



ORGANIC ACID COATED MAGNETIC NANOPARTICLES AS ADSORBENT FOR ORGANIC POLLUTANTS IN AQUEOUS SOLUTION

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by

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DECLARATION

I declare that this dissertation is my own work. It is being submitted for the Degree Magister Technologiae to the Department of Chemistry, Vaal University of Technology, Vanderbijlpark and has not been submitted before for any degree or examination to any other University.

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CO-SUPERVISOR

DEDICATION

To my loving parents, Musa and Lizzy Masuku.

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TABLE OF CONTENTS

DECLARATION	i
DEDICATION	ii
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	iv
LISTS OF FIGURES	xi
LIST OF TABLES	xiv
ABSTRACT	xix
CHAPTER 1.....	1
1 INTRODUCTION.....	1
1.1 BACKGROUND.....	1
1.2 PROBLEM STATEMENT	2
1.3 AIM	3
1.4 THESIS LAYOUT.....	3
CHAPATER 2.....	7
2. LITERATURE REVIEW	7
2.1 WATER, WATER SCARCITY, AND POLLUTION.....	7
2.1.1 Water pollution.....	7
2.1.2 Sources of wastewater	8
2.1.2.1 Municipal wastewater.....	8
2.1.2.2 Agricultural wastewater	8
2.1.2.3 Industrial wastewater	8
2.1.3 Organic pollutants in water	9
2.1.3.1 Volatile organic compounds (VOCs).....	9
2.1.3.2 Benzene, Toluene, and Xylenes (BTX)	9
2.1.3.2.1 Benzene properties and its uses	10
2.1.3.2.2 Toluene properties and its uses.....	10
2.1.3.2.3 Xylene properties and its uses	10
2.1.3.3 Sources of BTX in the environment	11

2.1.3.4 Health and environmental effects of BTX.....	11
2.1.3.5 Legislation on allowable levels of BTX compounds in water	12
2.2 METHODS OF WASTEWATER TREATMENT	13
2.2.1 Activated sludge treatment process	13
2.2.2 Wet air oxidation process	14
2.2.3 Chemical precipitation	14
2.2.4 Ion-exchangers.....	14
2.2.5 Membrane filtration	15
2.2.6 Electrochemical treatment	15
2.2.7 Chemical oxidation process.....	15
2.2.8 Biological treatment process	16
2.2.9 Adsorption process	16
2.2.9.1 Physisorption.....	16
2.2.9.2 Chemisorption.....	17
2.2.9.3 Exchange adsorption or ion - exchange	17
2.3 ADVANTAGES OF THE ADSORPTION PROCESS	18
2.3.1 Adsorption mechanism.....	18
2.3.2 Factors affecting adsorption	19
2.4 TYPES OF ADSORBENTS	19
2.4.1 Commercial adsorbents.....	20
2.4.1.1 Activated carbon.....	20
2.4.1.2 Zeolites	20
2.4.1.3 Silica gel.....	21
2.4.1.4 Clay minerals	21
2.5 IRON OXIDE MAGNETIC NANOPARTICLES	21
2.5.1 Uses of Iron oxide nanoparticles	22
2.5.2 Advantages of Iron oxide nanoparticles as an adsorbent in wastewater treatment	22
2.5.3 Preparation of Superparamagnetic Iron Oxide Nanoparticles	23
2.5.4 Production of magnetic nanoparticles via co-precipitation method..	23
2.5.5 Production of magnetic nanoparticles via microwave heating	23
2.5.6 Production of magnetic nanoparticles by thermal decomposition	24
2.5.7 Magnetite-organic acid composites.....	25

2.5.7.1 Organic modification	25
2.5.7.1.1 Surfactants	25
2.5.7.1.2 Modification of the iron oxide nanoparticles using organic acid ...	26
2.5.7.1.3 Potential adsorption mechanism	27
2.6 RESPONSE SURFACE METHODOLOGY (RSM).....	28
2.6.1 The design procedure (RSM)	28
2.6.2 Central Composite Design (CCD)	29
2.7 MODELING OF ADSORPTION EXPERIMENTAL DATA	30
2.7.1 Kinetic studies.....	30
2.7.1.1 Pseudo-first-order	31
2.7.1.2 Pseudo-second-order.....	31
2.8 CONCLUSION	31
2.9 REFERENCES	32
3 EXPERIMENTAL PROCEDURES	56
3.1 INTRODUCTION	56
3.2 SAMPLE PREPARATION	56
3.2.1 Materials	56
3.2.2 Synthesis of the magnetite-organic acids composites via microwave method	57
3.2.2.1 Proposed reactions for the magnetite-organic acid composites	57
3.2.3 Experimental design for the synthesis of magnetite-organic acid composites and statistical analysis.....	58
3.3 CHARACTERIZATION OF THE MAGNETITE-ORGANIC ACID COMPOSITE	59
3.3.1 X-Ray Fluorescence (XRF)	59
3.3. 2 Conductivity (S/cm).....	59
3.3.3 Fourier-Transform Infra-Red spectroscopy (FTIR).....	59
3.3.4 Thermogravimetric Analysis (TGA).....	60
3.3.5 X-Ray Diffraction spectroscopy (XRD)	60
3.3.6 Transmission Electron Microscopy (TEM)	60
3.3.7 Vibrating Sample Magnetometer (VSM)	60
3.3.8 Brunauer-Emmett-Teller Surface Area (BET)	61
3.4 APPLICATION OF THE PREPARED ADSORBENTS ONTO BTX UPTAKE IN AQUEOUS SOLUTION	61

3.4.1 pH at point zero charge	61
3.4.2 Effect of solution pH.....	61
3.4.3 Adsorbent dose	62
3.4.4 Effect of initial concentration.....	62
3.4.5 Adsorption kinetics.....	62
3.3.5 Desorption studies	62
3.5 REFERENCE	63
CHAPATER 4.....	64
4 OPTIMIZATION STUDIES BY STATISTICAL EXPERIMENTAL DESIGN	64
4.1 INTRODUCTION	64
4.2 REACTION SCHEME.....	64
4.3 EXPERIMENTAL DESIGN.....	64
4.4 DEVELOPMENT OF REGRESSION MODEL EQUATION AND STATISTICAL ANALYSIS USING MAGNETITE-OLEIC ACID COMPOSITE	65
4.5 EFFECTS OF PREPARATION VARIABLES ON THE % Fe CONTENT	71
4.6 EFFECTS OF PREPARATION VARIABLES ON THE CONDUCTIVITY (S/cm)	72
4.7. EFFECTS OF PREPARATION VARIABLES ON BTX	72
4.7.1 Benzene adsorption capacity.....	72
4.7.2 Toluene adsorption capacity	72
4.7.3 Xylene adsorption capacity	73
4.8 VALIDATION OF MODEL AND RESPONSE SURFACE PLOT	73
4.9 THREE DIMENSIONAL RESPONSE SURFACE PLOTS.....	75
4.9.1 3D Response Surface plots for % Fe content.....	75
4.9.2 3D Response Surface plots for conductivity on the adsorbent.....	75
4.9.3 3D Response Surface plots for BTX adsorption capacity	75
4.9.3.1 Benzene adsorption capacity	75
4.9.3.2 Toluene adsorption capacity.....	76
4.9.3.3 Xylene adsorption capacity.....	76
4.10 RESPONSE SURFACE MODEL FITTING BY (CCD) USING MAGNETITE-PALMITIC ACID COMPOSITE	79

4.11 EFFECTS OF PREPARATION VARIABLES ON THE % Fe CONTENT.....	85
4.12 EFFECTS OF PREPARATION VARIABLES ON THE CONDUCTIVITY (S/cm)	86
4.13 EFFECTS OF PREPARATION VARIABLES ON BTX	86
4.13.1 Benzene adsorption capacity	86
4.13.2 Toluene adsorption capacity	87
4.13.3 Xylene adsorption capacity	87
4.14 VALIDATION OF MODEL AND RESPONSE SURFACE PLOT	87
4.15 THREE-DIMENSIONAL RESPONSE SURFACE	89
4.15.1 3D Response Surface plots for % Fe content.....	89
4.15.2 3D Response Surface plots for conductivity on the adsorbent.....	89
4.13.3 3D Response surface plots for BTX adsorption capacity	89
4.13.3.1 Benzene adsorption capacity	89
4.13.3.2 Toluene adsorption capacity.....	90
4.13.3.3 Xylene adsorption capacity.....	90
4.16 CONCLUSION	93
4.17 REFERENCES	94
CHAPATER 5.....	95
5 RESULTS AND DISCUSSION (PART 1): THE CHARACTERIZATION OF PURE MAGNETITE, MAGNETITE-OLEIC AND MAGNETITE-PALMITIC ACID COMPOSITE.....	95
5.1 INTRODUCTION	95
5.2 FTIR SPECTROSCOPY.....	95
5.2.1 FTIR of pure magnetite nanoparticles	95
5.2.2 FTIR of magnetite-oleic acid composite	96
5.2.3 FTIR of magnetite-palmitic acid composite.	98
5.3 THERMOGRAVIMETRIC ANALYSIS (TGA) AND DERIVATIVE THERMOGRAVIMETRIC ANALYSIS (DTA)	100
5.3.1 TGA/ DTA of Pure magnetite	100
5.3.2 TGA/DTA of magnetite-oleic acid composite.....	101
5.3.3 The TGA/DTA of magnetite-palmitic acid composite.....	102
5.4 X-RAY DIFFRACTION (XRD).....	103
5.4.1 XRD of pure magnetite	103

5.4.2 XRD of magnetite-oleic acid composite	104
5.4.3 XRD of magnetite-palmitic acid composite	104
5.5 TRANSMISSION ELECTRON SPECTROSCOPY (TEM)	106
5.5.1 TEM of pure magnetite nanoparticles	106
5.5.2 TEM of magnetite-oleic acid composite.....	106
5.5.3 TEM of magnetite-palmitic acid composite.....	107
5.6 SCANNING ELECTRON MICROSCOPY (SEM)	109
5.6.1 SEM of pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid composites	109
5.7 ELECTRON DISPERSIVE SPECTROSCOPY (EDX)	110
5.7.1 EDX of pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid composites	110
5.8 BRUNAUER-EMMETT-TELLER (BET) SURFACE AREA	111
5.8.1 BET of pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid composites	111
5.9 VIBRATING SAMPLE MAGNETOMETER (VSM)	113
5.9.1 VSM of pure magnetite nanoparticles	113
5.9.2 VSM of magnetite-oleic acid composite.....	114
5.9.3 VSM of magnetite-palmitic acid composite.....	115
5.10 POINT ZERO CHARGE (pH_{pzc}).....	116
5.11 CONCLUSION	119
5.12 REFERENCE	120
CHAPATER 6.....	129
6. RESULTS AND DISCUSSION (PART 2)	129
6.1 INTRODUCTION	129
6.2 OPTIMISATION OF KINETIC PARAMETERS.....	129
6.2.1 Effect of solution pH.....	129
6.2.2 Adsorbent dose	133
6.3 KINETIC STUDIES	135
6.3.1 Effect of adsorption time on kinetics	136
6.3.2 Effect of concentration on the uptake of Benzene, Toluene and Xylene	137
6.4 KINETIC MODELLING	143
6.4.1. Kinetic modelling for MNP	143

6.4.2 Kinetic modelling for MNP-PA.....	148
6.4.3 Kinetic modelling for MNP-OA.....	153
6.4.4 Desorption and Reuse.....	159
6.4.5: Reusability of MNP, MNP-PA and MNP-OA for BTX adsorption	162
6.5 CONCLUSION.....	165
6.6 REFERENCE	166
CHAPATER 7.....	169
7 CONCLUSION AND RECOMMENDATIONS.....	169
7.1 CONCLUSION.....	169
7.2 RECOMMENDATIONS.....	172

LISTS OF FIGURES

Figure 2.1: Schematic diagram of adsorption model.....	18
Figure 3.1: Proposed reaction in the preparation of MNP-oleic acid.....	58
Figure 3.2: Proposed reaction in the preparation of MNP-palmitic acid.....	58
Figure 4.1: Plot of actual values against predicted values for (a) % Fe content,(b) conductivity, (c) benzene adsorption capacity, (d) toluene adsorption capacity (e) xylene adsorption capacity.....	76
Figure 4.2: 3D interaction for (a-e): % Fe content, conductivity (S/cm) and BTX adsorption capacity (mg/g).....	79
Figure 4.3: Plot of actual values against predicted values of (a) % Fe, (b).....	90
Figure 4.4: 3D plots of (a-e) for % Fe, conductivity, benzene, toluene and xylene adsorption capacity.....	93
Figure 5.1: FTIR spectra pure magnetite nanoparticles.....	98
Figure 5.2: FTIR spectra of pure magnetite, pure oleic and magnetite-oleic acid composite.....	100
Figure 5.3: FTIR spectra of pure magnetite, pure palmitic and magnetite-palmitic acid composite	101
Figure 5.4: Thermal stability of the magnetite nanoparticles.....	102
Figure 5.5: Thermal stability of the magnetite-oleic acid composite.....	103
Figure 5.6: Thermal stability of the magnetite-palmitic acid composite.....	104
Figure 5.7: XRD diagram of pure magnetite nanoparticles.....	105
Figure 5.8: XRD of magnetite-oleic acid composite.....	106
Figure 5.9: XRD of magnetite- palmitic acid composite.....	107
Figure 5.10: TEM images of pure magnetite nanoparticles.....	106
Figure 5.11: TEM images of magnetite-oleic acid composite	109
Figure 5.12: TEM images of magnetite-palmitic acid composite	110
Figure 5.13 SEM images of (a) Pure, (b) magnetite-oleic and (c) magnetite-palmitic acid composite.....	111
Figure 5.14: EDX of (a) Pure magnetite, (b) magnetite-oleic and (c) magnetite-palmitic acid composite.....	113
Figure 5.15: N ₂ adsorption–desorption isotherms of pure magnetite, magnetite-oleic and magnetite-palmitic acid composite.....	114
Figure 5.16: Magnetization curve of pure magnetite nanoparticles.....	115

Figure 5.17: Magnetization curve of magnetite-oleic acid composite.....	116
Figure 5.18: Magnetization curve of magnetite-palmitic acid composite.....	117
Figure 5.19: Point zero charge of pure magnetite and magnetite-oleic acid composite.....	118
Figure 5.20: Point zero charge of pure magnetite and magnetite-palmitic acid composite.....	119
Figure 6.1: Effects of initial solution pH on Benzene uptake on MNP, MNP-PA and MNP-OA composites.....	132
Figure 6.2: Effects of initial solution pH on Toluene MNP, MNP-PA and MNP-OA composites	133
Figure 6.3: Effects of initial solution pH on Xylene MNP, MNP-PA and MNP-OA composites.....	134
Figure 6.4: Effect of adsorbent dose on the uptake of BTX onto MNP.....	136
Figure 6.5: Effect of adsorbent dose on the uptake of BTX onto MNP-OA.....	136
Figure 6.6: Effect of adsorbent dose on the uptake of BTX onto MNP-PA.....	137
Figure 6.7: Effect of time on the uptake of BTX onto MNP.....	138
Figure 6.8: Effect of time on the uptake of BTX onto MN-PA.....	139
Figure 6.9: Effect of time on the uptake of BTX onto MNP-OA.....	139
Figure 6.10: Adsorption kinetics of Benzene on MNP. Initial pH: 7, adsorbate dose: 1.0 g/dm ³ , solution volume: 10 mL, agitation speed: 300 rpm, temperature.....	141
Figure 6.11: Adsorption kinetics of Toluene on MNP. Initial pH: 8, adsorbate dose: 1.0 g/dm ³ , solution volume: 10 mL, agitation speed: 300 rpm, temperature: 299 K.....	141
Figure 6.12: Adsorption kinetics of Xylene on MNP. Initial pH: 8, adsorbate dose: 1.0 g/dm ³ , solution volume: 10 mL, agitation speed: 300 rpm, temperature: 299 K.....	142
Figure 6.13: Adsorption kinetics of Benzene on MNP-PA composite. Initial pH: 7, adsorbate dose: 1.0 g/dm ³ , solution volume: 10 cm ³ , agitation speed: 300 rpm, temperature: 299 K.....	142
Figure 6.14: Adsorption kinetics of Toluene on MNP-PA composite Initial pH: 8, adsorbate dose: 1.0 g/dm ³ , solution volume: 10 cm ³ , agitation speed: 300 rpm, temperature: 299 K.....	143

Figure 6.15: Adsorption kinetics of Xylene on MNP-PA composite. Initial pH: 8, adsorbate dose: 1.0 g/dm ³ , solution volume: 10 cm ³ , agitation speed: 300 rpm, temperature: 299 K.....	143
Figure 6.16: Adsorption kinetics of Benzene on MNP-OA. Initial pH: 7, adsorbate dose: 1.0 g/dm ³ , solution volume: 10 mL, agitation speed: 300 rpm, temperature: 299 K.....	139
Figure 6.17: Adsorption kinetics of Toluene on MNP-OA. Initial pH: 8, adsorbate dose: 1.0 g/dm ³ , solution volume: 10 mL, agitation speed: 300 rpm, temperature: 299 K.....	139
Figure 6.18: Adsorption kinetics of Xylene on pure magnetite. Initial pH: 8, adsorbate dose: 1.0 g/dm ³ , solution volume: 10 mL, agitation speed: 300 rpm, temperature: 299 K.....	145
Figure 6.19: Comparison of predicted equilibrium capacities of kinetic models with experimental data for BTX adsorption onto MNP	146
Figure 6.20: Comparison of predicted equilibrium capacities of kinetic models with experimental data for BTX adsorption onto MNP-PA.....	151
Figure 6.21: Comparison of predicted equilibrium capacities of kinetic models with experimental data for BTX adsorption onto MNP-OA.....	156
Figure 6.22: Desorption efficiency of BTX using different solvents for MNP	162
Figure 6.23: Desorption efficiency of BTX using different solvents for MNP-PA.....	161
Figure 6.24: Desorption efficiency of BTX using different solvents for MNP-OA	163
Figure 6.25: Reusability of MNP for Benzene, Toluene and Xylene adsorption....	165
Figure 6.26: Reusability of MNP for Benzene, Toluene and Xylene adsorption....	166
Figure 6.27: Reusability of MNP for Benzene, Toluene and Xylene adsorption.....	166

LIST OF TABLES

Table 2.1: Basic characteristics of BTX compounds.....	11
Table.2.2: Comparisons between physisorption and chemisorption mechanism.....	17
Table.3.1: Range and levels of independent variables for experimental design using CCD	59
Table 4.1: CCD Experimental design of five independent variables and three responses.....	68
Table 4.2: CCD Experimental design of five independent variables and three responses.....	69
Table 4.3: CCD Experimental design of five independent variables and three responses.....	70
Table 4.4 : Benzene ANOVA for Response Surface Quadratic Model.....	71
Table 4.5: Toluene ANOVA for Response Surface Quadratic Model.....	72
Table 4.6: Xylene ANOVA for Response Surface Quadratic Model.....	73
Table 4.7: Optimum values for magnetite-oleic composite.....	80
Table 4.8: CCD Experimental design of five independent variables and three responses.....	82
Table 4.9: CCD Experimental design of five independent variables and three responses.....	83
Table 4.10: CCD Experimental design of five independent variables and three responses.....	84
Table 4.11: Benzene ANOVA for Response Surface Quadratic Model.....	85
Table 4.12: Toluene ANOVA for Response Surface Quadratic Model.....	86
Table 4 13: Xylene ANOVA for Response Surface Quadratic Model.....	87
Table 4.14: Optimum values.....	94
Table 5.1: Elemental analysis of pure magnetite and magnetite-oleic and magnetite-palmitic acid composites magneti.....	112
Table 5.2: pH _{pzc} values of pure magnetite and organic acid coated magnetite (oleic and palmitic) samples.....	118
Table 6.1: Pseudo-first-order Kinetic data for BTX adsorption onto MNP.....	148

Table 6.2: Pseudo-second-order Kinetic data for BTX adsorption onto MNP.....	149
Table 6.3: Pseudo-first-order Kinetic data for BTX adsorption onto MNP-PA.....	153
Table 6.4: Pseudo-second-order Kinetic data for BTX adsorption onto MNP-PA.....	154
Table 6.5: Pseudo-first-order Kinetic data for BTX adsorption onto MNP-OA.....	158
Table 6.6: Pseudo second order Kinetic data for BTX adsorption onto MNP-OA..	159
Table 6.7: Pseudo second order capacities of different adsorbents.....	160

LISTS OF ABBREVIATIONS AND SYMBOLS

q_e	Equilibrium capacity
q_t	Equilibrium capacity at time t
k_1	Pseudo-first order rate constant
k_2	Pseudo-second order rate constant
$t^{0.5}$	The time in min raised to the power of 0.5
r^2	Coefficient of determination
C_o	Initial Concentration
C_e	Equilibrium concentration
m	Mass of the adsorbent
V	Solution volume
% R	Percentage removal
h	The initial sorption rate
$q_{e,m}$	Equilibrium capacity obtained by calculating from model
VOCs	Volatile organic compounds
BTX	Benzene, Toluene, Xylene
Fe ₃ O ₄ /MNP	Magnetite nanoparticles
MNP-OA	Magnetite-oleic acid
MNP-PA	magnetite-palmitic acid
RSM	Response Surface Methodology
CCD	Central Composite Design
XRF	X-Ray fluorescence
S/cm	Conductivity

FTIR	Fourier-transform infrared spectroscopy
XRD	X-ray diffraction
TGA	Thermogravimetric analysis
TEM	Transmission Electron Microscopy
VSM	Vibrating Sample Magnetometer
pH _{pzc}	pH at point zero charge
BET	Brunauer-Emmett-Teller
EDX	Electron dispersive spectroscopy
SEM	Scanning electron microscopy
UV-vis	Ultra-violet-visible spectroscopy

PRESENTATIONS

The work presented in this dissertation has been presented at national conferences.

Conferences contributions

Makhosazana Masuku, Augustine E.Ofomaja, Agnes. Polosi. The effect of chain length on magnetite organic acid composite (magnetite-oleic and magnetite-palmitic) for the removal of benzene, toluene and xylene (BTX) pollutants from aqueous solution. The 3rd Vaal University of Technology (VUT) Interdisciplinary Research and Postgraduate Conference, 17 October 2018 (Vanderbijlpark).

Makhosazana Masuku, Augustine E.Ofomaja, Agnes. Polosi. The removal of Benzene from aqueous solution using magnetite-oleic acid composite: Response Surface Methodology. The water Institute of South African (WISA) Conference, Cape town (CTICC), June 2018.

Makhosazana Masuku, Augustine E.Ofomaja, Agnes. Polosi. The synthesis, characterization of magnetite-organic acid composite and adsorption studies (effect of pH and adsorbent dose) for removal of benzene and toluene from aqueous solution using. The 2nd Vaal University of Technology (VUT) Interdisciplinary Research and Postgraduate Conference, November 2017 (Vanderbijlpark).

ABSTRACT

Benzene, toluene and xylene (BTX) are water pollutants that appear very often in chemical and petrochemical wastewaters due to gasoline leakage from storage tanks and pipelines. These BTX compounds can cause adverse health effects on humans even at very low concentrations. Amongst the available pollutant removal methods from wastewater, adsorption has been used due to its ease of operation, simplicity and cost-effectiveness. Different adsorbents have been used for BTX removal, however the use of Magnetite-organic acid composites as an adsorbent seems to offer a much cheaper alternative. This work seeks to develop a one-step microwave synthesis and optimization of magnetite-oleic (MNP-OA) and magnetite-palmitic (MNP-PA) acid) composites.

Response surface methodology was used to optimize the magnetite-organic acid composites. The optimum conditions estimated for MNP-OA acid composite were 78.3 % Fe content, 1561.9 S/cm conductivity, 82.2, 84.1, 85.3 mg/g for BTX adsorption capacity. The MNP-PA composite were 75.6 % Fe content, 1325.66 S/cm conductivity, 60.55, 64.47, 63.06 mg/g for BTX adsorption capacity. The materials were characterized, and the adsorption process was optimized for BTX removal from aqueous solution. X-ray analysis confirmed the formation of magnetite by the presence of both ferric and ferrous ion states on the surface. It was noted that after modification, the magnetite-organic acids characteristics peaks became broad and the height of the peaks decreased indicating that surface modification with organic acid controls the crystallinity of the material. The average crystalline size of MNP, MNP-OA, and MNP-PA composites were 19.7, 17.1 and 17.9 nm. FTIR analysis confirmed the target materials were produced and also to determine if the organic acids were immobilised on the surface of the magnetite. TEM images presented that the MNP, MNP-OA, and MNP-PA composites were spherical in shape with particle average sizes of 18.4 ± 0.5 , 15.6 ± 0.5 and 16.5 ± 0.5 nm. The magnetite-organic acids show the particles with better isolated as compared to that of the MNP. The BET isotherms of the materials were described by a type IV characteristic related to uniform mesoporous materials. The magnetic saturation value for MNP, MNP-OA, and MNP-PA composites were 62.9, 59.0 and 51.0 emu/g. The decrease in magnetization was explained by the presence of the non-magnetic layer on magnetite surface. The pH_{pzc} of MNP, MNP-OA, and

MNP-PA composites were 6.9, 6.4 and 6.1. The decrease in pH_{pzc} after modification was due to the charging acid-base interaction mechanism of metal oxide nanoparticles.

The optimum pH for the adsorption of BTX onto MNP, MNP-OA, and MNP-PA composites was determined to be pH 7 for benzene, pH 8 for toluene and xylene. Among the three pollutants, xylene had the highest adsorption capacity followed by toluene and benzene. The optimum adsorbent dose for the adsorbents for the adsorption process was 0.1 g/dm^3 . The effect of time on the uptake of BTX onto MNP, MNP-OA, and MNP-PA composites show that initial adsorption of BTX occurred between 0 and 3 min of contact time. The effect of initial concentration results shows the initial concentration of BTX increases from 100 to 350 mg/dm^3 with an increase in adsorption capacity. The results suggest that the adsorption process is controlled by concentration driving force. The experimental data was fitted to the pseudo-first and pseudo-second-order kinetic models for all adsorbents and all pollutants. The pseudo-second-order models showed good correlation as compared to the first-pseudo model. Desorption studies for benzene, toluene and xylene using the pure magnetite, magnetite-palmitic and magnetite oleic acid composites indicate adsorption mechanism can be explained in relation to acid-base chemistry. Electron donation from the phenyl ring of each benzene, toluene and xylene compound to surface iron atoms of magnetite has been suggested. The CH_3OH and H_2O desorbing agents were used and regeneration using five cycles show that the percentage desorption decreases from Benzene < Toluene < Xylene. The reduction in adsorption capacity after the cycles are attributed to decomposition of the adsorbents active sites and mass loss of the sample.

CHAPTER 1

1 INTRODUCTION

1.1 BACKGROUND

Volatile organic compounds (VOCs) are harmful organic pollutants which are introduced into water systems by mainly petrochemical and pharmaceutical industrial processes. Among the well-known volatile organic compounds are benzene, toluene, and xylene (BTX). BTX are nonionic compounds with moderate solubility in water at 20 °C (benzene: 22 mM; toluene: 5.1 mM and xylenes: 1.5 mM) (Hussein and Ahmed, 2016, Russo *et al.*, 2018). These BTX organic compounds present in industrial wastewater may lead to groundwater contamination and depletion in water quality because they are nonbiodegradable. BTX has been found to have a mutagenic and carcinogenic effect on human health even when present at a low concentration (Masih *et al.*, 2017, Wang *et al.*, 2019). Strict rules on the discharge of the harmful pollutants in industrial wastewater make it important to develop removal technologies for BTX compounds in solution. These techniques include biological treatment, advanced oxidation process, condensation, membrane filtration, adsorption, chemical and electrochemical treatments (Alabi *et al.*, 2014, Zhang *et al.*, 2017, Kim *et al.*, 2018, Bustillo-Lecompte *et al.*, 2018, Crini *et al.*, 2018). Among these approaches, adsorption is still the most versatile and widely used method because it is found to be superior in reducing pollutants from industrial effluent. Advantages of adsorption method include low-cost, high removal efficiency, minimization of chemical or biological sludge, ease of operation, flexibility, the simplicity of design and ease of regeneration of the adsorbent (Makhathini and Rathilal, 2017, Kim *et al.*, 2018, Katheresan *et al.*, 2018). Adsorption is not complicated as is the case with some of the separation methods earlier mentioned. The extent of the pollutant removal using the adsorption process varies from 90 to 99 % (Gupta *et al.*, 2012).

Several cation and anion adsorbents such as modified clays, activated carbon, carbon nanotube, diatomite and zeolites have been found to be efficient in removal of BTX pollutants from aqueous solution (Aivalioti *et al.*, 2012, Makhathini and Rathilal, 2017, Mor *et al.*, 2017, Katheresan *et al.*, 2018). However, they are limited by their high operating costs, secondary waste production, low sorption capacity, regeneration problems and their inability to remove BTX from solution. (Makhathini and Rathilal, 2017, Mor *et al.*, 2017, Crini *et al.*, 2018). Magnetite nanoparticles produced via the coprecipitation method have been used as a good adsorbent for the removal of organic pollutants in wastewater due to their low cost, magnetisation, high sorption capacity, and reusability (Zhao *et al.*, 2016, Gutierrez *et al.*, 2017, Tyagi *et al.*, 2017). Although magnetite adsorbents are effective in removing organic pollutants in water, their hydrophilic surface is a limitation for the hydrophobic BTX compounds removal from aqueous solution. This research then seeks to synthesize a low-cost magnetite-organic acid composite (magnetite-oleic and magnetite-palmitic acid) via a one-step microwave synthesis method as a replacement for current conventional methods of removing BTX from aqueous solution.

1.2 PROBLEM STATEMENT

Different adsorbents have been prepared and applied for wastewater treatment. Although these adsorbents are effective, they show some major limitation for benzene, toluene, and xylene (BTX) removal in solution. BTEX are non-ionic, hydrophobic aromatic hydrocarbons. They are more toxic and carcinogenic in aqueous solution and they cannot be removed by cation and anion exchangers such as polymeric organic resins, agricultural biosorbents, activated carbon, zeolites, organoclays, and iron oxide magnetite nanoparticles. Hence there is a need to develop an adsorbent capable of removing these non-ionic pollutants from aqueous solution. Magnetite nanoparticles are good adsorbents due to their large surface area and reusability properties, however their hydrophilic surface charge is a disadvantage for removing BTX pollutants. Therefore, this research seeks to improve on the above weaknesses by use of magnetite-organic acid composites (magnetite-oleic and magnetite-palmitic acid). Specifically, it is envisaged that the carboxylic functional group from oleic and palmitic acid would impact hydrophobic characteristics on the surface of the magnetite, make them stable in air and increase sorption sites for BTX removal.

1.3 AIM

The aim of the study is to develop a one-step microwave synthesis and optimization of magnetite-organic acid composite using a microwave route. The synthesized adsorbent will then be applied for the removal of BTX from aqueous solution by achieving the following research objectives:

1. To synthesize the magnetite-organic acid composite (magnetite-oleic and magnetite-palmitic acid) using microwave method.
2. To apply Response surface methodology in optimizing the synthesis procedures.
3. To characterize the magnetite-organic acid composite using: FTIR, TGA, XRD, TEM, SEM, VSM and BET for surface area.
4. To optimize the adsorption of benzene, toluene and xylene on the prepared adsorbent.
5. To determine the kinetics of benzene, toluene and xylene onto the adsorbents.
6. To determine the adsorption mechanism and reusability of the prepared adsorbent for benzene, toluene and xylene.

1.4 THESIS LAYOUT

The thesis is divided into seven chapters: with two introductory chapters followed by 5 chapters each including a brief introduction, methodology, results and discussions and a conclusion.

Chapter 1:

The chapter covers the introduction, problem statement, aim and objectives of the research. It gives an insight into the research project.

Chapter 2:

This chapter looks at the literature review of pollutants in industrial wastewater and current techniques used for their removal in water systems. Adsorption method is presented as an alternative method for toxin removal from aqueous systems. Using magnetic nanoparticles as an adsorbent, their advantages and limitations are also discussed together with methods of modification and use of modified adsorbents. Kinetic models used to treat adsorption experimental data are presented.

Chapter 3:

This chapter presents the different techniques employed to characterise optimum samples obtained from RSM technique. The kinetic experiments are described in detail.

Chapter 4:

The chapter presents and discusses the use of Response surface methodology (RSM) using Central composite (CCD) approach. The CCD approach was used to optimize preparation of the magnetite-organic acid (magnetite-oleic and magnetite-palmitic acid) for the removal of benzene, toluene and xylene from aqueous solution.

Chapter 5

The chapter presents different sections. In this section results of the characterization of pure magnetite nanoparticles, magnetite-palmitic and magnetite-oleic acid composites were presented. The characterization was employed to confirm if the target materials were produced, to determine the effect of organic acid coating and to show the effect of different chain lengths of surfactant molecules (hydrophobicity).

Chapter 6:

The chapter presents and discusses the effects of adsorption parameters such as effect of solution pH, adsorbent dose and kinetics of BTX uptake at different initial concentrations and the kinetics data were also modelled using the pseudo-first and second-order models.

Chapter 7:

The final chapter presents the overall conclusion and recommendations of the study for future work based on the research finding.

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CHAPTER 2

2. LITERATURE REVIEW

2.1 WATER, WATER SCARCITY, AND POLLUTION

Water is the earth's most important liquid while portable water has a tremendous impact on all aspects of life. Its abundance in nature has led to human civilization and economic development through its use in agriculture as well as power generation. Although water is an important commodity for human wellbeing and welfare, it has not gone unnoticed that water scarcity has become a major global challenge in the 21st century.

Water scarcity is a major problem that affects a large part of the global population (Eslamian, 2016). It results when the water demand exceeds the available water supply. Several factors contribute to water scarcity. These factors include population growth, industrialization, urbanization, increase in agricultural activities, global changes as well as improper waste disposal of inorganic and organic compounds (Aivalioti *et al.*, 2012, Ali *et al.*, 2018). The United Nations in 2010 and the World Health Organization in 2018 estimated that 884 million people lack access to adequate potable water and 1.8 million children die every year due to water-related diseases. Today, this number has doubled (Odlare, 2014, WHO, 2014). Given the preceding alarming statistics, it is necessary to embark on water remediation research projects.

2.1.1 Water pollution

Water pollution is a result of pollutants being directly and indirectly deposited into water resources without being treated to eliminate harmful compounds (Jodeh *et al.*, 2015). Globally, water pollution caused by organic and inorganic contaminants is a serious problem. It decreases clean water supply.

Wastewater can be defined as spent water that emanates from domestic, agricultural and industrial processes. They are high in organic compounds, phosphorus and nitrogen.

2.1.2 Sources of wastewater

2.1.2.1 Municipal wastewater

The main sources of municipal wastewater are households, commercial buildings and educational institutions. In many networks, household wastewater accounts for 50 to 80% of the total waste (Shakir *et al.*, 2017). Household wastewater from sewage, sinks, dishwashers, washing machines, bathtubs, and showers consists of nitrogen, phosphate, trace elements (e.g. iron and manganese), dissolved salts, (such as sodium chloride), and in some cases, bicarbonates (HCO_3^-) (Karunanithi *et al.*, 2016, Niazi *et al.*, 2016, Ejhed *et al.*, 2018). Pathogens (viruses, bacteria, fungal) and other microorganisms (parasites) enter the marine environment mainly through municipal wastewater (Feichtmayer *et al.*, 2017).

2.1.2.2 Agricultural wastewater

Agriculture has the highest water demands, representing about 70% of global freshwater withdrawals worldwide (Eslamian *et al.*, 2016, Intriago *et al.*, 2018). Agricultural wastewater is the excess water that normally runs off the field at the low end of furrows, border strips, basins, and flooded areas during surface irrigation. Fertilizers, antibiotics, pesticides or toxic metals used on farmlands discharged into aquatic systems (Nikinmaa, 2014, Wei *et al.*, 2018). Masoud *et al.* 2016 reported that disposal of agricultural by-products such as rice husk from rice milling industry is a source of water pollution.

2.1.2.3 Industrial wastewater

Industries are high water consumers generating high quantities of liquid effluent. The growth in industrial developments in South Africa over the years has resulted in increased industrial wastewater (Ercin and Hoekstra, 2012, Jagtap *et al.*, 2012). Examples of industries with huge waste include, mining (Iron and steel), food (dairy and vegetable oil), textile, leather, cosmetics, plastic and organic chemicals (petroleum and pharmaceuticals) industries (Muralikrishna and Manickam, 2017, Das *et al.*, 2018, Huang *et al.*, 2018, Monteiro *et al.*, 2018).

Industrial wastewater contains significant quantities of toxic chemicals, persistent organic pollutants, micro-pollutants and heavy metals (examples, chromium) (Badmus *et al.*, 2018). Major components of these pollutants are sulphates, nitrates, antibiotics, pesticides, dyes, polynuclear aromatic hydrocarbons (PAHs), polychlorinated phenyls (PCBs), polybrominated diphenyl ethers (PBDEs), plasticizers, phenols, drug residues, cleaning detergents, benzene,

toluene, xylene, and ethylbenzene (El-Naas *et al.*, 2014, Rozi *et al.*, 2017). Notably, hydrocarbons of high molecular mass are difficult to remove from wastewater because they are the most water soluble petroleum compounds (El-Naas *et al.*, 2014). To avoid the toxic effect associated with industrial effluent, it is imperative for companies to work with scientists and government to ensure proper waste disposal (Brezonik and Arnold, 2012).

2.1.3 Organic pollutants in water

A number of organic pollutants in domestic and industrial wastewater pose danger to the environment and human health even when present at low concentrations (Salman, 2017). Such organic pollutants include phenols, nitroaromatics and volatile organic compounds such as benzene, toluene and xylenes (Feichtmayer *et al.*, 2017, Wang *et al.*, 2018). These pollutants have health effects on the immune, reproductive, cardiovascular, nervous, and endocrine systems (Feichtmayer *et al.*, 2017). Liver, kidney, skin and eye irritation have also been reported (Konggidinata *et al.*, 2017). In addition, these organic pollutants are carcinogenic, and overexposure cause vascular inflammation and atherosclerosis (Lee *et al.*, 2018)

2.1.3.1 Volatile organic compounds (VOCs)

Volatile organic compounds (VOCs) are organic chemicals that when released into the atmosphere can react with sunlight and nitrogen oxides to form tropospheric (ground-level) ozone (Marty *et al.*, 2010, Jin and Holloway, 2015). They may be of anthropogenic or natural origin with a boiling point of 100 °C and/or a vapor pressure greater than 1 mm Hg at 25 degrees Celsius (Salthammer, 2016).

Among VOCs discharged into water bodies are acetaldehyde, chloroform, benzene, toluene, xylene (BTX), formaldehyde and styrene. BTX emanating from petroleum products are the most poisonous ones. The second group is halogenated VOCs such as n-propyl bromide used as a degreaser and solvent. The third group includes chlorinated organic disinfection by-products, particularly trihalomethanes (Tisserand and Young, 2014).

2.1.3.2 Benzene, Toluene, and Xylenes (BTX)

Benzene, toluene and xylene (BTX) are used in the petrochemical industry. Their demand has substantially increased over the past years (Mohite, 2014, Ghorbannezhad *et al.*, 2018, Siqueira *et al.*, 2018). They are monocyclic aromatic compounds (Bolden *et al.*, 2015, Peng *et al.*, 2015).

2.1.3.2.1 Benzene properties and its uses

Benzene (C_6H_6) is composed of six (6) carbon atoms joined in a ring, with one (1) hydrogen atom attached to each carbon atom. The Environmental Protection Agency(EPA) stated that it has a molecular mass of 78.11 g/mol and boiling point of 176.2 °F (80.1°C) with a density of 876.50 kg/m³ and melting point 41.9 °F (5.5 °C) (EPA, 2015). It is clear, colorless at room temperature and has a sweet aromatic odour (Vulimiri *et al.*, 2017). It is extremely stable due to its aromatic structure, but has poor solubility and is highly flammable (Tilley and Fry, 2015, Vulimiri *et al.*, 2017). Benzene is used for the production of detergents, resins, plastics, synthetic fiber, dyes and as a solvent (Vulimiri *et al.*, 2017). It is also used for the production of chemical compounds such as maleic anhydride cumene, and styrene (Mendelsohn *et al.*, 2014). As a gasoline additive, benzene improves the octane rating and reduces knocking (Hussein and Ahmed, 2016, Russo *et al.*, 2018).

2.1.3.2.2 Toluene properties and its uses

Toluene (C_7H_8) is an aromatic compound (a methyl-substituted benzene derivative), its molar mass is 92.14 g/mol, density 866.90 kg/m³ and boiling point 231.1 °F (110.6 °C). It is a water-insoluble and colourless volatile compound (Vulimiri *et al.*, 2017). Toluene is also used in the industry as a solvent for paints, thinners, cleaners, coatings, adhesives, inks, coatings, fingernail polish, production of rubber, nylon, plastics as well as in leather tanning (Vulimiri *et al.*, 2017).

2.1.3.2.3 Xylene properties and its uses

Xylene (C_8H_{10}) is a monocyclic aromatic compound, the structure consists of two methyl groups attached to the benzene ring (Ravishankar *et al.*, 2018). It is a colorless, ignitable and hydrophobic liquid with a pungent smell. Its density is 861 k/gm², molar mass is 106.16 g/mol and boiling point is 281°F. It is used in industry in the form of isophthalic acids (m-xylene), phthalic anhydride (o-xylene), terephthalic acid and dimethyl terephthalate (p-xylene) for resin films (Ghorbannezhad *et al.*, 2018, Ravishankar *et al.*, 2018). It is also extensively used as a solvent in dye, manufacturing of rubber, coal, leather, insecticide, and covering industries (Saravanan and Rajamohan, 2009, Pourzamani *et al.*, 2017).

Table 2.1: Basic characteristics of BTX compounds (Mitra and Roy, 2011, El-Naas *et al.*, 2014).

Compound	Chemical Formula	Molecular weight g/mol	Boiling point °C	Solubility in water (ppm)	Density (g/ml)	Vapour pressure (torr)
Benzene	C ₆ H ₆	78.11	80.1	1780	0.88	75
Toluene	C ₆ H ₅ CH ₃	92.1	110.8	515	0.77	262
O-Xylene	C ₆ H ₄ (CH ₃) ₂	106.17	144.4	175	0.88	6

2.1.3.3 Sources of BTX in the environment

The increased demand for petroleum products with BTX content has caused an increase in environmental pollution (Bustillo-Lecompte *et al.*, 2018). Most BTX production is based on the recovery of aromatics derived from the catalytic reforming of naphtha (reformate) or pyrolysis gasoline in a petroleum refinery.

Large amounts of these compounds find their way into water bodies through the leakage of petroleum products and fuel oil from underground storage tanks, spillages from road accidents, transportation, cracked pipelines as well as improper waste disposal practices (Bolden *et al.*, 2015, Yang *et al.*, 2016, Alves *et al.*, 2017).

BTX compounds can further be found in effluent streams due to the release of large amounts of these pollutants during the extraction process, refining processes of coal tar, vehicle exhaust, storage tanks, chemical plants, composting facilities and waste incinerators (El-Naas *et al.*, 2014, Tamaddoni *et al.*, 2014, Bandura *et al.*, 2015).

Other sources include, the printing and leather industries, rubber manufacturing, plastics decomposition, solvent extraction, agricultural effluents, gases, personal care products industries as well as improper disposal of oils (Su *et al.*, 2010, Szala *et al.*, 2015, Bandura *et al.*, 2016, Sostaric *et al.*, 2016).

2.1.3.4 Health and environmental effects of BTX

The large quantity of wastewater produced by industries and discharged into the environment and their associated health hazard to mankind is a major concern (Bustillo-Lecompte *et al.*, 2018). Among the three BTX compounds, benzene is the most harmful mono-aromatic

compound of all. Benzene in the air is recognizable at 60 to 100 parts per million (ppm) and 0.5 to 4.5 ppm is enough for people to taste benzene in water. Additionally, it was reported that about 5 to 10 min exposure to more than 10,000 ppm of benzene can result in death (Tilley and Fry, 2015). Exposure to between 700 and 3,000 ppm can lead to brain damage, embryotoxicity, neurological, respiratory, genetic, excretory system damage, eye irritation, mucous membranes and mutagenicity effects (Picone, 2012, Shekarrizfard *et al.*, 2015, Khodaei *et al.*, 2017, Salvi *et al.*, 2017). Other effects reported include leukemia, lymphomas, dysfunction of the kidney, liver, weakened nervous systems, skin irritation and reduced bone marrow function (Shekarrizfard *et al.*, 2015, Salvi *et al.*, 2017). The International Agency for Cancer Research (IARC) and the Environmental Protection Agency (EPA) and other researchers have stated that benzene is a high-risk factor as it is known to be very carcinogenic, occupying sixth place on the priority list of dangerous substances (IARC, 1982, EPA, 2002, Szala *et al.*, 2015, Szczurek *et al.*, 2017, Vulimiri *et al.*, 2017). Besides health concerns benzene has also been associated with environmental pollution. Due to its high volatile nature, it contributes to the formation of ground-level, greenhouse effect global warming and toxic peroxyacyl nitrates through atmospheric photochemical reactions (Mo *et al.*, 2016). Whereas toluene is not carcinogenic however its exposure over a long period affects the central nervous system. Inhalation of 50 to 1,500 ppm of toluene for long hours can cause fatigue, drowsiness, impaired cognitive function and irritation to the eyes and throat (Council and Levels, 2009). Long-term exposure can lead to mental retardation, cerebellar dysfunction, abnormal encephalograms, and visual impairment (Sostaric *et al.*, 2016, Szczurek *et al.*, 2017). In addition, oral exposure to toluene can also lead to damage to the kidneys and the reproduction system (Yang *et al.*, 2016, Stahelin *et al.*, 2018). Exposure to xylene can cause eye irritation (Siqueira *et al.*, 2018). Despite all these health factors reported on the dangers of BTX compounds in human lives and the environment, large amounts of these compounds are still being used in many countries of the world because of the extent of their applications (Carla *et al.*, 2012).

2.1.3.5 Legislation on allowable levels of BTX compounds in water

It has not gone unnoticed that a considerable effort has been dedicated in the past years concerning the removal of these compounds from wastewater and government authorities have placed very stringent environmental standards for the maximum allowable levels of BTX compounds in water for human consumption. Worldwide, there are numerous existing

legislations for allowable BTX levels in the drinking water system. The United States Environmental Protection Agency has set maximum allowable levels of these contaminants in water for public consumption to be 0.005 mg L⁻¹ (benzene), 1.0 mg L⁻¹ (toluene), 0.7 mg L⁻¹ and 10 mg L⁻¹ (total xylene), while the Brazilian National Environment Council set its values for discharges into water bodies to be 1.2 ppm (benzene) and (toluene), and 1.6 ppm for xylene (CONAMA 430, 2011, US EPA, 2016).

The Sasol industries in South Africa are the main source of petrochemical products using large amounts of BTX in their products. The South African local municipality sewage clearance system does not have specifications for the limits of BTX compounds. However, it is anticipated that in the upcoming times, stringent regulations in South Africa will be compulsory on the concentrations of these compounds in wastewater before discharge (Makhathini and Rathilal, 2017).

2.2 METHODS OF WASTEWATER TREATMENT

The method of choice is an important factor in the removal of organic pollutants from wastewater. Scientists are working endlessly to find the best pollutants removal methods. Bhatnagar and Sillanpaa, 2010 reported that a number of key factors should be considered before choosing an appropriate method. These factors include the availability of space for treatment facilities, equipment resources, waste disposal controls, desired completed water quality and initial and maintenance costs (Barakat, 2011, Chen *et al.*, 2012, Imran Ali *et al.*, 2012). The various processes currently used for organic pollutants include, gas flotation, photocatalytic, chemical oxidation, air stripping, biological treatment activated sludge treatment, wet air oxidation, coagulation, flocculation, precipitation and oxidation (either chemical or photochemical), adsorption, ion exchange and filtration (Dickhout *et al.*, 2017, Sheikholeslami *et al.*, 2018, Konggidinata *et al.*, 2017).

2.2.1 Activated sludge treatment process

The activated sludge treatment process for wastewater is considered as a simple, convenient and relatively economically friendly. Although this method has several advantages it has limitations. The microorganisms employed can deal with only chemical wastewater containing relatively low concentration (< 100 mg/L) and it even acclimatizes due to low biodegradability and/or inhibitory effects to microorganisms of BTX. As a result, this process fails to resolve

problems associated with a very high concentration of wastewater produced from various kinds of chemical and petrochemical wastewaters (Zheng *et al.*, 2013, Huang and Li, 2014).

2.2.2 Wet air oxidation process

The use of wet air oxidation process is favorable. It is efficient and effective, fast and can oxidize a high concentration of organic compounds in the aqueous phase at elevated pressures and temperatures. This advantage can also be its disadvantage since elevated pressures and temperatures make it difficult to maintain reaction conditions. Other known limitations of this process involve high capital and operational cost (Davies, 2016, Bahri *et al.*, 2018).

2.2.3 Chemical precipitation

The chemical precipitation method is characterized as one of the most used in the removal of organic effluent from wastewater. Metal ions from aqueous solution can be precipitated by coagulants such as limestone, aluminium, calcium or ferric ions (Oncel *et al.*, 2013, Yelten-Yilmaz and Yilmaz, 2018). A typical example of one of the widely used precipitation techniques is hydroxide treatment. Its advantages include the relatively low cost of precipitant (lime), simple operation, as well as ease of automatic pH control. However, it has limitations due to the large production of sludge, high disposal cost, slow metal precipitation, poor settling and the aggregation of metal precipitates (Bhatnagar *et al.*, 2015, Ali *et al.*, 2018).

2.2.4 Ion-exchangers

This method is currently used in wastewater treatment to remove organic and inorganic pollutants. The ion-exchangers entails a process whereby the soluble ions from the liquid phase can be attracted to the solid phase. Ion exchange resins have an active ion group. There are different types of ion exchange such as anionic and cationic exchange resins. They are classified into insoluble substances which absorb negatively and positively charged ions from an electrolyte solution and release other ions with the same charges into the solution in an equivalent amount. The examples of negatively charged ions include sulphates and nitrates while the positively charged ions includes zinc and copper. Ion exchangers have proved to be very cost effective, can remove inorganic and organic compounds at very low concentrations of removal up to 95 % (Gupta *et al.*, 2012, Gebrewold, 2017). It is a reversible process and requires low energy contents. However, they are limited by high sensitivity to effluent pH, sludge disposal problem, require high-tech operation and maintenance which is expensive.

Additionally, it fails in handling concentrated metal solutions as the matrix gets easily fouled by organics and other solids in the wastewater (Gupta *et al.*, 2012, Kaleta *et al.*, 2018).

2.2.5 Membrane filtration

Various organic pollutants have been separated by this technique. There are different types of membrane filtration investigated and these include ultrafiltration (UF), reverse osmosis (RO), microfiltration (MF), and nanofiltration (NF) (Barakat, 2011). The process involves three basic principles: sieving, adsorption, and electrostatic phenomenon (Kontos *et al.*, 2018, Rezakazemi *et al.*, 2018). Barakat *et al.*, 2011 reported this method as an effective and efficient technology. Its advantages include: no chemicals addition as well as the minimum solid waste problem, however disadvantages such as high working pressures, high energy consumption, the high cost of the membrane, membrane fouling and the complexity of the process design and operation make it the less favorable technique for BTX removal in wastewater (Padaki *et al.*, 2015, Rezakazemi *et al.*, 2018).

2.2.6 Electrochemical treatment

This method uses electricity to pass current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode (Fleck *et al.*, 2018, Orts *et al.*, 2018). Electrochemical treatments of wastewater involve electro-deposition, electrocoagulation, electro-flotation, and electro-oxidation. The technology does not require chemicals and can be engineered to tolerate suspended solids. It is moderately metal selective and treats effluent to $>2000 \text{ mg/dm}^3$. Nevertheless, demerits include high electricity cost and sludge production and pollution from chlorinated organics and heavy metals due to indirect oxidation.

2.2.7 Chemical oxidation process

Chemical oxidation uses influential chemical oxidizers to ensure complete elimination of organic contaminants within the contaminated wastewater (Fleck *et al.*, 2018, Oturan *et al.*, 2018). Oxidizing agents used in water decontamination include potassium, ozone, permanganate, chloride, chlorine dioxide as well as hydrogen peroxide. The advantages are; low cost, no secondary pollutants while limitations include very slow reaction rates with organic compounds and its self-disintegration.

2.2.8 Biological treatment process

The biological treatment process can be characterized by its very low costs and low toxicity of product (El-Naas *et al.*, 2014, Tan *et al.*, 2018). The anaerobic (without oxygen) and anoxic (oxygen deficient) treatments are similar to aerobic treatment but use microorganisms that do not require the addition of oxygen. These microorganisms use compounds other than oxygen to catalyze the oxidation of biodegradable organics and other contaminants, resulting in innocuous by-products (Bahri *et al.*, 2018, Tan *et al.*, 2018). Conventional aerobic biological wastewater treatment processes are commonly used to treat wastewater streams containing benzene, toluene, meta-xylene, ortho-xylene and para-xylene (BTX). However, these processes are not often out of compliance with the current national Emissions Standards for Hazardous Air Pollutants regulations, due to the stripping of the volatile compounds from the aqueous phase into the atmosphere (Makhathini, 2015).

2.2.9 Adsorption process

Adsorption is one of the most efficient and commonly used methods to treat volatile organic compounds such as BTX, especially at very low concentrations (Konggidinata *et al.*, 2017, Wang *et al.*, 2018). The method involves the build-up of matter at the interface between two phases such as liquid, gas and solid, (Ali *et al.*, 2012). The solid on which adsorption occurs is called an adsorbent while the matter that accumulates at the interface is referred to as an adsorbate. Adsorption is defined as a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by chemical or physical interactions (Worch, 2012). Unbalanced forces of attraction between the liquid and solid phases result in an increase of the concentration of the component (s) on the solid phase. Because of the high affinity of the adsorbent for the adsorbate species, the adsorbate is attracted and bound to the adsorbent by different mechanisms.

2.2.9.1 Physisorption

A process in which the increase in the adsorbate concentration at the interface is due to non-specific (i.e., not dependent on the substance nature) van der Waals forces, hydrogen bonds, polarity, dipole-dipole π - π interaction (Ramos-Jacques *et al.*, 2018).

2.2.9.2 Chemisorption

Chemisorption is due to chemical reactions between the adsorbate and the adsorbent which create covalent or ionic bonds (Tripathi and Ranjan, 2015, Ramos-Jacques *et al.*, 2018).

2.2.9.3 Exchange adsorption or ion - exchange

The process involves ions exchanged from the adsorbent surface with adsorbate ions having charges of the same magnitude but greater affinity. It is generally reversible and proceeds stoichiometrically (Kammerer *et al.*, 2011).

Table 2.2: Comparisons between the physisorption and chemisorption mechanism (Kralik, 2014).

Property	Physical	Chemical
Type of bonding forces	Van der Wals	Similar to chemical bond
Adsorption heat	Low, 10–40 kJ mol ⁻¹	High, 20–400 kJ mol ⁻¹
Chemical change of adsorptive	None	Formation of a surface compound
Temperature range	Negative	Positive
Specificity of adsorbate-adsorbent interactions	Very low	High
Reversibility	Fully reversible	Irreversible
Activation energy	Low (close to zero)	High, similar to chemical reaction

2.3 ADVANTAGES OF THE ADSORPTION PROCESS

The adsorption process is the best method for wastewater treatment. When compared with conventional methods, especially the biological method, adsorption is favorable due to its superiority in reducing organic pollutants from industrial effluents (Varghese *et al.*, 2017). Investigations conducted by water researchers showed that adsorption method can remove up to 99.9 % (Makhathini and Rathilal, 2017). Additionally, the technique has a high impact in wastewater treatment in terms of low maintenance, profitability, high removal efficiency, minimization of chemical or biological sludge, ease of operation, flexibility, regeneration as well as the production of high-quality treated effluents (Kandisa *et al.*, 2016, Lima and safety, 2018). Other benefits of the adsorption method include removal of organic pollutants such as phenols, nitrophenols and nitrobenzene pollutants present in aqueous solution even at very low concentrations (Lima and safety, 2018).

Fig 2.1 shows the basic definition of adsorption (Konggidinata, 2017). Three major interactions existing in aqueous solution adsorption processes include aqueous-surface interaction, adsorbate-aqueous interaction as well as adsorbate-surface interaction. The solubility of the adsorbate is used to determine the interaction between adsorbate-aqueous whereas the surface chemistry is used to determine the aqueous-surface and adsorbate-surface interaction (Crittenden *et al.*, 2012, Konggidinata, 2017).

2.3.1 Adsorption mechanism

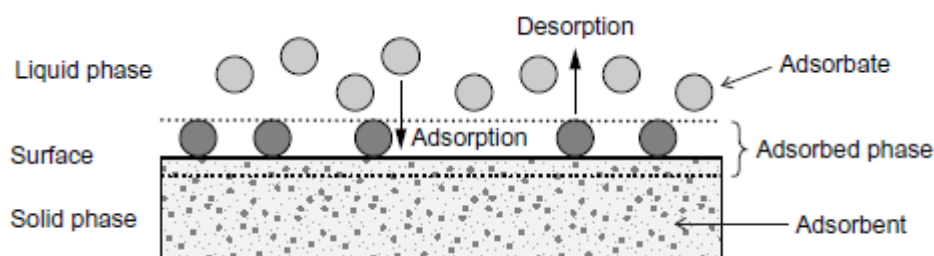


Figure 2.1: Schematic diagram of adsorption model (Worch, 2012, Konggidinata, 2017).

2.3.2 Factors affecting adsorption

The factors affecting the adsorption process include: the nature of the adsorbent, adsorbate, adsorbent surface area (large size implies a greater adsorption capacity), particle size (smaller particle size reduces internal diffusional and mass transfer limitation to the penetration of the adsorbate inside the adsorbent) the adsorbent should be capable of being easily regenerated (Le-Minh *et al.*, 2018).

The pollutants and adsorbent functional groups interactions are not only dependent on the nature of the adsorbent but also on the solution chemistry. The sorption capacity of many adsorbents depends on many experimental parameters: solution pH (the degree of ionization of a species is affected by the pH), the temperature at which the experiments are carried out, initial concentration of the aqueous solution, the mixing strength, contact time or residence time (the longer the time the more complete the adsorption will be), competing ions (effluent composition), affinity of the solute for the adsorbent, porosity, surface chemistry solubility of adsorbate in wastewater, hydrophobicity, acidity or basicity and differences in molecular weight or polarity which results in several molecules being strongly bonded on the surface than others (Barkakati *et al.*, 2010, Le-Minh *et al.*, 2018).

2.4 TYPES OF ADSORBENTS

An adsorbent is a porous substance having a high micropore volume and can adsorb substances onto its surface by intermolecular forces (Pholosi *et al.*, 2013). Adsorbents may be of organic, mineral or biological origin (Crini *et al.*, 2018) The choice of an adsorbent, technical applicability and cost-effectiveness are the key factors that determine the selection of the most suitable adsorbent (Wang *et al.*, 2018).

It is evident from the literature that the success or failure of adsorption separation mainly depends on the performance of the adsorbents in both kinetics and equilibrium studies. For example, an adsorbent with good capacity but slow kinetics is not a good choice as it takes adsorbate molecules too long a time to reach the particle interior (De Folly D'auris, 2012). On the other hand, an adsorbent with fast kinetics but low capacity is not good either as a large amount of solid is required for a given throughput. It can be concluded that a good adsorbent is the one that provides good adsorptive capacity as well as good kinetics by satisfying these two aspects.

2.4.1 Commercial adsorbents

In order to control pollution, researchers have employed different adsorbents in wastewater such as organoclays, activated carbon, silica gel, zeolites, activated alumina (Bhatnagar *et al.*, 2015, Hokkanen *et al.*, 2016, Singh and Gupta, 2016).

2.4.1.1 Activated carbon

Activated carbon is a black powdered solid substance naturally occurring from carbonaceous materials such as coal, coconut shells, lignite, and wood (Konggidinata *et al.*, 2017). It is produced using one of the two basic activation methods: physical and chemical process. The methods involve dehydration and carbonization followed by activation. Different organic and inorganic pollutants such as anions, metal ions, phenols and chlorinated hydrocarbons have been removed from wastewater using activated carbon (Zhang *et al.*, 2016). Advantages of activated carbon include low cost, large mesopores, and micropore volumes (specific surface area 100–2000 m²/g), pore size ranging from (less than 2 nm) to micropores more than 50 nm (Fu and Wang, 2011, Deliyanni *et al.*, 2015, Wjihi *et al.*, 2017). Despite the success of activated carbons inorganic and organic pollutant removal from wastewater, their applications are limited by lower adsorption capacity due to the inaccessibility of some sorption sites to the adsorbates, higher cost during synthesis, restricted by regeneration problems, pore clogging, lower selectivity and limited modification flexibility (Ren *et al.*, 2016, Konggidinata *et al.*, 2017). For this reason, scientists have attempted to synthesise other low-cost adsorbents to replace activated carbons.

2.4.1.2 Zeolites

Zeolites are microporous crystalline, hydrated aluminosilicates of alkali and alkaline earth metals, having infinite, three-dimensional structures (Choi *et al.*, 2016). These three-dimensional structures of zeolite possess large channels containing negatively charged sites resulting from Al³⁺ replacement of Si⁴⁺. The structure of zeolite has properties such as ion exchange, molecular sieving, catalytic and adsorption properties (Wdowin *et al.*, 2014, Bandura *et al.*, 2015, Kyzioł-Komosińska *et al.*, 2015, Woszuik and Franus, 2016). They can be of natural or synthetic origin, and the advantages include high surface area, stability, ion exchange, adsorption and molecular sieving (Guarino Bertholini, 2016, Moshoeshoe *et al.*, 2017).

2.4.1.3 Silica gel

Silica gels prepared by the coagulation of colloidal silicic acid results in the formation of porous and nanocrystalline granules of different sizes (Curdts *et al.*, 2015). They can be classified into three forms: low density, regular, and intermediate gels. Silica gel shows a higher surface area, high porosity and extremely low densities due to the open pore structure of the mesopore (Twej *et al.*, 2016). Intermediate and low-density silica gels have low surface areas, about 300-350 and 100-200 m²/g (Bhatnagar and Sillanpaa, 2010, Mishra, 2016). Silica gels are utilized in the dehumidification process due to their great pore surface area and good adsorption capacity (Abtab *et al.*, 2018). Modified forms of silica have been used for the sequestration of different pollutants (Guerra *et al.*, 2018).

2.4.1.4 Clay minerals

Natural clays in wastewater treatment have been investigated for several years. Their advantages include good sorption properties, low cost, natural occurrence. The three main types of clays are smectites (bentonites), mica and kaolinite (Ismadji *et al.*, 2015). Among these, bentonites (montmorillonite) hold the highest cation exchange capacity, it can be regenerated, and it is highly selective (Tripathi and Ranjan, 2015). Despite the advantages, organoclays are deemed unsuccessful for the removal of non-polar hydrophobic, and non-ionic organic contaminants due to the hydrophilic nature of their surfaces and charges, high costs of the stabilizing agent and regeneration problems (Carvalho *et al.*, 2012, Anjum *et al.*, 2018).

2.5 IRON OXIDE MAGNETIC NANOPARTICLES

Magnetic nanoparticles can be described as materials composed of polymeric shell and magnetic cores (Rakhshae and Panahandeh, 2011, Nasirimoghaddam *et al.*, 2015). Iron oxide magnetic nanoparticles are part of nanomaterials which can be easily manipulated under a magnetic field. The crystalline forms of iron oxide include magnetite (Fe₃O₄), Wüstite (FeO), hematite (α -Fe₂O₃) and maghemite (γ -Fe₂O₃, β -Fe₂O₃, ϵ -Fe₂O₃) (Estelrich *et al.*, 2015). When compared to the other iron oxides, for example, maghemite (γ -Fe₂O₃), magnetite (Fe₃O₄) have better advantages due to their superparamagnetic properties (Baharuddin *et al.*, 2018, Fernández-Bertolez *et al.*, 2018). Both maghemite and magnetite are part of a class of compounds known as inverse spinel ferrites. In magnetite, iron ions fully occupy the

octahedral (Oh) and tetrahedral (Td) sites of the spinel structure while in maghemite cationic vacancies exist within the octahedral site (Ahmed *et al.*, 2018).

2.5.1 Uses of Iron oxide nanoparticles

Magnetite has received much attention due to its better saturation magnetization values compared to maghemite. It has been applied in different areas of research as contrast agents for magnetic resonance imaging (MRI), separation of biochemical products, magnetically targeted drug delivery, catalysis, hyperthermia treatment processes, enzyme immobilization and thermoablation agents as well as wastewater treatment (Sharma *et al.*, 2015, Zamora-Mora *et al.*, 2015, Kaamyabi *et al.*, 2016, Baghayeri *et al.*, 2018). Magnetism is an independently unique physical property that helps in water refinement by influencing the physical properties of contaminants in water (Zaidi *et al.*, 2014). Adsorption processes and magnetic separation have been extensively used in wastewater treatment (Simonsen *et al.*, 2018).

2.5.2 Advantages of Iron oxide nanoparticles as an adsorbent in wastewater treatment

The application of magnetic adsorbent technology to solve environmental problems has received considerable attention in recent years. Choosing the best method and material for wastewater treatment is a complex task. To do this, a number of factors like the quality standards, cost, efficiency and reusability are important (Oller *et al.*, 2011, Crini *et al.*, 2018). The physical, biological and chemical properties of iron oxide make it of interest and it is considered an alternative adsorbent over classical adsorbents (Lu and Astruc, 2018). Some of the advantages of iron oxide nanoparticles includes: low-cost, large surface area to volume ratio due to high active sites, less toxicity, superparamagnetic properties and reusability (Abbas *et al.*, 2014, Al-Hussain *et al.*, 2018, Fleck *et al.*, 2018, Lu and Astruc, 2018).

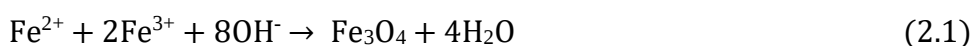
Although iron oxide nanoparticles are highly efficient for wastewater treatment, they have limitations. They can easily aggregate, and their magnetic properties can be altered in complex environmental and biological systems. In order to improve the stability and biocompatibility, the superparamagnetic iron oxide nanoparticles are often modified with some surfactants or polymers (Mahmoudi *et al.*, 2011).

2.5.3 Preparation of Superparamagnetic Iron Oxide Nanoparticles

Iron oxide nanoparticles with appropriate surface chemistry can be synthesized via different methods. The available methods are thermal decomposition, coprecipitation, solvothermal, sonolysis, spray and laser pyrolysis, hydrothermal and high-temperature synthesis, nanoreactors, such as protein cages, vesicles, microemulsions, and microwave-assisted synthesis. Among these methods, the most commonly used are coprecipitation, thermal decomposition and microwave-assisted synthesis (Moosavi *et al.*, 2017, Pourgolmohammad *et al.*, 2017).

2.5.4 Production of magnetic nanoparticles via co-precipitation method

The co-precipitation method has been given much attention in recent years. This method is based on precipitation of magnetite by adding a strong base to a solution of ferrous/ferric salts in water in an alkaline medium (Rashad *et al.*, 2018). Nanoparticles of small size have been synthesized using this simple and cost-effective co-precipitation method (Rashad *et al.*, 2018). The composition of particles and particle size may be controlled by optimizing parameters such as the Fe (II)/Fe (III) salt ratio, synthesis conditions such as reaction temperature, pH, time, amount of base and ionic strength (Saif *et al.*, 2016). During the synthesis of iron oxide nanoparticles, complete precipitation occurs between pH 8 and 14 (Ali *et al.*, 2016, Macias-Martinez *et al.*, 2016). The nanoparticles produced by the co-precipitation method are highly aggregated with a spherical shape (Wang *et al.*, 2015). The inlet of nitrogen to the reaction helps to stop the magnetite from oxidation and helps reduce the magnetite particle size. Nanoparticles of size ranging between 10-20 nm have been produced using the co-precipitation method (Rashad *et al.*, 2014). The main limitations of co-precipitation are that at the particle size is not, relatively, small and monodispersed enough for specific applications (Kumar *et al.*, 2015, Rashad *et al.*, 2018). Equation 2.1 shows the overall reaction leading to the precipitation of black magnetite (Wang *et al.*, 2015).



2.5.5 Production of magnetic nanoparticles via microwave heating

The microwave technique can be used to heat dielectric materials due to electromagnetic radiation (Li *et al.*, 2013, Wong and Gupta, 2015). The difference in conventional and microwave heating is the way in which the heat is generated (Mello *et al.*, 2014). In

microwave heating, the energy is easily transformed into heat within the particles by dipole rotation and ionic conduction (Anwar *et al.*, 2015). As soon as a high-frequency voltage is applied to a sample material, the molecules with an induced dipole moment, due to the applied electrical field, align in the direction opposite to that of the applied field. Thus, the heat is directly generated by dipole-dipole rotation of molecules and friction within a matrix (microwave irradiation) (Destandau *et al.*, 2013, Mello *et al.*, 2014). Therefore, a large temperature gradient develops from the interior of the sample particle to its cool surface (Mello *et al.*, 2014).

Nanoparticles produced by the fast and simple microwave-assisted process of the spinel structured $M^{II}Fe_2O_4$ ($M = Co, Mn$) have diameters less than 20 nm (Sunija Sukumaran, 2018). The decrease in particle sizes is attributed to the fast and homogeneous reactions that occur during synthesis. They asserted that the microwave heating method is highly effective for the synthesis of magnetite (Fe_3O_4) and hematite ($\alpha-Fe_2O_3$) using $FeCl_3$, polyethylene glycol, and $N_2H_4.H_2O$. The $N_2H_4.H_2O$ influences the final phase of Fe_3O_4 , while the microwave heating plays an important role in the shape of nanocrystals. At higher amounts of $N_2H_4.H_2O$ only the single phase of Fe_3O_4 can be formed but at lower amounts, the product consists of mixtures of Fe_3O_4 and $\alpha-Fe_2O_3$ (Faraji *et al.*, 2010). Ellipsoidal $\alpha-Fe_2O_3$ nanoparticles have been prepared by microwave heating while a mixture of irregular $\alpha-Fe_2O_3$ NPs and rods have also been prepared by the oil bath (Sunija Sukumaran, 2018).

The application of microwave heating into the reaction system has many advantages when compared to the co-precipitation method, this includes: efficient heating to the desired temperature, high phase purity, increased reaction kinetics, easy functionalization, high crystallinity, and good reliability and reproducibility (Zhu and Chen, 2014, Ali *et al.*, 2016, Gharibshahian *et al.*, 2017, Farinas *et al.*, 2018). The synthesis of large amounts of magnetic nanoparticles in a short time shows great potential for industrial production.

2.5.6 Production of magnetic nanoparticles by thermal decomposition

The synthesis of magnetic nanoparticles using a decomposition technique generally involves the chemical decomposition of the substance at an elevated temperature which breaks the chemical bonds. The technique specifically involves thermal decomposition of iron-oleate complex derived from an iron precursor such as iron cup ferrates iron pentacarbonyl, and iron oxyhydroxide (Hufschmid *et al.*, 2015). This is achieved using organic solvents and stabilizing

surfactants such as oleic acid and stearic acid (Majewski and Thierry, 2007, Hufschmid *et al.*, 2015). Magnetic nanoparticles of between 4 and 40 nm have been produced by this method. The decomposition method offers much better control over the size of the magnetic nanoparticles. However, the major limitation of this method is the use of surfactants which may decrease the biocompatibility of the product (Hufschmid *et al.*, 2015, Lassenberger *et al.*, 2017). The iron precursor (iron oxo-hydrate), surfactant (oleic acid), and solvent (1-octadecene) give an intermediate iron-oleate complex that is thermally decomposed upon heating the reaction mixture at 320 °C to form magnetic nanoparticles (Bauer *et al.*, 2016, Lassenberger *et al.*, 2017).

2.5.7 Magnetite-organic acid composites

Surface coating of the nanoparticles provide colloidal stability by steric and/or electrostatic repulsion and prevents aggregation (Araujo-Neto *et al.*, 2014). A number of organic and inorganic coating agents have been used, examples are polymers (e.g., chitosan, polyethylene glycol and dextran), inorganic materials (examples are silica, gold, carbon and alumina), and liposome and carboxylic (oleic, palmitic and citric) acids (Karimi *et al.*, 2013, Araújo-Neto *et al.*, 2014). Sodium oleate and oleic acid have high affinity to the surface of iron oxide particles, being effective in the stabilization of nanoparticles by steric repulsion. (Liu *et al.*, 2018).

2.5.7.1 Organic modification

2.5.7.1.1 Surfactants

The surface of magnetite can be stabilized with different organic, stabilizing agents. Coatings displaying different functional groups such as amines, thiols, and carboxylic acids can improve the stability of MNPs by adjusting their hydrophobicity and their surface charge (Liu *et al.*, 2018). Among these organic surfactants, oleic acid is the most favorable capping agent because oleic acid binds strongly to the surface of metals with native oxides through the carboxyl group. Oleic acid is shown to be superior when compared to other surfactants like stearic acid, citric and myristic acid and palmitic acid (Wu *et al.*, 2010, Vorobiova *et al.*, 2017). Synthesized Co NPs were used to investigate the difference between the capping agents in their ability to affect the controlling size, distribution and air stability of MNPs. It was revealed that using stearic acid resulted in poor stability due to its linear conformation

(Vorobiova *et al.*, 2017). Unlike oleic acid, there is no C = C double bonding in the chain of stearic acid.

The interaction of double bonding within oleic acid assists in the formation of a densely packed layer on the surface of Co nanoparticles (Jovanovic *et al.*, 2014). The overlapping of double bonds between adjacent molecules enhances the hardness of the capping layer by impacting a densely packed surface layer which is harder than those formed from aliphatic acids. The existence of a double bond in oleic acids makes it possible to form magnetic gels by polymerizing and cross-linking the double bonds during the evaporation of the solvent (Aggarwal, 2014).

2.5.7.1.2 Modification of the iron oxide nanoparticles using organic acid

Two methods used in the surface modification are the electrostatic and steric method (Yu *et al.*, 2017). For steric modification, the oleic acid is the most used, (Soares *et al.*, 2014). Oleic acid is an odorless, colourless fatty acid found naturally in various vegetables, animal fats, and oils (Kumar *et al.*, 2017). In nature, oleic acid is a monounsaturated omega-⁹ fatty acid and has a chemical formula of $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$. Oleic acid is derived from olive oil. While palmitic is one of the most common saturated fatty acids found in animals and plants and has a chemical formula of $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$. Oleic and palmitic acid have similar properties but differ in the carbon chain length with oleic acid possessing higher carbon chain (C_{18}) and palmitic having shorter carbon chain (C_{16}). Electrostatic stabilization can be obtained by applying such mechanisms as preferential adsorption of ions, dissociation of surface charged species, isomorphic substitution of ions, accumulation or depletion of electrons at the surface, and physical adsorption of charged species onto the surface (Yu *et al.*, 2017, Klekotka *et al.*, 2018).

Oleic and palmitic carboxylic acids are the most used small molecules which are biocompatible with magnetite (Cano *et al.*, 2012, Agrawal *et al.*, 2017). They act as a surfactant and help to reduce the particle size of MNPs. The surface of magnetite nanoparticles can be stabilized in an aqueous dispersion by the adsorption of carboxylate acid because of the strong chemical bond between the carboxylic acid and the amorphous iron oxide nanoparticles (Gruar *et al.*, 2015, Wu *et al.*, 2015, Klekotka *et al.*, 2018).

Oleic acid and palmitic acid have a non-polar hydrocarbon tail with an affinity for the non-polar liquid medium and a polar carboxylic acid head group with an affinity for the hydrophilic particle surface (Bateer *et al.*, 2013, Shete *et al.*, 2015). The carboxylate anions are known to coordinate with the surface of magnetite, presumably through coordination of iron atoms with both the carboxylate oxygen (Bateer *et al.*, 2013, Korpany *et al.*, 2017). The polar head group is anchored on the magnetite surface and the non-polar tail extends into solution causing the magnetite to be hydrophobic and dispersible in organic solvents (Shete *et al.*, 2015). The cis double bond in the structure is the dominant feature responsible for the lack of aggregation among particles. Studies have reported the adsorption of this long chain fatty acid onto magnetite in monolayer coverage via formation of chelating bidentate with surface iron atoms (Zhang *et al.*, 2006, Hajdu *et al.*, 2008). The incorporation of capping ligands immediately after nanoparticle formation was ideal due to the ability of organic coating cis to inhibit growth and to maintain the already-formed MNPs at a size with no additional enhancement in diameter. surfactants capable of nanoparticles growth control are commonly associated with the production of smaller and more monodispersed MNPs (Connie and Ariya, 2015).

2.5.7.1.3 Potential adsorption mechanism

The BTX adsorption mechanism onto Fe_3O_4 nanoparticles can be described in relation to acid-base chemistry (Eltouny *et al.*, 2012). Studies conducted by Joseph *et al.*, 2000; Sasaki and Tanaka, 2011 suggested that the adsorption mechanism involves the electron donation from the phenyl ring of each BTX compound to surface iron atoms of the magnetite. The interaction of π -electrons highly depends on the availability of numbers of surface-active sites on adsorbent, structure, orientation as well as the configuration of the adsorbate which could potentially activate side chain interactions (Joseph *et al.*, 2000).

Qualitative data on adsorption angles suggests a perfectly flat configuration of the phenyl group onto the nanoparticles surface to be most favorable (Joseph *et al.*, 2000). The electron donating substituent group of benzene, toluene and xylene supplies electrons to the aromatic ring and in turn provides electron density to unoccupied 3d orbitals of iron cations which display Lewis acid character (Joseph *et al.*, 2000; Sasaki and Tanaka, 2011). Without an electron donating substituent group, benzene is insufficient in establishing a favorable

interaction through π -electrons; as such would perturb the resonance stability in the aromatic ring.

2.6 RESPONSE SURFACE METHODOLOGY (RSM)

RSM is one of the oldest techniques used by researchers. Recently, it has been used in food science, chemistry, and chemical engineering. It is currently gaining more attention in wastewater treatment. It was introduced by Box and Wilson (1951). Box and Wilson described RSM as a collection of mathematical and statistical techniques that are useful for modeling and analysis of problems in which a response of interest is influenced by numerous variables and the aim is to optimize this response. Other researchers also concurred with Wilson to say that RSM is one of the most efficient statistical methods for the modeling and optimization of various variables to predict the best performance conditions with a minimum number of experiments (Montgomery *et.al.*, 2017). In RSM methodology, regression is performed on the data collected where the observed variable (response) is approximated based on a functional relationship between the estimated input variables. Factors or independent variables are experimental variables that can be changed independently of each other. Levels of a variable are different values of a variable at which the experiments must be carried out. Responses or dependent variables are the measured values of the results from experiments. Residual is the difference between the calculated and experimental result for a determinate set of conditions. A good mathematical model fitted to experimental data should present low residual values (Ali *et al.*, 2018).

2.6.1 The design procedure (RSM)

The design procedure of RSM have several stages, these can be sourced out from Steppan, 1998 as follows: (1) The selection of the most important independent variables and their level on the system through screening studies; (2) The choice of the experimental design and carrying out the experiments according to the selected experimental matrix; (3) The mathematic–statistical treatment of the obtained experimental data through the fit of a polynomial function (4) The evaluation of the model's fitness; (5) The verification of the necessity and possibility of performing a displacement in the direction of the optimal region and (6) Obtaining the optimum values for each variable.

2.6.2 Central Composite Design (CCD)

The Central Composite Design (CCD) was employed by Ghorbannerzhad et al (2018) to investigate the linear, quadratic, cubic and cross-product effects of the three experimental parameters on the combined effects of operating parameters such as pyrolysis temperature, biomass ratio, and the acidity of the HZSM-5 catalyst. Mehrizard et al (2016) also used the CCD approach to study four experimental parameters such as initial 1-chloro-4-nitrobenzene (1C4NB) (mg/L^{-1}), carbon nanofibers (CNFs) dose (mg/L^{-1}), initial pH of the solution and contact time (min). The results obtained by these researchers confirms that RSM by CCD approach is one of the most effective and fast methods to optimize working conditions. The central composite design comprises a two-level full factorial design, star points, and centre points. In CCD the value of α is fixed at 2. The complete design matrix of the experiments and results are normally given in the form of a table. The experiment sequence is randomized to minimize the effects of the uncontrolled factors. Each response is used to develop a mathematical model that correlates it to the experimental variables through first order, second order, third order and interaction terms, according to a third order polynomial equation with equation (2.3) as an illustration.

Normally the design experiments are repeated several times and the one that is close to average is recorded. Additionally, if all variables are assumed to be measurable, the response surface can be expressed as follows:

$$y = f(x_1, x_2, \dots, x_k) \quad (2.2)$$

$$Y = \beta_0 + \sum_{j=1}^4 \beta_j X_j + \sum_{i,j=1}^4 \beta_{ij} X_i X_j + \sum_{j=1}^4 \beta_{jj} X_j^2 + \sum_{k,i,j=1}^4 \beta_{kij} X_k X_i X_j + \sum_{j=1}^4 \beta_{jjj} X_j^3 \quad (2.3)$$

The goal is to optimize the response variable y . It is assumed that the independent variables are continuous and controllable by experiments with negligible errors. It is required to find a suitable approximation for the true functional relationship between independent variables and the response surface. Usually, a second-order model is utilized in response surface methodology, (2.3) where ε is a random error. The β coefficients, which should be determined in the second-order model, are obtained by the least square method. In general, (2.3) can be written in matrix form.

$$Y = bX + E \quad (2.4)$$

where Y is defined to be a matrix of measured values, X to be a matrix of independent variables. The matrixes b and E consist of coefficients and errors, respectively. The solution of (2.4) can be obtained by the matrix approach.

$$b = (XTX)^{-1}XTY \quad (2.5)$$

where XT is the transpose of the matrix X and $(XTX)^{-1}$ is the inverse of the matrix XTX .

The mathematical models are evaluated for each response by means of multiple linear regression analysis. The modelling starts with a quadratic model including linear, squared and interaction terms. The significant terms in the model are found by analysis of variance (ANOVA) for each response. The significance is normally judged by determining the probability level that the F-statistic calculated from the data is less than 5 %. The model adequacies are checked by R^2 , adjusted- R^2 , predicted- R^2 and prediction error sum of squares (PRESS). A good model will have a large predicted R^2 and a low PRESS. After the model fitting is performed, the residual analysis is conducted to validate the assumptions used in the ANOVA. This analysis includes calculating case statistics to identify outliers and examining diagnostic plots such as normal probability plots and residual plots.

2.7 MODELING OF ADSORPTION EXPERIMENTAL DATA

2.7.1 Kinetic studies

The experimental data is analyzed using kinetic parameters to determine the mechanism and efficiency of the adsorption process. Adsorption reaction orders are studied using different kinetics adsorption reaction models such as pseudo-first-order and pseudo-second-order models. Reaction order of adsorption systems based on solution concentration has also been investigated (Sud *et al.*, 2008; Ofomaja *et al.*, 2013). Adsorption and desorption are both dependent on time. Predicting the rate at which adsorption takes place is an important factor in adsorption system design and evaluation of adsorbent. Hence, it is of great importance to determine the adsorption and desorption kinetics and compute the parameters characterizing the transport of adsorbate within adsorbents. This study, therefore, focuses on the incorporation of oleic and palmitic acids onto magnetite and examines the kinetics and

mechanism of the BTX uptake and competitive BTX adsorption from aqueous solution. It uses the nonlinear regression program of the KyPlot 2.0 software, with a Quasi-Newton algorithm for finding the parameter values that minimize the sum of the squares of the errors (ERRSQ). The variance error methods were applied in the determination of best fit.

2.7.1.1 Pseudo-first-order

The Pseudo-first-order is when the adsorption follows diffusion through a boundary, the kinetics was proposed by Lagergren (1898). It is represented as:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (2.6)$$

The nonlinear form of the pseudo-first-order equation can be written as

$$q_t = q_e(1 - \exp^{-k_1 t}) \quad (2.7)$$

where q_t and q_e are the amounts sorbed at time t and at equilibrium and k_1 is the rate constant of the pseudo-first-order.

2.7.1.2 Pseudo-second-order

The pseudo-second-order chemisorption kinetics may be expressed as (Ho, 1999).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2.8)$$

This equation can be rearranged to the nonlinear form.

$$q_t = \frac{t k_2 q_e^2}{1 + k_2 t q_e} \quad (2.9)$$

2.8 CONCLUSION

Substantial research has been done to investigate the adsorptive capability of pure and coated magnetite nanoparticles for removal of organic pollutants. A literature search shows that modifying the pure magnetite using long chain carboxylic acids improves its stability and makes the surface of the magnetite hydrophobic so that it can remove non-ionic compounds however the adsorptive capabilities of BTX has not been attempted. It is the aim of this research to synthesize a hydrophobic adsorbent using oleic and palmitic acid via microwave method and explore its ability to remove BTX from aqueous solution as this has not yet been attempted.

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CHAPTER 3

3 EXPERIMENTAL PROCEDURES

3.1 INTRODUCTION

This chapter describes the synthesis and characterization of adsorbent materials used in this study including the pure magnetite, magnetite-oleic acid and magnetite-palmitic acid composites. The experimental procedures used for sample preparation and the modification of the magnetite nanoparticles by oleic and palmitic acid are also explained in detail. Response surface methodology using Central Composite Design, (CCD) approach was used to optimize the preparation of the magnetite-organic acid composite. A total number of 50 samples of the magnetite-oleic and magnetite-palmitic acid composites using one-step microwave method were produced. The microwave technique was used due to advantages such, increased product yield, reduction in synthesis time (from hours to minutes), and improved material properties (e.g. small particle size), when compared to the conventional heating methods (Charde *et al.*, 2012). The coating procedure of the pure magnetite using the two organic acids was done to stabilize the magnetite nanoparticles and make them hydrophobic. The adsorbents were characterised using Rigaku NEX-QC model X-ray fluorescence (XRF), conductivity (S/cm) meter, Fourier transform infrared instrument (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscope (SEM), electron dispersive x-ray spectroscopy (EDX), vibrating-sample magnetometer (VSM), transmission electron microscope (TEM), (Brunauer–Emmett–Teller) BET surface area and pH_{pzc} . The chapter also presents a section that involves the application of the pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid for the uptake of BTX from aqueous solution. The batch adsorption studies, and kinetic studies were also determined.

3.2 SAMPLE PREPARATION

3.2.1 Materials

Ammonium hydroxide (NH_4OH , 25 %) was supplied by Labchem (South Africa). Hydrochloric acid (25 %), Sulphuric ($\text{H}_2\text{SO}_4 > 98\%$) and ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O} > 98\%$) were supplied by Merck. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O} > 99\%$), oleic acid $\geq 99\%$, palmitic acid $\geq 95\%$, benzene, for HPLC, $\geq 99.9\%$, toluene, 99.8%, xylene, 99.0 %, ethanol, 96% and were purchased from Sigma-Aldrich. All chemicals were used without any further

purification. All syntheses were carried out under nitrogen atmosphere with vigorous stirring to ensure uniform dispersions.

3.2.2 Synthesis of the magnetite-organic acids composites via microwave method

A stock solution of 0.2 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.1 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was freshly prepared in an acidic medium of HCl and H_2SO_4 respectively. The one-step synthesis of magnetite-oleic acid composite was carried out in a three-neck flask by mixing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution at a ratio of 1:2. Ammonium hydroxide was used as a precipitating agent. The solution was purged with nitrogen gas to minimize oxidation and was heated at 70 °C under constant magnetic stirring at 300 rpm for 10 min. After 10 min a black precipitate was formed, oleic acid was added into the black solution to introduce hydrophobicity, the solution was left to continue stirring for 5 more min after the oleic acid was added. The magnetite-oleic acid composite was then subjected to domestic Kelvinator microwave oven heating for another 5 min at a microwave power of 200 W. The black magnetite-oleic acid precipitate formed was separated by magnetic decantation. The precipitate was washed several times with distilled water to remove any impurities present then washed with ethanol and dried at 60 °C for 2 hrs and later used for further characterization. The magnetite-palmitic acid composite material was prepared in a one-step synthesis method similar to the method described above for magnetite-oleic acid composite.

3.2.2.1 Proposed reactions for the magnetite-organic acid composites

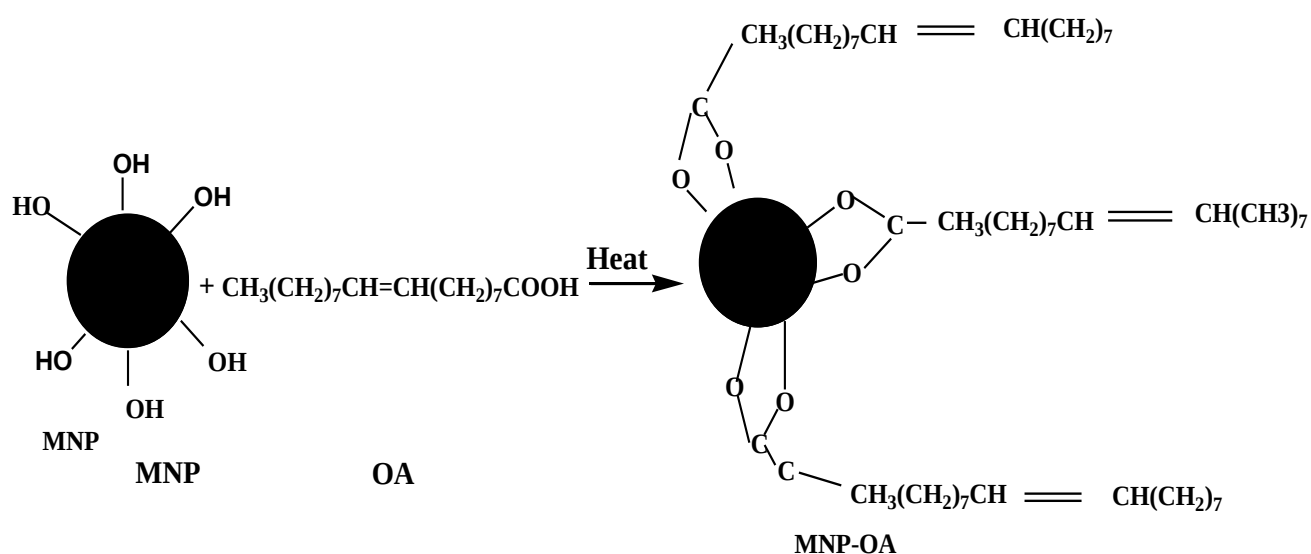


Figure 3.1: Proposed reaction for the preparation of magnetite-oleic acid composite.

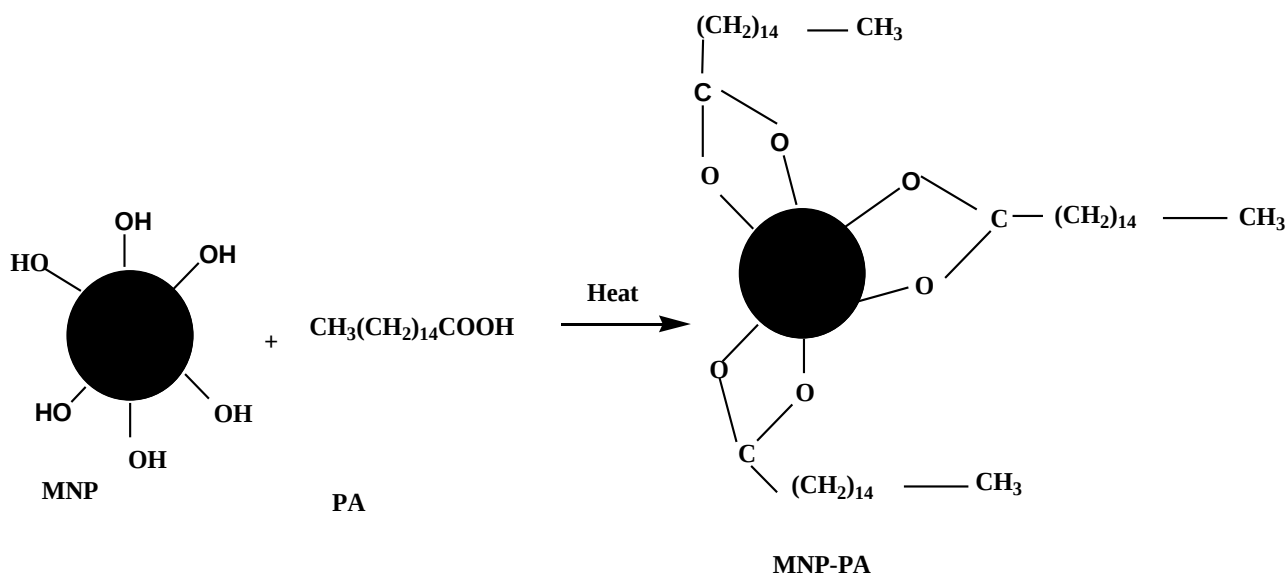


Figure 3.2: Proposed reaction in the preparation of magnetite-palmitic acid composite.

3.2.3 Experimental design for the synthesis of magnetite-organic acid composites and statistical analysis

The Response Surface Method (RSM) using Central Composite Design (CCD) approach was used to determine the optimum values. A total number of 50 experiments were done to optimize the working condition of the magnetite-oleic and magnetite-palmitic acid composites, respectively. The number of experimental runs created from a partial factorial design had five variables and three responses. The variables contained 32 factorial points, 10 axial points and eight replicates at the center points. The five experimental parameters were: the $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution (mL), microwave power (W), NH_4OH volume (mL), reaction time (min), and volume of acid (oleic and palmitic) (mL). The percentage of iron (% Fe), conductivity, BTX adsorption process were the responses of the study. The fitting of the quadratic and as cross-products effects was also obtained from the RSM software.

Table 3.1: The range and levels of independent variables for experimental design using central composite design (CCD).

Factor	Name	Units	Minimum	Maximum	Coded	Values	Mean
A	Fe ³⁺ /Fe ²⁺	mL	0.50	2.0	-1.0 = 0.5	1.0 = 2.0	1.25
B	Microwave Power	W	200	800	-1.0 = 200	1.0 = 800	500
C	Volume of NH ₄ OH	mL	2.0	8.00	-1.0 = 2.0	1.0 = 8.0	5.0
D	Time	Min	5.0	15.00	-1.0 = 5.0	1.0= 15.0	10.0
E	Volume of Acid	mL	0.2	4.00	-1.0 = 0.2	1.0 = 4.0	2.10

3.3 CHARACTERIZATION OF THE MAGNETITE-ORGANIC ACID COMPOSITE

3.3.1 X-Ray Fluorescence (XRF)

XRF was employed to determine the % Fe in the magnetite-organic acid composites (magnetite-oleic and magnetite-palmitic). The method is quick and highly reliable because of its accuracy. The % Fe₃O₄ content was measured with a Rigaku NEX-QC model X-ray fluorescence (XRF) machine, using magnetite analysis application mode.

3.3. 2 Conductivity (S/cm)

The effect of the synthesis variables on the conductivity (S/cm) of the magnetite-organic acid composites were assessed by dissolving the adsorbent in 10 mL of distilled water and 20 mL ethanol mixture. The mixture was sonicated for 10 min, a conductivity meter (Oakton™ PC 700 pH/conductivity, Pittsburgh,1902) was then inserted in the sonicated solution and the reading observed were recorded.

3.3.3 Fourier-Transform Infra-Red spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy was carried out on a PerkinElmer spectrum 400 FT-IR/NIR spectrometer to determine surface functional groups and the effects of magnetite-organic acid composite (magnetite-oleic and magnetite-palmitic acid) (Ofomaja, 2010, Yang *et al.*, 2010).

3.3.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) technique was used to measure the amount and rate of change in the weight of a sample as a function of temperature in an inert environment. The adsorbents were weighed into quartz crucibles and subjected to pyrolysis from 30 to 900 °C in a N₂/air environment at a heating rate of 10 °C/min using Perkin- Elmer STA 6000, of Perkin-Elmer life and analytical sciences 710 Bridgeport Avenue Shelton, Connecticut 06484 (USA).

3.3.5 X-Ray Diffraction spectroscopy (XRD)

X-ray diffraction (XRD) analysis was conducted to identify the chemical crystallographic structure of the pure magnetite and magnetite-oleic and magnetite-palmitic acid composites. An X'Pert PRO X-ray diffractometer (PANalytical, PW 3040/60 XRD; CuK α anode; λ = 0.154 nm) was used to obtain the XRD patterns. The samples were placed in an aluminum holder and scanned at 45 kV and 40 mA from 10 to 120° 2 θ , the exposure time for each sample was 20 minutes and a step size of 0.02 °. The Debye-Scherrer equation was used to determine particle sizes of the three prepared adsorbents, (Burton *et al.*, 2009, Li *et al.*, 2010).

$$d = \frac{0.89 \lambda}{\beta \cos \theta} \quad (3.1)$$

Where, d is the particle size (nm), λ is the 0.154 nm (CuK α), β is $\frac{\text{FWHM}}{360 \times 2\pi}$ (FWHM is Full Width at Half Maximum) and θ is half of 2 θ (centre of peak).

3.3.6 Transmission Electron Microscopy (TEM)

The particle morphology, size and structure of MNP, MNP-PA and MNP-PA were determined on a FEI Tecnai F20 transmission electron microscope (TEM) at an acceleration voltage of 200kV High Resolution images of the materials for shape and size measurements were obtained

3.3.7 Vibrating Sample Magnetometer (VSM)

The magnetic properties of the MNP, MNP-PA and MNP-OA adsorbents was characterized using vibrating sample magnetometer of VSM. Magnetic measurements were carried out on a Lake Shore model 735 vibrating sample magnetometer at room temperature

3.3.8 Brunauer-Emmett-Teller Surface Area (BET)

The sample surface area, pore volume, and pore size of the MNP, MNP-PA and MNP-OA adsorbents were determined by N₂ adsorption at -196 °C using a Tristar 3000 analyser coupled to VacPrep 061 degassing unit. These instruments were both supplied by Micromeritics Instrument Corporation.

3.4 APPLICATION OF THE PREPARED ADSORBENTS ONTO BTX UPTAKE IN AQUEOUS SOLUTION

3.4.1 pH at point zero charge

To determine the pH at point zero charge (pH_{pzc}) of the of the MNP, MNP-PA and MNP-OA composites, the solid addition method was used (Ofomaja *et al.*, 2014). To a series of 100 mL conical flasks, 45 mL of 0.01 mol.dm⁻³ of a KNO₃ solution of known concentration was transferred. The pH values of the solution were adjusted from pH 3 to 12 by adding either 0.10 mol.dm⁻³ of HCl or NaOH. The total volume of the solution in each flask was made up to 50 mL by adding KNO₃ of the same strength. The pH_i values of the solution were accurately noted, and 0.1 g of either pure magnetite, magnetite-oleic and magnetite-palmitic acid composites was added to the flask, which was securely capped immediately. The suspension was shaken and allowed to equilibrate for 48 hrs with intermittent manual shaking. The pH value of the supplements liquids was noted. The difference between the initial and the final pH values ($\Delta\text{pH} = \text{pH}_i - \text{pH}_f$) was plotted against the pH_i. The point of intersection of the resulting curve at which $\Delta\text{pH} = 0$ gave the pH_{pzc}.

3.4.2 Effect of solution pH

The effect of solution pH on the equilibrium uptake of benzene, toluene and xylene (BTX) was investigated by accurately weighing 0.05 g of MNP, MNP-PA and MNP-OA materials in ten separate 250 mL beakers. To each of the 250 mL beakers, 50 mL of the 100 mg/dm³ BTX whose pH had been adjusted to several values between 3 to 12 by using 0.1 M HCl and 0.1 M NaOH solution were then separately added, ultrasonicated for one hour. Each solution was then separately transferred into a tornado instrument for agitation. The agitation speed and temperature were fixed at 300 rpm for 2 hrs at 299 K respectively then filtered to stop the adsorption process. After equilibrium, a clear organic solution was taken and analyzed with a Perkin-Elmer (USA) Lambda 25 UV-visible (UV-vis) spectrometer.

3.4.3 Adsorbent dose

The adsorbent dose on the equilibrium uptake of BTX was performed by agitating known masses (0.05, 0.1, 0.5, 1.0, and 1.5 g) of the three different materials (MNP, MNP-PA and MNP-OA). The experiment was investigated by adding each of the five known masses to five 250 mL beakers containing 100 mg/dm³ solution of benzene at pH 7, at pH 8 for toluene and at pH 8 for xylene. All the samples were separately ultrasonicated for an hr then each transferred into a tornado instrument in which they were agitated at a speed of 300 rpm and a temperature of 299 K for 2 hrs and then filtered. The filtrate was analyzed using a UV-Vis spectrometer.

3.4.4 Effect of initial concentration

To determine the effect of initial solution concentration, 0.1 g of all adsorbents were mixed with benzene, toluene and xylene solutions of concentrations of 100, 200, 250, 300 and 350 mg/dm³, agitated at 300 rpm for 2 hrs at constant pH, adsorbent dosage and contact time. The samples were then filtered and analysed using a Perkin-Elmer (USA) Lambda 25 UV-visible (UV-vis) spectrometer to determine the amounts of benzene, toluene, and xylene left in the solution.

3.4.5 Adsorption kinetics

Kinetic experiments were conducted with 0.1 g of adsorbent contacted with 100 mL of benzene, toluene and xylene, solutions of concentrations ranging from 100, 200, 250, 300 and 350 mg/dm³, agitated at 300 rpm for 2 hrs. An aliquot of sample (10 cm³) was withdrawn at various time intervals until equilibrium was reached. The samples were then filtered and analysed using a Perkin-Elmer (USA) Lambda 25 UV-visible (UV-vis) spectrometer to determine the amounts of benzene, toluene, and xylene left in the solution.

3.3.5 Desorption studies

Experiments on the desorption of (BTX) and reuse of the spent adsorbents were performed by subjecting the various adsorbents to five adsorption/desorption cycles. The adsorbents residue used in the system of 0.5 g MNP, MNP-PA and MNP-OA adsorbents were mixed with 100 mL of 200 mg/dm³ of benzene, toluene and xylene solution which was separated by centrifugation and washed with distilled water. The washed residue solid was dried overnight and stirred in 100 cm³ of 0.5 mol/dm³ of each of the desorbing solvents, CH₃OH and H₂O. After shaking the flask for 2hrs at 300 rpm, the solid adsorbent MNP-PA and MNP-OA composites were filtered off and the amount of the leached BTX ions were determined by PerkinElmer (USA) Lambda 25 UV-visible(UV-vis) spectrometer.

3.5 REFERENCE

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CHAPATER 4

4 OPTIMIZATION STUDIES BY STATISTICAL EXPERIMENTAL DESIGN

4.1 INTRODUCTION

The chapter presents and discusses the use of Response surface methodology (RSM) using Central composite (CCD) approach. The CCD approach was used to optimize preparation of the magnetite-oleic and magnetite-palmitic acid composites for the removal of benzene, toluene and xylene from aqueous solution. The optimization was performed by varying experimental parameters such as $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution (mL) (A), microwave power (W) (B), NH_4OH volume (mL) (C), reaction time (min) (D), and volume of acid (oleic and palmitic) (mL) (E), respectively while recording the response such as % Fe, conductivity (S/cm), and adsorption capacity (mg/g). The interaction between any two parameters on the responses were also determined with 3-dimentional plots. The final optimized condition was then obtained from the CCD software.

4.2 REACTION SCHEME

The aim of the experiment is to produce magnetite-organic acids composites (magnetite-oleic and magnetite-palmitic) of different chain length and their application for adsorption of BTX. To obtain the optimized adsorbent several reaction parameters need to be varied and the simultaneous effect on the adsorption properties on the final material determined. Experiment parameters such as the microwave power, volume of ammonium hydroxide for coprecipitation, $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution and total iron content in the preparation method determines the particle size and magnetic properties of the product. Whereas the amount of organic acid coated on the magnetite nanoparticles affects the conductivity and hydrophobicity of the final product which in turn affects the adsorption capacity of the adsorbent for BTX in solution. Therefore, these reaction parameters must be optimized in such a way that none of these properties will be compromised.

4.3 EXPERIMENTAL DESIGN

The Central composite (CCD) approach was used to correlate variables and responses. The experimental variables chosen were coded as: $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution (mL) (A), microwave power (W) (B), NH_4OH volume (mL) (C), reaction time (min) (D), and volume of acid (oleic and

palmitic) (mL) (*E*). The % Fe content, conductivity (S/cm), and adsorption capacity (mg/g) were then measured as a response to the experimental variables. In the experimental design, a total of 50 experiments runs were performed and the number of experimental runs (*N*) created from a partial factorial design for the five variables contained 32 factorial points, 10 axial points and 8 replicates at the center points as calculated from Eq. (4.1)

$$N = 2n + 2n + nc \quad (4.1)$$

where *n* is the number of the variable factor (which is 5 for the present study) and *n_c* is a constant which has a value of 8.

4.4 DEVELOPMENT OF REGRESSION MODEL EQUATION AND STATISTICAL ANALYSIS USING MAGNETITE-OLEIC ACID COMPOSITE

The five parameters, Fe³⁺/Fe²⁺ solution (mL) (*A*), microwave power (W) (*B*), NH₄OH volume (mL) (*C*), reaction time (min) (*D*), and volume of oleic acid (mL) (*E*) are presented in Table 4.1 to 4.3. The *A*, *B*, *C*, *D* and *E* were chosen as the independent variables while the three responses % Fe content, conductivity (S/cm), and BTX adsorption capacity (mg/g) were dependent variable of the study. Tables 4.4 to 4.6 also shows the ANOVA (Analysis of Variance) results to evaluate second-order response surface models including interactions for responses of % Fe content, conductivity (S/cm), and BTX adsorption capacity (mg/g). The Regression Eqs. (4.2) - (4.6) are shown below.

$$\begin{aligned} \% \text{ Fe} = & +78.02 - 2.09C - 0.81 D - 6.53 E + 1.77AC - 2.10 + 2.00 AE + 1.40 BC - 2.35 BD - 1.19 \\ & CD - 1.99 CE - 2.57 DE - 1.89 A^2 + 158 B^2 - 232 D^2 \end{aligned} \quad (4.2)$$

$$\begin{aligned} \text{Conductivity} = & +267.42 + 135.03B - 133.21C + 163.63D + 198.52E + 415.23BD + 91.38 AB \\ & + 387.89 AD - 222.35 AE + 454.64 BD + 106.29 BE - 107.50 CE + 228.03 C^2 - 13.97E^2 \end{aligned} \quad (4.3)$$

$$\begin{aligned} \text{Benzene Adsorption capacity} = & +59.80 - 5.92 A + 3.88 C - 25.06 E - 4.58 AB + 5.47AD + 6.29 \\ & BC - 2.76 CD - 6.26 CE - 3.45 DE - 23.22 A^2 - 30.22 B^2 - 7.22 C^2 + 9.78 D^2 + 33.20A^2 \end{aligned} \quad (4.4)$$

$$\begin{aligned} \text{Toluene adsorption capacity} = & +31.53 - 4.09 A + 4.76 B + 1.65 C + 3.41 D - 1.68 E + 1.06 AC \\ & + 1.12 AD + 0.69 AE - 4.50 BC - 2.94 BD - 1.25 BE - 1.44 CD - 1.12 CE + 0.69 DE - 5.92 \\ & B^2 + 7.07 C^2 + 6.58 E^2 \end{aligned}$$

(4.5)

$$\begin{aligned} \text{Xylene adsorption capacity} = & + 48.41 - 4.15 A + 5.62 B + 2.15 C - 1.18 D - 6.66 AB + 4.84 AD \\ & - 2.09 AE + 1.34 BC - 4.91 BD - 6.34 BE - 4.84 DE - 10.19 A^2 - 4.69 E^2 \end{aligned}$$

(4.6)

The coefficients with one factor represent the effect of the particular factor, while the coefficients with two factors represent the interaction between the two factors. The positive sign in front of the terms indicates a synergistic effect, whereas a negative sign indicates an antagonistic effect (Montgomery, 2017, Ghorbannezhad *et al.*, 2018).

Table 4.1: CCD Experimental design of five independent variables and three responses.

Variables						Responses		
Runs	Fe ³⁺ /Fe ²⁺ (mL)	Microwave power (W)	NH ₄ OH volume (mL)	Time (min)	Volume of acid (mL)	% Fe	Conductivity (S/cm)	Benzene Adsorption capacity (mg/g)
1	1.25	500.00	2.00	10.00	2.10	77.4	657	37.56
2	1.25	500.00	5.00	10.00	2.10	78.9	1261	62.616
3	2.00	800.00	2.00	15.00	4.00	58.7	2954	39.656
4	0.50	200.00	2.00	5.00	0.20	58.5	1608.4	62.074
5	2.00	800.00	8.00	15.00	0.20	76.7	2455	30.78
6	2.00	800.00	2.00	5.00	4.00	73.1	1715	25.78
7	0.50	800.00	2.00	5.00	4.00	55.1	556	22.88
8	1.25	500.00	8.00	10.00	2.10	77.2	1344	33.7
9	1.25	500.00	5.00	10.00	4.00	69.1	799	77.67
10	0.50	200.00	2.00	5.00	4.00	50.6	2621	34.158
11	2.00	800.00	8.00	15.00	4.00	55.1	2341	37.148
12	0.50	800.00	5.00	10.00	2.10	77.9	387	51.842
13	0.50	800.00	2.00	15.00	4.00	65.4	1837.93	21.764
14	1.25	200.00	5.00	10.00	2.10	82.2	105	87.002
15	1.25	500.00	5.00	10.00	2.10	80.8	272	62.47
16	1.25	500.00	5.00	10.00	2.10	78.6	259	60.99
17	1.25	500.00	5.00	10.00	2.10	76	253	67.398
18	0.50	200.00	8.00	15.00	4.00	52.4	804.5	45.13
19	0.50	200.00	2.00	15.00	0.20	80	472	71.406
20	1.25	500.00	5.00	10.00	2.10	75.3	251	61.664
21	2.00	800.00	2.00	5.00	0.20	70.3	427	46.35
22	1.25	500.00	5.00	10.00	2.10	77.7	257	61.55
23	0.50	200.00	2.00	15.00	4.00	64.7	1063	57.542
24	0.50	200.00	8.00	15.00	0.20	79.5	319	37.634
25	2.00	200.00	8.00	15.00	4.00	50.3	248	37.284
26	0.50	800.00	8.00	15.00	4.00	58.7	1101	31.036
27	2.00	200.00	8.00	5.00	4.00	64.9	202	28.084
28	0.50	200.00	8.00	5.00	4.00	46.4	1976	34.1
29	2.00	200.00	8.00	5.00	0.20	76.8	627	24.42
30	2.00	200.00	2.00	5.00	4.00	69.2	237	42.47
31	1.25	500.00	5.00	15.00	2.10	69.3	446	47.688
32	2.00	200.00	2.00	15.00	4.00	58.3	461	54.486
33	2.00	800.00	8.00	5.00	4.00	74.4	259	42.358
34	2.00	800.00	2.00	15.00	0.20	68.9	2381.01	47.276
35	1.25	500.00	5.00	5.00	2.10	69.8	71	44.486
36	0.50	200.00	8.00	5.00	0.20	65.9	1318.02	44.1
37	2.00	200.00	2.00	5.00	0.20	69.6	609.18	49.542
38	0.50	800.00	2.00	15.00	0.20	80.1	318	40.478
39	2.00	200.00	2.00	15.00	0.20	74.1	462	62.1
40	0.50	800.00	8.00	5.00	4.00	58.1	349	32.099
41	2.00	200.00	8.00	15.00	0.20	75.1	694.71	29.41
42	1.25	800.00	5.00	10.00	2.10	84.7	454	75.672
43	1.25	500.00	5.00	10.00	2.10	80.6	265	63.398
44	0.50	800.00	8.00	15.00	0.20	80.4	202	30.35
45	0.50	800.00	2.00	5.00	0.20	58.3	237	43.946
46	1.25	500.00	5.00	10.00	2.10	78.9	281	64.98
47	2.00	500.00	5.00	10.00	2.10	80	453	49.77
48	1.25	500.00	5.00	10.00	0.20	79.9	455	81.888
49	0.50	800.00	8.00	5.00	0.20	72	66	46.368
50	2.00	800.00	8.00	5.00	0.20	85.1	444	44.908

Table 4.2: CCD Experimental design of five independent variables and three responses.

Variables						Responses		
Runs	Fe ³⁺ /Fe ²⁺ (mL)	Microwave power (W)	NH ₄ OH volume (mL)	Time (min)	Volume of acid (mL)	% Fe	Conductivity (S/cm)	Toluene Adsorption capacity (mg/g)
Runs	Fe ³⁺ /Fe ²⁺ (mL)	Microwave power (W)	NH ₄ OH volume (mL)	Time (min)	Volume of acid (mL)	% Fe	Conductivity (S/cm)	Toluene Adsorption capacity (mg/g)
1	1.25	500.00	2.00	10.00	2.10	77.4	657	39.88
2	1.25	500.00	5.00	10.00	2.10	78.9	1261	65.67
3	2.00	800.00	2.00	15.00	4.00	58.7	2954	40.01
4	0.35	500.00	2.00	15.00	2.10	58754	160857	264345
5	2.00	500.00	5.00	15.00	2.10	78879	24561	724383
6	2.00	800.00	2.00	15.00	4.00	75817	12954	429666
7	0.50	200.00	2.00	5.00	0.20	55815	16686	7226245
8	2.00	500.00	8.00	15.00	0.20	77627	12455	405187
9	2.00	500.00	2.00	15.00	4.00	69311	1795	357659
10	0.50	200.00	2.00	5.00	4.00	56561	26536	326512
11	2.00	500.00	8.00	15.00	2.10	55712	2344	40.78
12	0.35	500.00	5.00	10.00	2.00	76991	380	856143
13	0.50	200.00	2.00	15.00	4.00	65046	1837623	442365
14	2.00	200.00	5.00	15.00	2.00	83521	2841	4789655
15	0.35	500.00	5.00	10.00	2.10	80789	262	6169467
16	0.35	500.00	2.00	15.00	2.00	76564	183758	316212
17	1.25	500.00	5.00	10.00	2.10	8262	253	968265
18	0.35	300.00	5.00	15.00	2.10	58048	8042	74856
19	0.35	300.00	3.00	15.00	2.10	7806	453	706933
20	1.25	500.00	5.00	10.00	2.10	7536	253	776674
21	0.90	200.00	8.00	15.00	4.00	79234	8643	55688
22	0.35	200.00	2.00	15.00	0.20	7780	272	81506
23	0.50	300.00	3.00	15.00	2.10	64573	1063	715466
24	0.50	300.00	2.00	15.00	0.20	79653	319	589458
25	2.00	300.00	5.00	15.00	2.10	5037	249	71645
26	0.50	200.00	2.00	15.00	4.00	5847	1103	6751
27	0.90	200.00	8.00	15.00	0.20	64695	203	472589
28	0.50	200.00	8.00	15.00	4.00	4603	1978	47684
29	0.90	800.00	8.00	15.00	4.00	7687	1901	24.45
30	2.00	200.00	8.00	5.00	4.00	68429	237	38448
31	0.35	500.00	8.00	15.00	4.00	6463	1976	41988
32	2.00	200.00	8.00	15.00	0.20	583	461	5923
33	2.00	200.00	2.00	5.00	4.00	7442	259	4323
34	2.00	500.00	2.00	15.00	0.20	6893	238101	7423
35	0.50	500.00	2.00	15.00	2.10	693	446	57254
36	0.50	800.00	8.00	5.00	4.00	659	131802	4212
37	2.00	200.00	2.00	15.00	0.20	744	659	52564
38	2.00	200.00	2.00	15.00	0.20	686	60918	5055
39	0.50	800.00	2.00	15.00	0.20	689	238101	57176
40	0.50	500.00	5.00	15.00	0.20	8098	318	4643
41	0.50	200.00	8.00	15.00	0.20	761	461	5446
42	0.50	200.00	8.00	15.00	0.20	659	131802	6434
43	0.50	800.00	2.00	5.00	4.00	581	349	3248
44	0.50	200.00	2.00	15.00	0.20	696	60918	5957
45	0.50	200.00	2.00	15.00	0.20	751	69471	2987
46	0.50	800.00	2.00	15.00	0.20	801	318	50478
47	2.00	800.00	2.00	15.00	0.20	847	454	7268
48	2.00	200.00	2.00	15.00	0.20	741	462	721
49	0.50	800.00	8.00	15.00	4.00	861	265	6531
50	0.50	800.00	8.00	15.00	0.20	804	202	4312
51	0.50	800.00	8.00	15.00	0.20	751	69471	3567
52	0.50	800.00	2.00	15.00	0.20	5837	237	4166
53	1.25	800.00	2.00	10.00	2.10	789	454	85342
54	1.25	500.00	2.00	10.00	2.10	806	281	6876
55	2.00	500.00	5.00	10.00	2.10	80	453	73862
56	0.50	800.00	8.00	15.00	0.20	804	702	4095
57	0.50	500.00	2.00	10.00	0.20	799	455	8765
58	0.50	800.00	8.00	15.00	0.20	583	237	53123
59	0.50	800.00	8.00	15.00	0.20	76	36	4978
60	2.00	500.00	5.00	10.00	0.20	859	484	7441
61	2.00	500.00	5.00	10.00	2.10	80	453	5907
62	1.25	500.00	5.00	10.00	0.20	79.9	455	71.126
63	0.50	800.00	8.00	5.00	0.20	72	66	56.458
64	2.00	800.00	8.00	5.00	0.20	85.1	444	54.143

Table 4.3: CCD Experimental design of five independent variables and three responses

Table 4.4: Benzene ANOVA for Response Surface Quadratic Model.

Source	% Fe		Conductivity		Benzene	
	F value	Prob> F	F value	Prob > F	F value	Prob > F
Model	140.6	< 0.0001	75.96	< 0.0001	81.79	< 0.0001
A-Fe ³⁺ /Fe ²⁺	3.48	0.0723	2.33	0.0593	53.91	< 0.0001
B-Microwave Power	0.012	0.9152	33.37	< 0.0001	1.16	0.2913
C-Volume of NH ₄ OH	119.3	< 0.0001	32.48	< 0.0001	23.10	< 0.0001
D-Time	17.85	0.0002	49.20	< 0.0001	0.068	< 0.7965
E-Volume of Acid	1160	< 0.0001	72.12	< 0.0001	965.24	< 0.0001
AB	1.11	0.3010	296.97	< 0.0001	30.38	< 0.0001
AC	80.05	< 0.0001	14.38	0.0007	0.058	0.8116
AD	113.3	< 0.0001	239.15	< 0.0001	43.26	< 0.0001
AE	102.8	< 0.0001	85.16	0.0007	2.85	0.1022
BC	50.11	< 0.0001	3.92	0.0571	57.19	< 0.0001
BD	141.5	< 0.0001	356.02	< 0.0001	1.64	0.2102
BE	0.63	0.4356	19.46	< 0.0001	2.49	0.1253
CD	36.45	< 0.0001	2.88	0.1006	11.05	0.0024
CE	101.8	< 0.0001	19.90	< 0.0001	56.64	< 0.0001
DE	168.8	< 0.0001	2.69	0.1119	17.20	0.0003
A ²	7.08	0.0126	2.90	0.0994	60.26	< 0.0001
B ²	4.93	0.0343	5.66	0.0359	102.07	< 0.0001
C ²	4.04	0.0538	6.92	0.0135	5.82	< 0.0001
D ²	10.65	0.0028	0.026	0.8730	10.70	0.0224
E ²	124.3	< 0.0001	16.73	0.0003	124.24	0.0028
Lack of Fit	2.25	0.1374	0.48	0.9102	1.84	0.025

Table 4.5:Toluene ANOVA for Response Surface Quadratic Model.

Source	% Fe		Conductivity		Toluene	
	F value	Prob> F	F value	Prob > F	F Value	Prob > F
Model	140.6	< 0.0001	75.96	< 0.0001	64.95	< 0.0001
A-Fe ³⁺ /Fe ²⁺	3.48	0.0723	2.33	0.0593	192.03	< 0.0001
B-Microwave Power	0.012	0.9152	33.37	< 0.0001	260.83	<0.0001
C-Volume of NH ₄ OH	119.3	< 0.0001	32.48	< 0.0001	31.17	< 0.0001
D-Time	17.85	0.0002	49.20	< 0.0001	133.74	< 0.0001
E-Volume of Acid	1160	< 0.0001	72.12	< 0.0001	32.29	< 0.0001
AB	1.11	0.3010	296.97	< 0.0001	0.38	0.5423
AC	80.05	< 0.0001	14.38	0.0007	12.21	0.0015
AD	113.3	< 0.0001	239.15	< 0.0001	13.69	0.0009
AE	102.8	< 0.0001	85.16	0.0007	5.11	0.0315
BC	50.11	< 0.0001	13.92	0.0571	218.97	< 0.0001
BD	141.5	<0.0001	356.02	< 0.0001	93.31	< 0.0001
BE	0.63	0.4356	19.46	< 0.0001	16.90	0.0003
CD	36.45	< 0.0001	2.88	0.1006	22.34	<0.0001
CE	101.8	< 0.0001	19.90	< 0.0001	13.69	< 0.009
DE	168.8	< 0.0001	2.69	0.1119	5.11	0.0315
A ²	7.08	0.0126	2.90	0.0994	0.15	0.7005
B ²	4.93	0.0343	5.66	0.0059	29.34	< 0.0001
C ²	4.04	0.0538	6.92	0.0135	41.84	< 0.0001
D ²	10.65	0.0028	0.026	0.8730	118.85	<0.0001
E ²	124.3	< 0.0001	16.73	0.0003	36.13	<0.0001
Lack of Fit	2.25	0.1374	0.48	0.9102	2.86	0.6262

Table 4.6: Xylene ANOVA for Response Surface Quadratic Model.

Source	% Fe		Conductivity		Xylene	
	F value	Prob > F	F value	Prob > F	F value	Prob > F
Model	140.6	< 0.0001	75.96	< 0.0001	55.16	< 0.0001
A-Fe ³⁺ /Fe ²⁺	3.48	0.0723	2.33	0.0593	69.21	< 0.0001
B-Microwave Power	0.012	0.9152	33.37	< 0.0001	126.99	< 0.0001
C-Volume of NH ₄ OH	119.3	< 0.0001	32.48	< 0.0001	18.55	0.0002
D-Time	17.85	0.0002	49.20	< 0.0001	5.57	0.0252
E-Volume of Acid	1160	< 0.0001	72.12	< 0.0001	0.014	0.9069
AB	1.11	0.3010	296.97	< 0.0001	167.81	< 0.0001
AC	80.05	< 0.0001	14.38	0.0007	1.63	0.2117
AD	113.3	< 0.0001	239.15	< 0.0001	88.86	< 0.0001
AE	102.8	< 0.0001	85.16	0.0007	16.60	0.0003
BC	50.11	< 0.0001	3.92	0.0571	6.84	0.0140
BD	141.5	< 0.0001	356.02	< 0.0001	91.17	< 0.0001
BE	0.63	0.4356	19.46	< 0.0001	152.42	< 0.0001
CD	36.45	< 0.0001	2.88	0.1006	2.31	0.1392
CE	101.8	< 0.0001	19.90	< 0.001	0.033	0.8565
DE	168.8	< 0.0001	2.69	0.1119	88.86	< 0.0001
A ²	7.08	0.0126	2.90	0.0994	30.40	< 0.0001
B ²	4.93	0.0343	566	0.0059	0.96	0.3357
C ²	4.04	0.0538	6.92	0.0135	0.011	0.9186
D ²	10.65	0.0028	0.026	0.8730	0.84	0.3679
E ²	124.3	< 0.0001	16.73	0.0003	6.44	0.0168
Lack of Fit	2.25	0.1374	0.48	0.9102	1.13	0.4663

4.5 EFFECTS OF PREPARATION VARIABLES ON THE % Fe CONTENT

The iron content (% Fe) of the magnetite-oleic acid composite was between 49.79 to 85.95 %, for BTX respectively. The Model F-value of 140.61 indicates the model was significant. The Lack of Fit F-value of 2.25 shows that it is not significant relative to the pure error. Non-significant lack of fit is good because we want the model to fit. The R-squared value (r^2) was 0.9898 indicating that only 0.01% of the total variations were not explained by the regression model. The predicted R-squared value (r_a^2) value was 0.9828. The r^2 value and the r_a^2 value are reasonably high and comparable showing that there is good agreement between the models and the experimental data. The coefficient of variation (CV) was < 4.5 indicating the high reliability of the experiments for the chosen model. The values of Prob > F that are less than 0.0500 indicates model terms are significant while values greater than 0.10 indicate the model terms are not significant. In this case the significant model are C, D, E, AC, AD, AE, BC, BD, CD, CE, DE, A², B², D², E² with the corresponding F-value of 119.31, 17.85, 1160.42, 80.05,

113.26, 102.81, 50.14, 141.48, 36.45, 101.78, 168. It was also observed that the interaction obeyed the following order $DE > BD > AD > AE > CE > AC > BC > CD$. The interaction of DE was the most significant due higher F-value of 168.80.

4.6 EFFECTS OF PREPARATION VARIABLES ON THE CONDUCTIVITY (S/cm)

The conductivity of the magnetite-oleic acid composite ranged from 66 to 2954 (S/cm). The model was favorable with F value of 75.96 implying the model is significant. There is only a 0.01% chance that an F-value could occur due to noise. The r^2 was 0.981, r_a^2 was 0.9683 and the lack of fit was 0.48. The coefficient of variation (CV) was < 4.5 indicating the high reliability of the experiments for the chosen model. The significant models were B, C, D, E, AB, AC, AD, AE, BD, BE, CE, C^2 , E^2 with the corresponding F-values of 33.37, 32.48, 49.20, 72.12, 296.97, 14.38, 259.15, 85.16, 356.02, 19.46, 19.90. The interaction obeyed the following order $BD > AB > AD > AE > CE > BE > AC$. The interaction of BD had the largest of F-value of 356.02 showing it is most significant.

4.7. EFFECTS OF PREPARATION VARIABLES ON BTX

4.7.1 Benzene adsorption capacity

The benzene adsorption capacity was between 0.5 to 116 mg/g. The F was 85.36, r^2 was 0.9888, r_a^2 was 0.9718 and lack of fit of 1.84. The coefficient of variation (CV) was < 4.5 . Values Probability $> F$ less than 0.05 shows that the models' terms are significant. In this case the significant models were A, C, E, AB, AD, BC, CD, CE, DE, A^2 , B^2 , C^2 , D^2 , E^2 with corresponding F-value of significant model terms 1.16, 23.10, 965.24, 30.38, 43.26, 57.19, 11.05, 56.64, 17.20. It was also observed the interaction obeyed the following order $AB > AD > BC > CD > CE > DE$. The interaction of BC had the largest significance due to higher F-value of 57.19.

4.7.2 Toluene adsorption capacity

The toluene adsorption capacity ranged from 1.0 to 82 mg/g. The F value was 55.63 r^2 was 0.9845 r_a^2 was 0.9571 and lack of fit was 2.86. The significant model were A, B, C, D, E, AC, AD, AE, BC, BD, BE, CD, CE, DE, B^2 , C^2 , D^2 , E^2 with the corresponding F-value of 192.03, 260.83, 31.17, 133.74, 32.29, 12.21, 13.69, 5.11, 218.97, 93.31, 16.90, 22.34, 13.69, 5.11, 29.34, 41.84, 118.85, 36.13. It was also observed that the interaction obeyed the

following order $BC > BD > CD > BE > CE > AD > AC > AE = DE$. The interaction of BC had the largest significance due to a higher F-value of 218.97.

4.7.3 Xylene adsorption capacity

The xylene adsorption capacity ranged from 10 to 89 mg/g, the F value was 61.42, r^2 to 0.9769, r_a^2 to 0.9610 and lack of fit of 1.13. Values of Probability > F less than 0.05 show that the significant models were A, B, C, D, AB, AD, AE, BC, BD, BE, DE, A^2 , E^2 with the corresponding F-value of 69.21, 126.99, 18.55, 5.57, 167.81, 88.86, 16.60, 6.84, 91.17, 152.42, 88.86. The interaction followed the order $AB > BE > BD > AD = DE > AE > BC$. The interaction of AB had the largest significance due to a higher F-value of 167.81.

4.8 VALIDATION OF MODEL AND RESPONSE SURFACE PLOT

The adequacy of the model equation in describing the experimental data was validated from the plot of predicted versus actual values. The relationship between predicted and actual values for % Fe content, conductivity (S/cm) and BTX adsorption capacity (mg/g) are shown in Fig. 4.1 (a-e) respectively. The results show that there is a high correlation between the predicted and actual values signifying that the predicted and actual values were in good agreement. The points also show that they are in constant range across the graph and near to the straight line. This means that the models well fitted the experimental data and was a good estimate of response for the system in the experimental range studied (Mehrizad and Gharbani, 2016, Ali *et al.*, 2018).

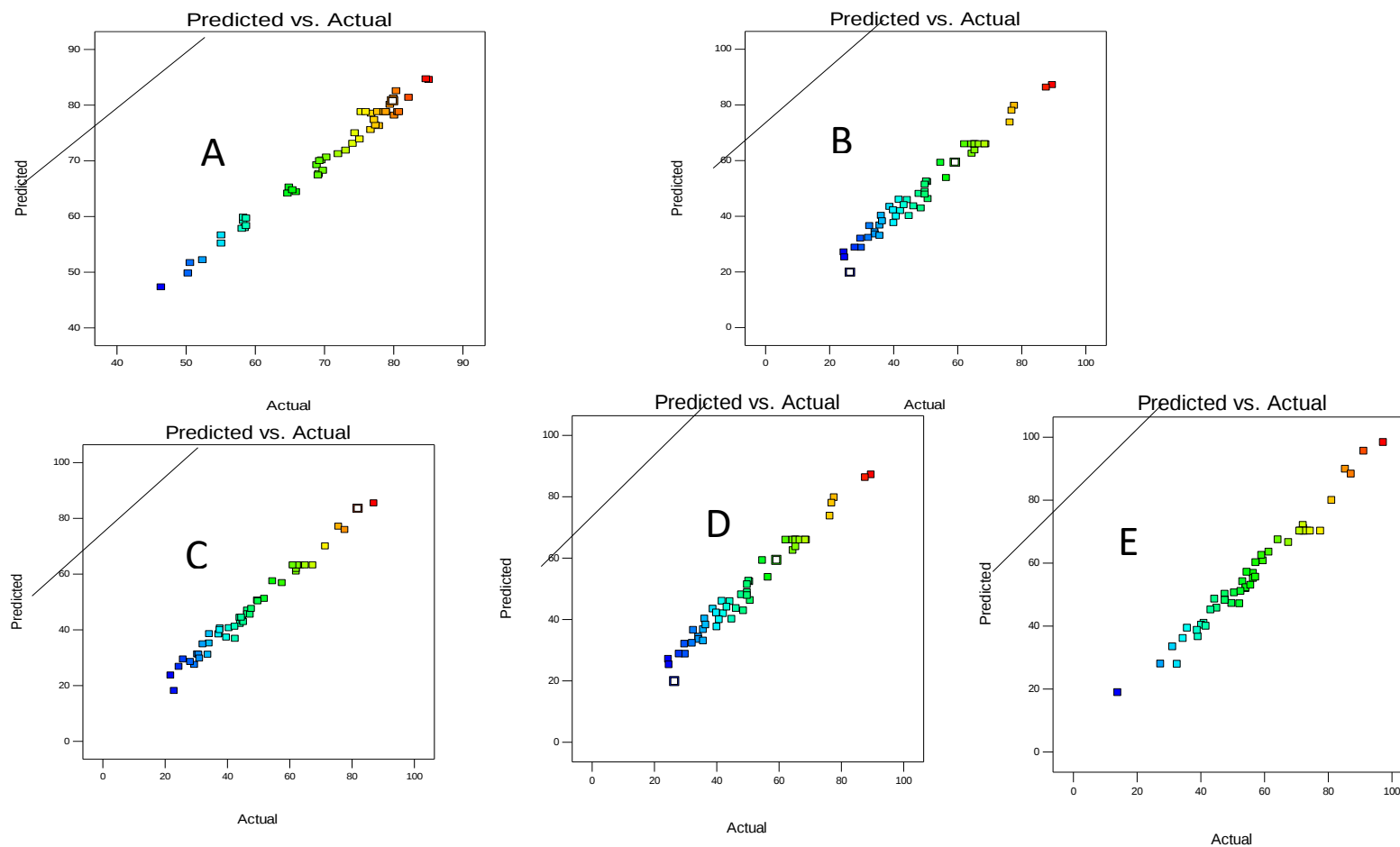


Figure 4. 1: Plot of actual values against predicted values of (a) % Fe content, (b) conductivity, (c) benzene adsorption capacity, (d) toluene adsorption capacity (e) xylene adsorption capacity.

4.9 THREE DIMENSIONAL RESPONSE SURFACE PLOTS

Three-dimensional (3D) response surface plots were done to gain a better understanding of the effects of the independent variables and their interactions on the dependent variables. Fig 4.2 (a-e) describe the 3D response surface plots for % Fe content, conductivity (S/cm) and BTX adsorption capacity (mg/g).

4.9.1 3D Response Surface plots for % Fe content

The 3D plot in Fig 4.2 (a) shows interaction of time and volume of oleic acid while maintaining $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution, microwave power and volume of NH_4OH at 1.25 mL, 500 W and 5.0 mL, respectively. The plot shows that increase in time from 5 to 10 min increases the % Fe content to 75.9 %, however, a further increase in time to 15 min results in the % Fe content slightly decreasing to 75.3 %. For the volume of oleic acid, the increment in the volume of acid from 0.2 to 5 ml the % Fe content was high at 75.8 % however further increment in the volume of acid later resulted in decrease in % Fe content to 63.99 %.

4.9.2 3D Response Surface plots for conductivity on the adsorbent

The 3D plot in Fig.4.2 (b) shows the interaction of microwave power and time while maintaining $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution, volume of NH_4OH and volume of oleic acid at 1.25 mL, 5.00 mL and 2.10 mL respectively. The plot shows at an increase in microwave power from 200 to 500 W the conductivity was low at 71 (S/cm), however further increases in microwave power to 800 W then resulted in an increase in conductivity to 454 (S/cm). For the plot of time versus microwave power, it was observed that an increase in time from 5 to 10 min the conductivity was reduced to 105 (S/cm) and further increase to 15 min the conductivity of the material also increases to 446 (S/cm).

4.9.3 3D Response Surface plots for BTX adsorption capacity

4.9.3.1 Benzene adsorption capacity

The 3D response surface plots of the quadratic models with respect to benzene adsorption capacity is shown in Fig.4.2 (c). The 3D plot shows the interaction of microwave power and volume of NH_4OH while maintaining $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution, time and volume of the oleic acid at 1.25 mL, 10 min, and 2.10 mL.

As shown in Fig 4.2 (c) increasing the microwave power from 200 to 500 W also increases the adsorption capacity to 48 mg/g, however a further increase in microwave power to 800W

later decreases the adsorption capacity to 28 mg/g. This could be due to reduction in number of active sites and some of the pores might be burnt off under higher radiation power. For the volume of ammonium hydroxide solution versus microwave power it was observed that an increase the volume of ammonium hydroxide solution from 2 to 5 mL decreases the adsorption capacity to 29.5 mg/g however further increase of the volume of ammonium hydroxide solution to 8.00 mL the adsorption capacity then increases to 55.5 mg/g.

4.9.3.2 Toluene adsorption capacity

The 3D response surface plots of the quadratic models with respect to toluene adsorption capacity is shown in Fig.4.2 (d). The plot shows at an interaction of microwave power and the volume of ammonium hydroxide solution while maintaining $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution, time and volume of the oleic acid coated magnetic nanoadsorbent, at 1.25 mL, 10 min, and 2.10 mL. It was observed that increase in microwave power from 200 to 500 W resulted in an increase in the adsorption capacity to 39 mg/g. However further increasing the microwave power to 800 W later resulted in a decrease in capacity to 29.1 mg/g. This may be due to the fact that some active sites may be blocked and burnt off by high radiation power or agglomeration may interfere with binding sites leading to lower capacity (Hesas *et al.*, 2013). For the volume of NH_4OH versus microwave power between 2 to 5 mL, low adsorption capacity of 23.0 mg/g was recorded, but further increase to 8.00 mL then later resulted in increased capacity to 39.0 mg/g.

4.9.3.3 Xylene adsorption capacity

The 3D response surface plots of the quadratic models with respect to xylene adsorption capacity is shown in Fig.4.2 (e). The plot shows the interaction of $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution and microwave power while maintaining the volume of ammonium hydroxide solution, time and volume of the oleic acid at 5.00 mL, 10 min, and 2.10 mL, respectively. The plot shows that increasing the $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution from 0.5 to 1.25 mL the adsorption capacity also increases to 46 mg/g but further increases to 2.0 mL decreases the adsorption capacity. The results also show that low microwave power adsorption capacity was a bit low at 44.0 mg/g however increment in microwave power to 800 W adsorption capacity also increases to 54.0 mg/g. The capacity was higher due to the fact that the high microwave power may facilitate the development of pore structure and then result in the formation of larger surface area and more number of active sites (Hesas *et al.*, 2013).

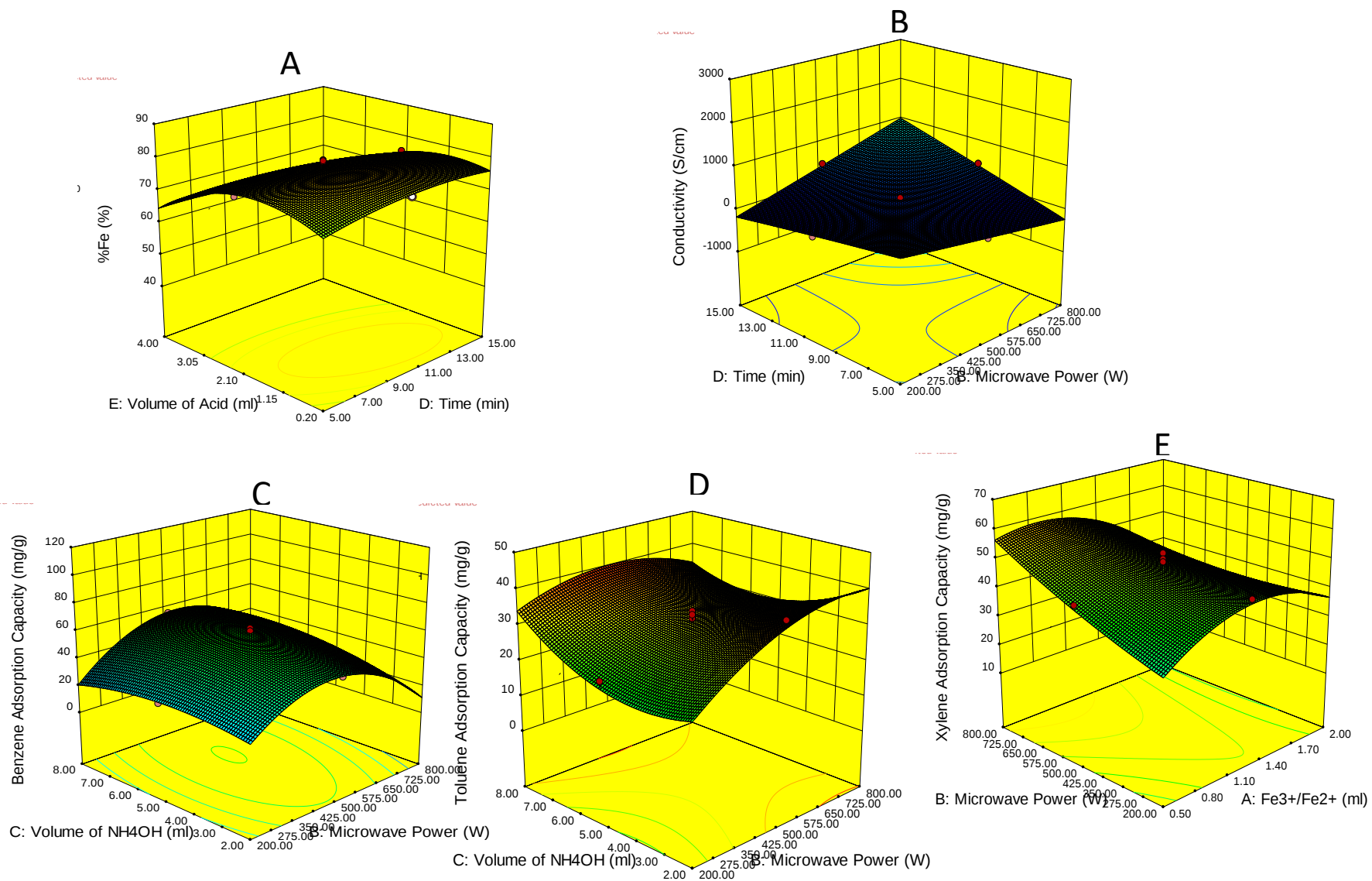


Figure 4.2: 3D interaction for (a-e): % Fe content, conductivity (S/cm) and BTX adsorption capacity (mg/g)

Table 4.7 : Magnetite-oleic acid composite optimum values

Pollutant name	Fe ³⁺ /Fe ²⁺ volume (mL)	Microwave power (W)	NH ₄ OH volume (mL)	Time (min)	Volume of acid (mL)	% Fe	Conductivity (S/cm)	Adsorption capacity (mg/g)	Desirability
Benzene	0.5	200	8.00	5.00	0.2	78.16	1561.92	82.20	0.92
Toluene	0.5	200	8.00	5.00	0.2	77.62	1203.91	80.41	0.90
Xylene	0.5	200	8.00	5.00	0.2	79.44	1395.59	85.25	0.96

4.10 RESPONSE SURFACE MODEL FITTING BY (CCD) USING MAGNETITE-PALMITIC ACID COMPOSITE

The three responses % Fe content, conductivity (S/cm), and BTX adsorption capacity (mg/g) were correlated with the five factors: Fe³⁺/Fe²⁺ solution (mL) (A), microwave power (W) (B), NH₄OH volume (mL) (C), reaction time (min) (D), and volume of acid (palmitic) (E), using the second-order polynomial and quadratic regression models were obtained from the experimental data, as shown in Eqs. (4.7) - (4.11).

$$\begin{aligned} \% \text{ Fe} = & + 78.30 + 2.46 A + 1.66 B - 1.77 C - 9.14 E + 2.06 AB - 4.77 AD + 1.65 AE + 1.95 BC \\ & - 2.28 BD - 3.78 CD - 3.70 CE - 3.58 DE - 5.75 A^2 + 3.75 B^2 - 4.25 C^2 - 8.70 E^2 \end{aligned} \quad (4.7)$$

$$\begin{aligned} \text{Conductivity} = & + 207.54 + 72.26 A + 2.19.94 B - 184.00 C + 75.29 D + 340.74 E + 102.03 \\ & AB - 48.84 AC - 69.22 AD + 169.22 AE - 72.78 BC + 152.22 BD + 187.84 BE + 83.47 CD - \\ & 63.91 CE - 142.47 DE + 374.30 E^2 \end{aligned} \quad (4.8)$$

$$\begin{aligned} \text{Benzene adsorption capacity} = & + 31.15 - 2.27 B - 2.34 C + 0.76 D - 1.88 E + 1.52 AB - 0.578 AC \\ & + 0.43 AE + 1.05 BC - 1.49 BD - 1.15 CD + 2.00 CE + 0.98 DE - 6.06 A^2 + 9.53 B^2 - 13.60 C^2 \\ & - 8.10 D^2 + 7.29 E^2 \end{aligned} \quad (4.9)$$

$$\begin{aligned} \text{Toluene adsorption capacity} = & + 29.30 - 5.02 B - 2.48 C + 1.63 D - 1.37 E - 2.25 AC - 1.44 AD + \\ & 3.12 AE + 3.43 BC - 1.57 BE - 1.85 CE + 19.93 A^2 + 5.83 B^2 - 9.29 C^2 - 10.19 D^2 - 13.61 E^2 \end{aligned} \quad (4.10)$$

$$\begin{aligned} \text{Xylene adsorption capacity} = & + 29.43 - 1.94 A - 5.16 B - 2.31 C + 1.67 D - 1.40 E - 20.73 AB - \\ & 2.31 AC - 1.63 AD + 3.05 AE + 3.47 BC - 1.74 BE - 1.7 CE + 19.99 A^2 + 5.90 B^2 - 10.07 C^2 - \\ & 10.13 D^2 - 13.20 E^2 \end{aligned} \quad (4.11)$$

Table 4.8: CCD Experimental design of five independent variables and three responses.

Variables					Responses			
Runs	Fe ³⁺ /Fe ²⁺ (mL)	Microwave power (W)	NH ₄ H volume (mL)	Time (min)	acid volume (mL)	% Fe	Conductivity (S/cm)	Benzene Adsorption capacity (mg/g)
1	1.25	500.00	2.00	10.00	2.10	71.4	1557	18.78
2	1.25	500.00	5.00	10.00	2.10	79.4	1261	31.308
3	2.00	800.00	2.00	15.00	4.00	58.7	2054	18.642
4	0.50	200.00	2.00	5.00	0.20	58.5	1205	31.037
5	2.00	800.00	8.00	15.00	0.20	76.7	1245	15.243
6	2.00	800.00	2.00	5.00	4.00	73.1	1015	12.316
7	0.50	800.00	2.00	5.00	4.00	55.1	690	11.981
8	1.25	500.00	8.00	10.00	2.10	77.2	144	16.308
9	1.25	500.00	5.00	10.00	4.00	69.1	799	35.912
10	0.50	200.00	2.00	5.00	4.00	50.6	1452	19.079
11	2.00	800.00	8.00	15.00	4.00	55.1	1667	18.574
12	0.50	500.00	5.00	10.00	2.10	77.9	287	25.921
13	0.50	800.00	2.00	15.00	4.00	65.4	1474	10.882
14	1.25	200.00	5.00	10.00	2.10	82.2	105	43.501
15	1.25	500.00	5.00	10.00	2.10	80.8	272	31.235
16	1.25	500.00	5.00	10.00	2.10	78.6	156	29.166
17	1.25	500.00	5.00	10.00	2.10	76	253	33.699
18	0.50	200.00	8.00	15.00	4.00	52.4	1017	22.565
19	0.50	200.00	2.00	15.00	0.20	80	272	35.703
20	1.25	500.00	5.00	10.00	2.10	75.3	251	30.832
21	2.00	800.00	2.00	5.00	0.20	70.3	1227	23.175
22	1.25	500.00	5.00	10.00	2.10	77.7	257	29.372
23	0.50	200.00	2.00	15.00	4.00	64.7	1063	28.771
24	0.50	200.00	8.00	15.00	0.20	79.5	219	18.817
25	2.00	200.00	8.00	15.00	4.00	50.3	648	18.642
26	0.50	800.00	8.00	15.00	4.00	58.7	1101	15.518
27	2.00	200.00	8.00	5.00	4.00	64.9	202	14.042
28	0.50	200.00	8.00	5.00	4.00	46.4	1159	17.05
29	2.00	200.00	8.00	5.00	0.20	76.8	427	12.21
30	2.00	200.00	2.00	5.00	4.00	69.2	337	21.235
31	1.25	500.00	5.00	15.00	2.10	69.3	146	23.844
32	2.00	200.00	2.00	15.00	4.00	58.3	661	27.243
33	2.00	800.00	8.00	5.00	4.00	74.4	459	21.179
34	2.00	800.00	2.00	15.00	0.20	68.9	1324	23.638
35	1.25	500.00	5.00	5.00	2.10	69.8	71	22.243
36	0.50	200.00	8.00	5.00	0.20	65.9	838	22.05
37	2.00	200.00	2.00	5.00	0.20	69.6	658	24.771
38	0.50	800.00	2.00	15.00	0.20	80.1	618	20.239
39	2.00	200.00	2.00	15.00	0.20	74.1	462	31.05
40	0.50	800.00	8.00	5.00	4.00	58.1	449	16.0499
41	2.00	200.00	8.00	15.00	0.20	75.1	343	14.7064
42	1.25	800.00	5.00	10.00	2.10	84.7	254	37.836
43	1.25	500.00	5.00	10.00	2.10	80.6	265	31.699
44	0.50	800.00	8.00	15.00	0.20	80.4	202	15.175
45	0.50	800.00	2.00	5.00	0.20	58.3	837	21.973
46	1.25	500.00	5.00	10.00	2.10	78.9	281	31.969
47	2.00	500.00	5.00	10.00	2.10	80	353	24.239
48	1.25	500.00	5.00	10.00	0.20	79.9	455	40.944
49	0.50	800.00	8.00	5.00	0.20	72	126	23.1817
50	2.00	800.00	8.00	5.00	0.20	85.1	444	19.707

Table 4.9: CCD Experimental design of five independent variables and three responses.

Variables						Responses		
Runs	Fe ³⁺ /Fe ²⁺ (mL)	Microwave power (W)	NH ₄ H volume (mL)	Time (min)	acid volume (mL)	% Fe	Conductivity (S/cm)	Toluene Adsorption capacity (mg/g)
1	1.25	500.00	2.00	10.00	2.10	71.4	1557	21.9
2	1.25	500.00	5.00	10.00	2.10	79.4	1261	31.703
3	2.00	800.00	2.00	15.00	4.00	58.7	2054	17.775
4	0.50	200.00	2.00	5.00	0.20	58.5	1205	31.037
5	2.00	800.00	8.00	15.00	0.20	76.7	1245	15.78
6	2.00	800.00	2.00	5.00	4.00	73.1	1015	15.909
7	0.50	800.00	2.00	5.00	4.00	55.1	690	9.019
8	1.25	500.00	8.00	10.00	2.10	77.2	144	16.308
9	1.25	500.00	5.00	10.00	4.00	69.1	799	14.509
10	0.50	200.00	2.00	5.00	4.00	50.6	1452	24.243
11	2.00	800.00	8.00	15.00	4.00	55.1	1667	11.817
12	0.50	500.00	5.00	10.00	2.10	77.9	287	51.372
13	0.50	800.00	2.00	15.00	4.00	65.4	1474	14.977
14	1.25	200.00	5.00	10.00	2.10	82.2	105	42.501
15	1.25	500.00	5.00	10.00	2.10	80.8	272	28.033
16	1.25	500.00	5.00	10.00	2.10	78.6	259	30.032
17	1.25	500.00	5.00	10.00	2.10	76	253	30.299
18	0.50	200.00	8.00	15.00	4.00	52.4	1017	25.235
19	0.50	200.00	2.00	15.00	0.20	80	272	36.703
20	1.25	500.00	5.00	10.00	2.10	75.3	251	27.832
21	2.00	800.00	2.00	5.00	0.20	70.3	1227	15.175
22	1.25	500.00	5.00	10.00	2.10	77.7	257	27.497
23	0.50	200.00	2.00	15.00	4.00	64.7	1063	33.771
24	0.50	200.00	8.00	15.00	0.20	79.5	219	33.703
25	2.00	200.00	8.00	15.00	4.00	50.3	648	19.965
26	0.50	800.00	8.00	15.00	4.00	58.7	1101	18.376
27	2.00	200.00	8.00	5.00	4.00	64.9	202	18.574
28	0.50	200.00	8.00	5.00	4.00	46.4	1159	16.11
29	2.00	200.00	8.00	5.00	0.20	76.8	427	15.821
30	2.00	200.00	2.00	5.00	4.00	69.2	337	39.235
31	1.25	500.00	5.00	15.00	2.10	69.3	146	19.11
32	2.00	200.00	2.00	15.00	4.00	58.3	661	41.235
33	2.00	800.00	8.00	5.00	4.00	74.4	459	8.821
34	2.00	800.00	2.00	15.00	0.20	68.9	1324	12.17
35	1.25	500.00	5.00	5.00	2.10	69.8	71	18.977
36	0.50	200.00	8.00	5.00	0.20	65.9	838	24.353
37	2.00	200.00	2.00	5.00	0.20	69.6	658	28.771
38	0.50	800.00	2.00	15.00	0.20	80.1	618	24.239
39	2.00	200.00	2.00	15.00	0.20	74.1	462	26.505
40	0.50	800.00	8.00	5.00	4.00	58.1	449	13.57
41	2.00	200.00	8.00	15.00	0.20	75.1	343	15.886
42	1.25	800.00	5.00	10.00	2.10	84.7	254	27.642
43	1.25	500.00	5.00	10.00	2.10	80.6	265	31.836
44	0.50	800.00	8.00	15.00	0.20	80.4	202	31.037
45	0.50	800.00	2.00	5.00	0.20	58.3	837	16.551
46	1.25	500.00	5.00	10.00	2.10	78.9	281	30.299
47	2.00	500.00	5.00	10.00	2.10	80	353	46.969
48	1.25	500.00	5.00	10.00	0.20	79.9	455	17.441
49	0.50	800.00	8.00	5.00	0.20	72	126	28.771
50	2.00	800.00	8.00	5.00	0.20	85.1	444	16.703

Table 4.10: CCD Experimental design of five independent variables and three responses.

Variables						Responses		
Runs	Fe ³⁺ /Fe ²⁺ (mL)	Microwave power (W)	NH ₄ H volume (mL)	Time (min)	acid volume (mL)	% Fe	Conductivity (S/cm)	Xylene Adsorption capacity (mg/g)
1	1.25	500.00	2.00	10.00	2.10	71.4	1557	23
2	1.25	500.00	5.00	10.00	2.10	79.4	1261	29
3	2.00	800.00	2.00	15.00	4.00	58.7	2054	19.88
4	0.50	200.00	2.00	5.00	0.20	58.5	1205	33.2
5	2.00	800.00	8.00	15.00	0.20	76.7	1245	17.6
6	2.00	800.00	2.00	5.00	4.00	73.1	1015	17.3
7	0.50	800.00	2.00	5.00	4.00	55.1	690	10.56
8	1.25	500.00	8.00	10.00	2.10	77.2	144	16.9
9	1.25	500.00	5.00	10.00	4.00	69.1	799	11.3
10	0.50	200.00	2.00	5.00	4.00	50.6	1452	29.243
11	2.00	800.00	8.00	15.00	4.00	55.1	1667	21.817
12	0.50	500.00	5.00	10.00	2.10	77.9	287	45.372
13	0.50	800.00	2.00	15.00	4.00	65.4	1474	61.977
14	1.25	200.00	5.00	10.00	2.10	82.2	105	12.501
15	1.25	500.00	5.00	10.00	2.10	80.8	272	18.033
16	1.25	500.00	5.00	10.00	2.10	78.6	259	40.032
17	1.25	500.00	5.00	10.00	2.10	76	253	40.299
18	0.50	200.00	8.00	15.00	4.00	52.4	1017	25.235
19	0.50	200.00	2.00	15.00	0.20	80	272	66.703
20	1.25	500.00	5.00	10.00	2.10	75.3	251	27.62
21	2.00	800.00	2.00	5.00	0.20	70.3	1227	15.175
22	1.25	500.00	5.00	10.00	2.10	77.7	257	27.497
23	0.50	200.00	2.00	15.00	4.00	64.7	1063	39.771
24	0.50	200.00	8.00	15.00	0.20	79.5	219	36.303
25	2.00	200.00	8.00	15.00	4.00	50.3	648	25.305
26	0.50	800.00	8.00	15.00	4.00	58.7	1101	22.16
27	2.00	200.00	8.00	5.00	4.00	64.9	202	19.55
28	0.50	200.00	8.00	5.00	4.00	46.4	1159	19.21
29	2.00	200.00	8.00	5.00	0.20	76.8	427	19.451
30	2.00	200.00	2.00	5.00	4.00	69.2	337	35.835
31	1.25	500.00	5.00	15.00	2.10	69.3	146	17.41
32	2.00	200.00	2.00	15.00	4.00	58.3	661	31.235
33	2.00	800.00	8.00	5.00	4.00	74.4	459	12.421
34	2.00	800.00	2.00	15.00	0.20	68.9	1324	15.57
35	1.25	500.00	5.00	5.00	2.10	69.8	71	20.227
36	0.50	200.00	8.00	5.00	0.20	65.9	838	26.33
37	2.00	200.00	2.00	5.00	0.20	69.6	658	26.711
38	0.50	800.00	2.00	15.00	0.20	80.1	618	22.329
39	2.00	200.00	2.00	15.00	0.20	74.1	462	28.45
40	0.50	800.00	8.00	5.00	4.00	58.1	449	15.57
41	2.00	200.00	8.00	15.00	0.20	75.1	343	16.126
42	1.25	800.00	5.00	10.00	2.10	84.7	254	37.642
43	1.25	500.00	5.00	10.00	2.10	80.6	265	33.56
44	0.50	800.00	8.00	15.00	0.20	80.4	202	21.037
45	0.50	800.00	2.00	5.00	0.20	58.3	837	26.551
46	1.25	500.00	5.00	10.00	2.10	78.9	281	30.49
47	2.00	500.00	5.00	10.00	2.10	80	353	36.969
48	1.25	500.00	5.00	10.00	0.20	79.9	455	22.441
49	0.50	800.00	8.00	5.00	0.20	72	126	35.771
50	2.00	800.00	8.00	5.00	0.20	85.1	444	33.703

Table 4.11: Benzene ANOVA for Response Surface Quadratic Model.

Source	% Fe		Conductivity		Benzene	
	F value	Prob > F	F value	Prob > F	F value	Prob > F
Model	53.52	< 0.0001	53.14	< 0.0001	81.76	< 0.0001
A-Fe ³⁺ /Fe ²⁺	29.26	< 0.0001	11.79	0.0018	3.74	0.0630
B-Microwave Power	13.32	< 0.0010	109.18	< 0.0001	94.08	< 0.0001
C-Volume of NH ₄ OH	15.22	0.0005	76.41	< 0.0001	99.86	< 0.0001
D-Time	1.74	0.1972	12.80	0.0012	10.66	0.0028
E-Volume of Acid	404.18	< 0.0001	262.04	< 0.0001	64.60	< 0.0001
AB	19.32	0.0001	22.11	< 0.0001	39.73	< 0.0001
AC	0.81	0.3753	5.07	0.0321	5.75	0.0231
AD	103.46	< 0.0001	10.18	0.0034	3.21	0.0835
AE	12.36	0.0015	60.83	< 0.0001	19.01	0.0001
BC	17.27	0.0003	11.25	0.0022	109.03	< 0.0001
BD	23.64	< 0.0001	49.22	< 0.0001	38.16	< 0.0001
BE	3.61	0.06733	74.96	< 0.0001	4.02	0.0544
CD	65.02	< 0.0001	14.80	0.0006	22.77	< 0.0001
CE	62.47	< 0.0001	8.68	0.0063	68.69	< 0.0001
DE	58.32	< 0.0001	43.12	< 0.0001	16.59	0.0003
A ²	11.62	0.0019	2.26	0.1436	48.84	< 0.0001
B ²	4.96	0.0338	2.64	0.1150	120.57	< 0.0001
C ²	0.69	0.4145	1.57	0.2201	245.73	< 0.0001
D ²	0.15	0.7046	0.32	0.5755	87.17	< 0.0001
E ²	26.62	< 0.0001	23.06	< 0.0001	70.52	< 0.0001
Lack of Fit	1.42	0.8120	0.33	0.974	0.85	0.6442

Table 4.12: Toluene ANOVA for Response Surface Quadratic Model.

Source	% Fe		Conductivity		Toluene	
	F value	Prob > F	F value	Prob > F	F Value	Prob > F
Model	87.31	< 0.0001	8.16	< 0.0001	62.53	< 0.0001
A-Fe ³⁺ /Fe ²⁺	60.82	< 0.0001	0.11	0.7419	33.70	< 0.0001
B-Microwave Power	33.21	< 0.0001	6.22	0.0185	236.99	< 0.0001
C-Volume of NH ₄ OH	5.34	0.0281	18.77	0.0002	57.81	< 0.0001
D-Time	9.08	0.0053	2.90	0.0995	25.05	< 0.0001
E-Volume of Acid	532.71	< 0.0001	12.25	0.0015	17.72	0.0002
AB	0.41	0.5271	23.31	< 0.0001	2.59	0.1187
AC	2.65	0.1146	0.100	0.7546	44.83	< 0.0001
AD	290.82	< 0.0001	8.27	0.0075	18.32	0.0002
AE	10.38	0.0031	7.18	0.0120	86.34	< 0.0001
BC	21.61	< 0.0001	2.66	0.1140	104.39	< 0.0001
BD	13.41	0.0010	13.48	0.0010	0.87	0.3576
BE	9.58	0.0043	0.21	0.6506	21.95	< 0.0001
CD	40.85	< 0.0001	2.09	0.1592	0.36	0.5532
CE	82.40	< 0.0001	0.82	0.3732	30.41	< 0.0001
DE	82.40	< 0.0001	11.62	0.0019	2.91	0.0987
A ²	0.14	0.7142	0.22	0.6445	271.98	< 0.0001
B ²	20.90	< 0.0001	1.22	0.2783	23.29	< 0.0001
C ²	15.77	0.0004	9.34	0.0048	59.06	< 0.0001
D ²	70.67	< 0.0001	4.16	0.0507	71.15	< 0.0001
E ²	14.32	0.0007	7.56	0.0102	122.33	< 0.0001
Lack of Fit	0.63	0.8120	0.33	0.9794	1.76	0.2263

Table 4 13: Xylene ANOVA for Response Surface Quadratic Model.

Source	% Fe		Conductivity		Xylene	
	F value	Prob > F	F value	Prob > F	F Value	Prob > F
Model	53.52	< 0.0001	53.14	< 0.0001	78.71	< 0.0001
A-Fe ³⁺ /Fe ²⁺	29.26	< 0.0001	11.79	0.0018	43.19	< 0.0001
B-Microwave Power	13.32	< 0.0010	109.18	< 0.0001	305.15	< 0.0001
C-Volume of NH ₄ OH	15.22	0.0005	76.41	< 0.0001	61.00	< 0.0001
D-Time	1.74	0.1972	12.80	0.0012	31.86	< 0.0001
E-Volume of Acid	404.2	< 0.0001	262.04	< 0.0001	22.41	< 0.0001
AB	19.32	0.0001	22.11	< 0.0001	5.69	0.0238
AC	0.81	0.3753	5.07	0.0321	57.80	< 0.0001
AD	103.5	< 0.0001	10.18	0.0034	28.81	< 0.0001
AE	12.36	0.0015	60.83	< 0.0001	100.51	< 0.0001
BC	17.27	0.0003	11.25	0.0022	129.77	< 0.0001
BD	23.64	< 0.0001	49.22	< 0.0001	1.84	0.1854
BE	3.61	0.06733	74.96	< 0.0001	32.79	< 0.0001
CD	65.02	< 0.0001	14.80	0.0006	0.028	0.8673
CE	62.47	< 0.0001	8.68	0.0063	31.45	< 0.0001
DE	58.32	< 0.0001	43.12	< 0.0001	3.74	0.0629
A ²	11.62	0.0019	2.26	0.1436	333.77	< 0.0001
B ²	4.96	0.0338	2.64	0.1150	29.01	< 0.0001
C ²	0.69	0.4145	1.57	0.2201	84.70	< 0.0001
D ²	0.15	0.7046	0.32	0.5755	85.73	< 0.0001
E ²	26.62	< 0.0001	23.06	< 0.0001	145.51	< 0.0001
Lack of Fit	1.42	0.8120	0.33	0.9794	1.01	0.5340

4.11 EFFECTS OF PREPARATION VARIABLES ON THE % Fe CONTENT

The iron content (% Fe) of the magnetite-palmitic acid composite was between 38.3 to 83.1% for benzene, toluene, and xylene, respectively. The Model F-value of 53.52 indicates the model was significant. The Lack of Fit F-value of 1.42 shows that it was not significant relative to the pure error. Non-significant lack of fit is good because the model is expected to fit. The Probability F values less than 0.05 shows that the models' terms are significant while values greater than 0.1 indicate the models, terms are not significant. The R-squared value (r^2) was obtained to be 0.9736 indicating that only 0.01% of the total variations were not explained by the regression model. The adjusted R-squared value (r_a^2) was 0.9554. The r^2 value and the r_a^2 value are reasonably high and comparable showing that there is a good agreement between the models and the experimental data. The coefficient of variation (CV) was < 4.5 indicating the high reliability of the experiments for the chosen model. The significant model terms were A, B, C, E, AB, AD, AE, BC, BD, CD, CE, DE, A², B², E² with corresponding F-value of significant model terms 29.26, 13.32, 15.22, 19.32, 103.46, 12.36,

17.27, 23.64, 65.02, 62.47, 58.32, 11.62, 4.96, 26.62. It was also observed that the model obeyed the following order $AD > CD > CE > DE > BD > AB > BC > AE$. The interaction of AD had F-value of 103.46 and was the most significant.

4.12 EFFECTS OF PREPARATION VARIABLES ON THE CONDUCTIVITY (S/cm)

The conductivity (S/cm) for the magnetite-palmitic acid composite was between 71-2354 (S/cm) for benzene, toluene, and xylene respectively. The coefficient of determination, r^2 was 0.9734 and the r_a^2 was 0.9551. In this case, the model was favourable with probability $> F$ and F value of 53.14 implies the model was significant. There is only a 0.01 % chance that an F-value could occur due to noise. The coefficient of variation (CV) was < 4.5 indicating the high reliability of the experiments for the chosen model. The significant model are A, B, C, D, E, AB, AC, AD, AE, BC, BD, BE, CD, CE, DE, E^2 with corresponding F-value of significant model terms 11.79, 109.18, 76.41, 1.80, 262.04, 22.11, 5.07, 10.18, 60.83, 11.25, 49.22, 74.96, 1480, 8.68, 43.12, 23.00. The model interactions obeyed the following order $BE > AE > BD > DE > CD > BC > AD > CE > AC > AB$. The interaction of DE was the most significant due to a higher F value of 74.96.

4.13 EFFECTS OF PREPARATION VARIABLES ON BTX

4.13.1 Benzene adsorption capacity

The benzene adsorption capacity ranged from 10.882 to 43.501 mg/g. The F-value was 81.76, r^2 was 0.9826, r_a^2 was 0.9706. There is only a 0.01 % chance that an F-value this large could occur due to noise. The lack of fit 0.85 was good since the model is expected to fit. The coefficient of variation (CV) was relatively small and is less than 4.5 and the adequate precision was 37.584 which is greater than 4 showing a high reliability of the experiments for the chosen model. The significant model are B, C, D, E, AB, AC, AE, BC, BD, CD, CE, DE, A^2 , B^2 , C^2 , with corresponding F-value of significant model terms 94.86, 99.86, 10.66, 64.60, 39.73, 5.75, 19.09, 109.03, 38.16, 22.77, 68.69, 16.59. It was also observed that the interaction were in the following order $BC > CE > AB > BD > CD > AE > DE > AC$. The interaction of BC had the largest significance due to a higher F-value of 109.03.

4.13.2 Toluene adsorption capacity

The toluene adsorption capacity ranged from 8.821 to 51.372 mg/g. The models F-values was 62.53. The r^2 values are 0.9819 and the r_a^2 was 0.9773. The significant models were A, B, C, D, E, AC, AD, AE, BC, BE, CE, A^2 , B^2 , C^2 , D^2 , E^2 with corresponding F-value of significant model terms 33.70, 236.99, 57.81, 25.05, 17.72, 44.83, 18.32, 86.34, 104.39, 21.95, 30.41, 271.98, 23.23, 59.06, 71.15. It was also observed that the interactions were in the following order $BC > AE > AC > CE > BE > AD$. The interaction of BC had largest significance due to a higher F-value of 104.39.

4.13.3 Xylene adsorption capacity

The xylene adsorption capacity ranged from 10.821 to 53.372 mg/g. The models F-values was 78.71. The r^2 values are 0.9819 and the r_a^2 was 0.9694 with lack of fit of 2.97. The significant model are A, B, C, D, E, AB, AC, AD, AE, BC, BE, CE, A^2 , B^2 , C^2 , D^2 , E^2 with corresponding F-value of significant model terms 43.19, 305.15, 61.00, 31.86, 22.41, 5.69, 57.80, 28.81, 100.51, 129.17, 1.84, 31.45, 333.77, 29.01, 84.70, 84.73, 145.51. The interaction was in the following order $BC > AE > AC > CE > AD > AC > BE$. The interaction of BC had greatest influence and was the most significant due to a higher F-value of 129.17.

4.14 VALIDATION OF MODEL AND RESPONSE SURFACE PLOT

The plots of predicted versus actual values for % Fe content, conductivity (S/cm) and BTX adsorption capacity (mg/g) are shown in Fig. 4.3 (a-e) respectively. The diagnostic plots help determine whether a model is satisfactory. In this case the results indicate that the predicted and actual value were closely distributed near the straight line indicating that the models well fitted the experimental data and all predictive models can be used to navigate the design space defined by CCD.

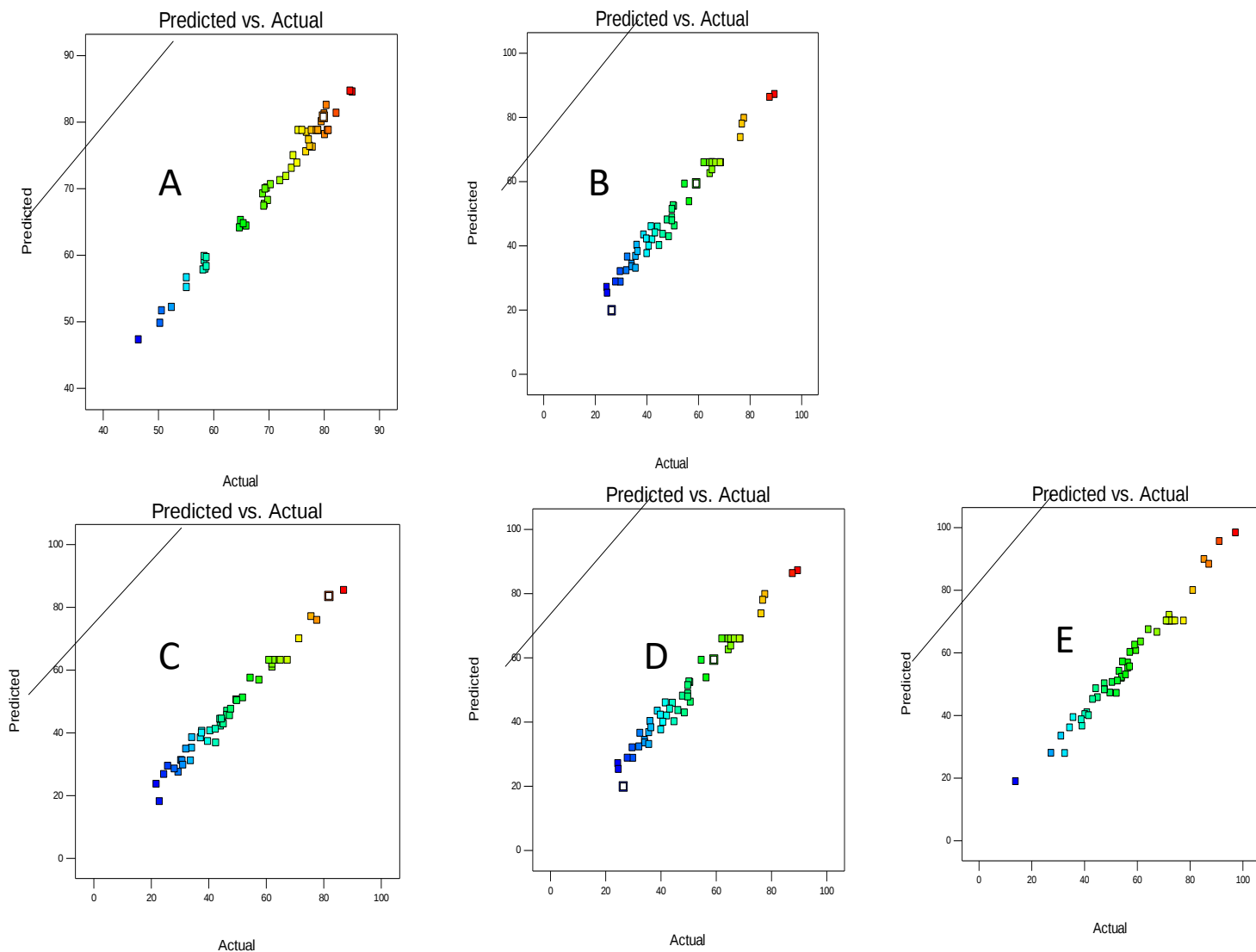


Figure 4.3: Plot of actual values against predicted values of (a) % Fe, (b) conductivity, (c) benzene adsorption capacity, (d) toluene adsorption capacity (e) xylene adsorption capacity.

4.15 THREE-DIMENSIONAL RESPONSE SURFACE

4.15.1 3D Response Surface plots for % Fe content

The 3D Response surface plots of the quadratic models with respect to % Fe content is shown in Fig.4.4 (a). The plot shows interaction of $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution and time while maintaining microwave power, the volume of ammonium hydroxide (NH_4OH) and volume of palmitic acid at 5.00 W, 5.00 mL, and 2.10 mL, respectively. Fig 4.4 (a) show that increasing the $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution from 0.5 to 1.25 mL increased the % Fe content to 79.8 %, however further increase to 2.00 mL then later resulted in slight decrease to 77 %. In the case of time versus the $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution increasing the time from 5 to 10 min, the % Fe content was low 67.9 % but further increase in time to 15 min the % Fe content also increased to 75.3%.

4.15.2 3D Response Surface plots for conductivity on the adsorbent

The 3D response surface plots of the quadratic models with respect to influence of synthesis variables on the conductivity (S/cm) of magnetite-palmitic acid composite. The plot of Fig. 4.4 (b) shows the interactions of microwave power and volume of palmitic acid while maintaining the $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution, the volume ammonium hydroxide time at 1.25 mL, 5.00 mL and 10 min, respectively. The plot shows that as the microwave power increase from 200 to 500 W low conductivity was achieved, 255 (S/cm), however further increase in microwave power to 800 W then resulted in increment of conductivity to 454 (S/cm). For the volume of palmitic acid versus microwave power it was observed that at low volume of acid between 0.2 to 2.10 mL the conductivity of the material was low, 105 (S/cm) but an increment in the volume of the palmitic to 4.00 mL then increases the conductivity of the material to 799 (S/cm).

4.13.3 3D Response surface plots for BTX adsorption capacity

4.13.3.1 Benzene adsorption capacity

The 3D surface plot in Fig.4.4 (c) shows the interactions of microwave power and the volume ammonium hydroxide while maintaining the $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution, volume of palmitic acid and time at 1.25 mL, 2.10 mL and 10 min respectively. The plot shows that at low microwave power the adsorption capacity was low at 18.78 mg/g but as the microwave power increase to 800 W the adsorption capacity increased to 37.84 mg/g. For the volume of the volume of ammonium hydroxide solution versus microwave power, the increase from 2.0 to 5.0 mL in the volume of ammonium hydroxide solution resulted in an increase in the adsorption capacity

of 43.5 mg/g but at a later stage when in the volume of ammonium hydroxide solution was 8.00 mL the adsorption capacity decreased drastically to 16.308 mg/g. The maximum point was achieved at 29.37 mg/g, microwave power of 500 W and the volume of ammonium hydroxide solution of 5.00 mL.

4.13.3.2 Toluene adsorption capacity

The 3D surface plot in Fig.4.4 (d) shows the interactions of microwave power and the volume of ammonium hydroxide while maintaining the $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution, volume of palmitic acid and time at 1.25 mL, 2.10 mL and 10 min, respectively. As the microwave power decreases from 200-500 W, adsorption capacity decreases, adsorption capacity at this point was 23 mg/g. However, an increase in microwave power to 800 W slightly increases the capacity to 27.64 mg/g. For the volume ammonium hydroxide solution the results show that the toluene adsorption capacity increased with increase in volume of ammonium hydroxide solution from 2.00 to 5.00 mL. The adsorption capacity of toluene at this point was achieved at 42.5 mg/g. The results also show further increment in the volume of ammonium hydroxide solution to 8.00 mL then resulted in decrease in capacity. The adsorption at this point was 16.9 mg/g. The maximum adsorption capacity achieved was 27.497 mg/g, microwave power of 500 W and volume of ammonium hydroxide at 5.00 mL.

4.13.3.3 Xylene adsorption capacity

The 3D surface plot in Fig.4.4 (e) shows the interaction of $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution and volume of palmitic acid while maintaining microwave power, the volume ammonium hydroxide and time at 500 W, 5.00 mL, and 10 min, respectively. The plot shows that for the volume of $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution between 0.5 to 1.25 mL, capacity was low and was 22.4 mg/g but when the $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution increased to 2.00 mL the capacity increased to 46.97 mg/g. For the volume of the volume of ammonium hydroxide solution between 0.5 to 5.00 mL the adsorption capacity was slightly high at 51.37 mg/g but when the volume of ammonium hydroxide solution increased to 8.00 mL the capacity drastically decreased to 16.9 mg/g. The maximum point for adsorption capacity was 27.50 mg/g, $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution at 1.25 mL and volume of acid at 5.00 mL.

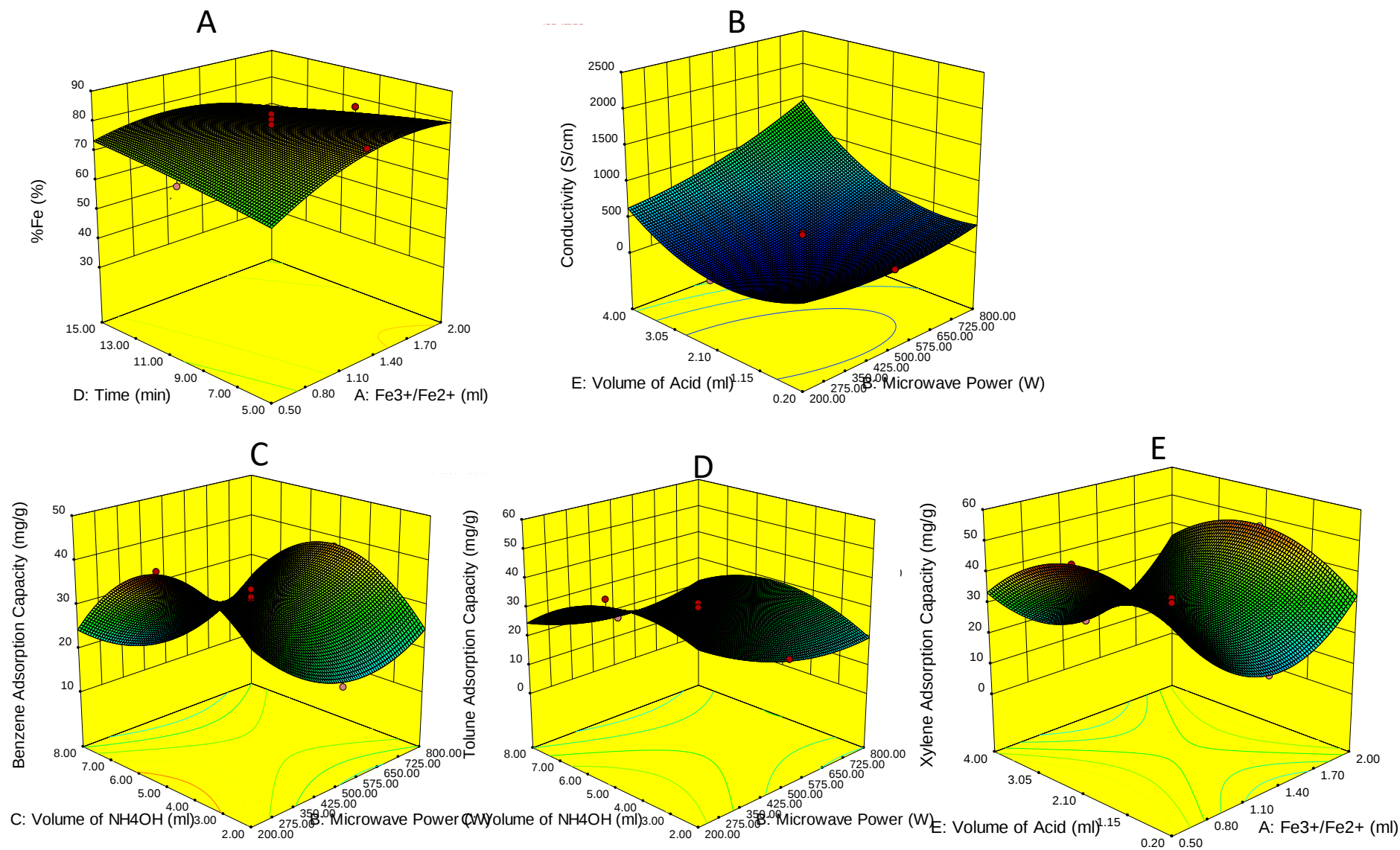


Figure 4.4: 3D plots of (a-e) for % Fe, conductivity, benzene, toluene and xylene adsorption capacity.

Table 4.14: Magnetite-palmitic acid composite optimum values

Pollutant name	Fe ³⁺ /Fe ²⁺ volume (ml)	Microwave power (W)	NH ₄ OH volume (ml)	Time (min)	Volume of acid (ml)	% Fe	Conductivity (S/cm)	Adsorption capacity (mg/g)	Desirability
Benzene	0.5	200	2.00	15.00	0.2	75.51	1011.34	60.55	0.96
Toluene	0.5	200	2.00	15.00	0.2	76.17	1325.66	64.47	0.95
Xylene	0.5	200	2.00	15.00	0.2	75.59	1039.45	63.06	0.97

4.16 CONCLUSION

The results show successful preparation of the magnetite-oleic and magnetite-palmitic acid composites. The most significant synthesis variables that controls reaction responses for both magnetite-oleic and magnetite-palmitic acid composites were the volume of oleic and palmitic acid, microwave power and $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution due to their high F-values. The optimum preparation conditions estimated by CCD for the synthesis of magnetite-oleic acid composite were: 0.5 mL of $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution, 200 W microwave power, 5 min microwave irradiation reaction time and 0.8 mL volume NH_4OH and 0.2 mL of oleic acid solution. The optimum condition for magnetite-palmitic acid composite were: 0.5 mL of $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution, 200 W microwave power, 15 min microwave irradiation reaction time and 0.8 mL volume NH_4OH and 0.2 mL of palmitic acid solution. The results showed that the optimum preparation conditions estimated by CCD for magnetite-oleic acid composite were 78.3 % Fe content, 1561.9 S/cm conductivity, 82.2 mg/g benzene, 84.1 mg/g and 85.3 mg/g xylene adsorption capacity. The optimum condition for palmitic-oleic acid composite were 75.6 % Fe content, 1325.66 S/cm conductivity, 60.55 mg/g benzene adsorption capacity, 64.47 mg/g toluene adsorption capacity and 63.06 mg/g xylene adsorption capacity.

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5 RESULTS AND DISCUSSION (PART 1): THE CHARACTERIZATION OF PURE MAGNETITE, MAGNETITE-OLEIC AND MAGNETITE-PALMITIC ACID COMPOSITE

5.1 INTRODUCTION

The chapter presents different sections. In this section results of the characterization of pure magnetite nanoparticles (MNP), pure oleic acid (OA), pure palmitic acid (PA), magnetite-oleic (MNP-OA) and magnetite-palmitic (MNP-PA) acid composites were presented. The characterization was employed to confirm if the target materials were produced, to determine the effect of organic acid coating and to show the effect of different chain lengths of surfactant molecules (hydrophobicity). Oleic and palmitic are mono-carboxylic acids, oleic acid has longer carbon chain length C_{18} and a double bond (monounsaturated) while palmitic acid has shorter carbon chain length C_{16} and has no double bond (saturated). The characterization techniques employed were Fourier Transform infrared (FTIR), Thermal Gravimetric Analysis (TGA). The X-Ray diffraction (XRD), Vibrating sample magnetometer (VSM), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Electron Dispersive Spectroscopy (EDX), Brunauer-Emmett-Teller Surface Area (BET) and the pH_{pzc} .

5.2 FTIR SPECTROSCOPY

To understand the adsorption mechanism of the oleic and palmitic acid on the surface of the magnetite nanoparticles Fourier-transform infrared (FTIR) spectroscopy measurements were conducted to study the different functional groups of the pure magnetite, pure oleic acid, pure palmitic acid and the changes in functional groups after coating the magnetite with oleic acid and palmitic acid. The functional groups on the FTIR spectrum show that the pure magnetite and magnetite-organic acid composites (magnetite-oleic and magnetite-palmitic) were successfully synthesised.

5.2.1 FTIR of pure magnetite nanoparticles

FTIR of pure magnetite nanoparticles is shown in Fig. 5.1. The spectrum shows a shoulder at 624 cm^{-1} and a strong absorbance band at 544 cm^{-1} assigned to the Fe–O band related to the magnetite stretching vibration modes (Tran *et al.*, 2010, Salem and Awwad, 2013, Soares *et*

al., 2014). The metal oxygen absorption bands at 435 cm^{-1} , was assigned to the octahedral Fe only and corresponds to the band of Fe-O of bulk magnetite (Pati *et al.*, 2013, Khanehzaei *et al.*, 2014, Pham *et al.*, 2016). The absorption peaks at 2983, 2899, 1624, 1403, 1052 and 870 cm^{-1} were attributed to ethanol and de-ionized water used as solvent (Chaki *et al.*, 2015) while the broad band at 3429 cm^{-1} represents the hydroxyls groups (O-H) stretching vibration mode ascribed to water on nanoparticles (Soares *et al.*, 2014, Muthukumaran and Philip, 2016).

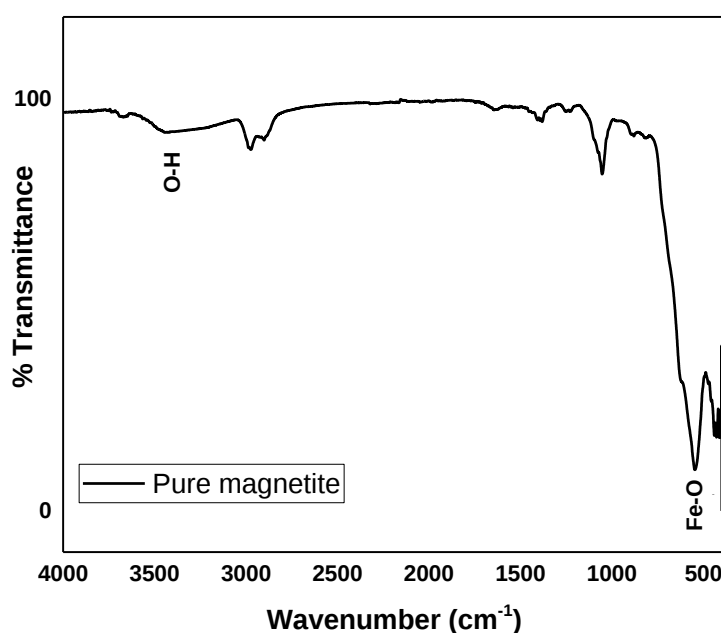


Figure 5.1: FTIR spectra of pure magnetite nanoparticles.

5.2.2 FTIR of magnetite-oleic acid composite

To confirm the interaction between the functional groups of magnetite and oleic acid. The FTIR spectrum of pure oleic acid and magnetite-oleic acid composite were performed separately.

The FTIR spectrum of pure oleic acid shown is in Fig. 5.2. The spectrum in Fig 5.2 shows prominent peaks at 2923 and 2859 cm^{-1} which are ascribed to asymmetric and symmetric stretching modes of CH_2 . The peak at 1709 cm^{-1} was due to C=O stretching, the 1407 and 1539 cm^{-1} are attributed to symmetric and asymmetric (COO^-) (Yang *et al.*, 2010). The peak at 1051 cm^{-1} was due to C-O stretching and the O-H out-of-plane bands occurred at 883 cm^{-1} (Mosafer *et al.*, 2017).

When magnetite nanoparticles were coated with oleic acid reduction in intensities and shift of certain peaks along with the disappearance of certain new peaks were observed. For example, the intensity of the broad peak at 3429 cm^{-1} decreased due to displacement of water by hydrophobic oleic acid. The bands representing asymmetric and symmetric CH_2 stretching of the oleic acid coating agent reduced in intensity, The results of the significant shift of these specific peaks to the lower frequency indicated that the hydrocarbon chains in the monolayer surrounding the nanoparticles were in a closed-packed, crystalline state (Nakamoto and Nakamoto, 1977, Bootdee *et al.*, 2012, Mahdavi *et al.*, 2013). Other factors could be that after stabilization by long chain carboxylic acid, the sample possesses hydrophobicity (Muthukumaran and Philip, 2016). The peak at 544 cm^{-1} and 624 cm^{-1} corresponding Fe-O were slightly shifted and this could attributed to the interaction of Fe atoms from the magnetite nanoparticles and carboxyl groups of oleic acid producing a partial single bond character of the carbonyl C=O group there by shifting the stretching frequency to a lower region (Li *et al.*, 2010, Yang *et al.*, 2010).

The bands that represents the asymmetric and symmetric carboxylic ion (COO^-) at 1404 and 1534 cm^{-1} (Yang *et al.*, 2010) were observed to shift from 1407 and 1539 cm^{-1} confirming the interaction between oleic acid and magnetite with these groups after capping of magnetite with oleic acid. The bands attest that the magnetite surface and the stabilizing agent are bonded as the esterification happens between the hydroxyl groups on the magnetite surface and the (COO^-) carboxyl group from the acid molecule (Yang *et al.*, 2010, Petcharoen and Sirivat, 2012, Lobato *et al.*, 2016).

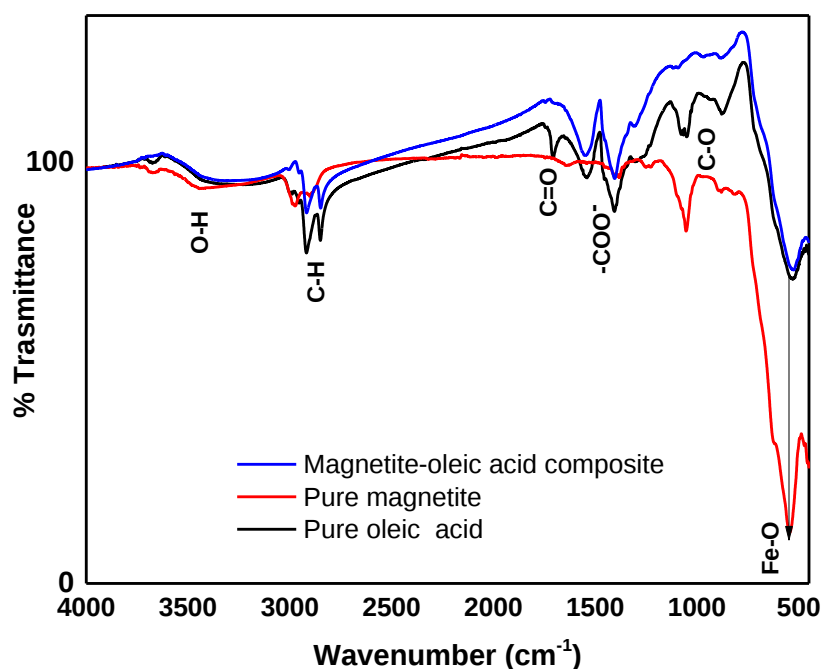


Figure 5.2: FTIR spectra of pure magnetite, pure oleic and magnetite-oleic acid composite.

5.2.3 FTIR of magnetite-palmitic acid composite.

The FTIR spectrum analysis of pure palmitic and magnetite-palmitic acid composite were performed to elucidate the different function groups present on the materials. The FTIR spectrum of pure palmitic acid is displayed in Fig. 5.3. Although there were no strong peaks for the initial pure palmitic acid, the CH_2 strong peaks corresponding to asymmetric and symmetric stretching modes were observed at 2912 and 2846 cm^{-1} (Choi and Lee, 2017). The sharp and strong peak at 1703 cm^{-1} indicates the $\text{C}=\text{O}$ stretching in the carboxyl ($-\text{COOH}$) group and the peaks at 1419 and 1539 cm^{-1} also observed in the sample indicates the symmetric and asymmetric (COO^-) (Choi and Lee, 2017). The bands at 1420 and 932 cm^{-1} were associated with the $-\text{OH}$ in-plane and out-of plane stretch, respectively (Harnchana *et al.*, 2018). The presence of the band at 1270 cm^{-1} is due to the $\text{C}-\text{O}$ stretch (Mosafer *et al.*, 2017).

After magnetite nanoparticles were coated with palmitic acid reduction in intensities and shift of certain peaks along with the disappearance of certain new peaks were observed. As the palmitic acid molecules are adsorbed to the surface of the magnetic nanoparticles, the FTIR

characteristic bands representing asymmetric and symmetric CH_2 stretching of the palmitic acid reduced in intensity were found to shift to lower wave number. This is due to that the hydrocarbon chains in monolayer surrounding the nanoparticles are in a closed-packed, crystalline state (Choi and Lee, 2017). In addition modification might have led to superhydrophobic surfaces on the composite (Muthukumaran and Philip, 2016). The peak at 544 cm^{-1} corresponding Fe-O were slightly shifted to lower wavelength and this could attributed to the interaction of Fe atoms from the magnetite nanoparticles and carboxyl groups of palmitic acid producing a partial single bond character of the carbonyl C=O group there by shifting the stretching frequency to a lower region (Li *et al.*, 2010, Yang *et al.*, 2010).

By comparison, the strong peak at 1703 cm^{-1} was displaced, and a new peak at 1578 cm^{-1} was formed in the spectrum for the palmitic coated magnetite particles surface, the same stretching peaks at $1540\text{--}1460\text{ cm}^{-1}$ were also observed in the sample. The new peak at 1578 cm^{-1} is assumed to correspond to C-O bond, which shifted from 1703 to 1578 cm^{-1} . This peak suggests that a chemical interaction between the palmitic coating molecule and the C -O bonding in the carboxyl group of palmitic acid occurred (Choi and Lee, 2017). Several authors have observed similar peaks for successful coating of palmitic acid to magnetite (Agrawal *et al.*, 2017, Choi and Lee, 2017, Harnchana *et al.*, 2018).

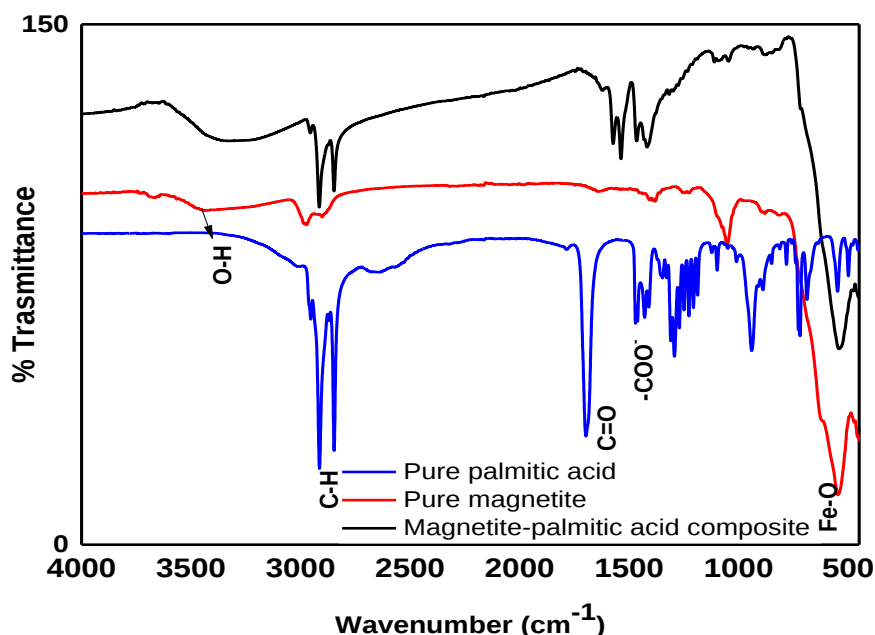


Figure 5.3: FTIR spectra of pure magnetite, pure palmitic acid and magnetite-palmitic acid composite.

5.3 THERMOGRAVIMETRIC ANALYSIS (TGA) AND DERIVATIVE THERMOGRAVIMETRIC ANALYSIS (DTA)

5.3.1 TGA/ DTA of Pure magnetite

The TGA and derivative weight loss percent of the pure magnetite nanoparticles were performed to understand the thermal stability of the sample. The analysis was performed under an inert environment, from 30 to 900 °C at a heating rate of 10 °C /min is shown in Fig 5.4. The initial weight loss at temperature of 54.5 °C correspond to the evaporation of adsorbed water (Abboud *et al.*, 2015). The thermogram of the pure magnetite shows that the weight loss in this range was about 3.6 %; the peak of the DTA isotherm at above 500 to 700 °C corresponds to the transformation of magnetite to iron (II) oxide because of the unstable phase of iron (II) oxide at higher temperatures (Zhang *et al.*, 2018).

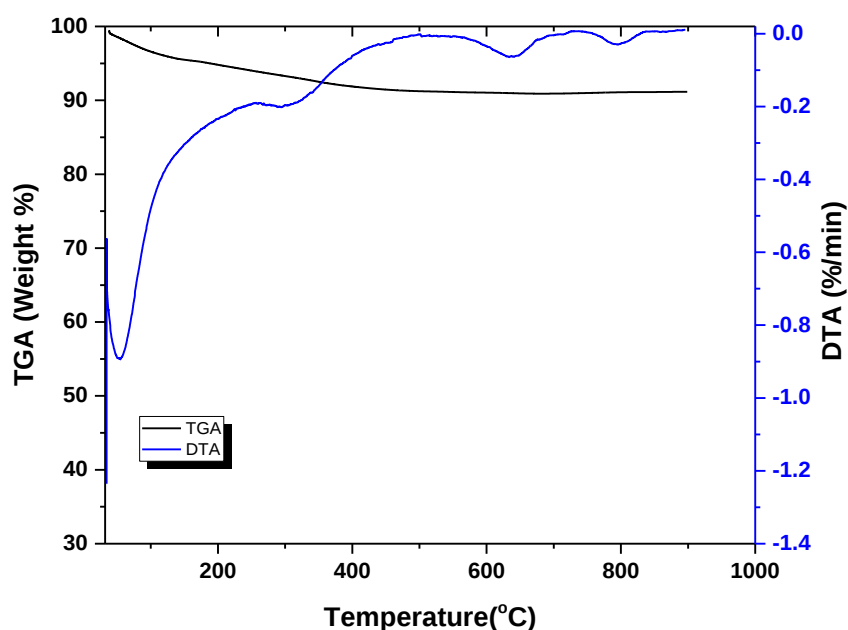


Figure 5.4: Thermal stability of the pure magnetite.

5.3.2 TGA/DTA of magnetite-oleic acid composite

The TGA and DTA of magnetite-oleic acid composite are presented in Fig. 5.5. The weight loss at a temperature of 97.4 °C, was attributed to the evaporation of adsorbed water molecules (Abboud *et al.*, 2015). No excess moisture was present after this initial stage considering the fact that the sample had a hydrophobic character. The weight loss at this stage was approximately 2.1 % (Abboud *et al.*, 2015). Moreover, the magnetite-oleic acid composite thermograms showed weight loss over the temperature range firstly between 97.4 and 214 °C and secondly between 214 to 340 °C. The first decomposition due to physically adsorbed water represents the decomposition of the oleic acid molecule layer with weight loss of 24.4 % (Dadwal and Joy, 2018). The second decomposition was due to chemically adsorbed water and showed weight loss of 28.8 % (Lobato *et al.*, 2016). Petcharoen and Sirivat, 212 observed the same trend in the TGA of magnetite-oleic acid composite. Lastly the weight loss due to the conversion of magnetite (Fe_3O_4) to ferrous oxide (FeO) appeared at 687 to 754 °C and had a percentage weight loss of 43.9% (Lobato *et al.*, 2016).

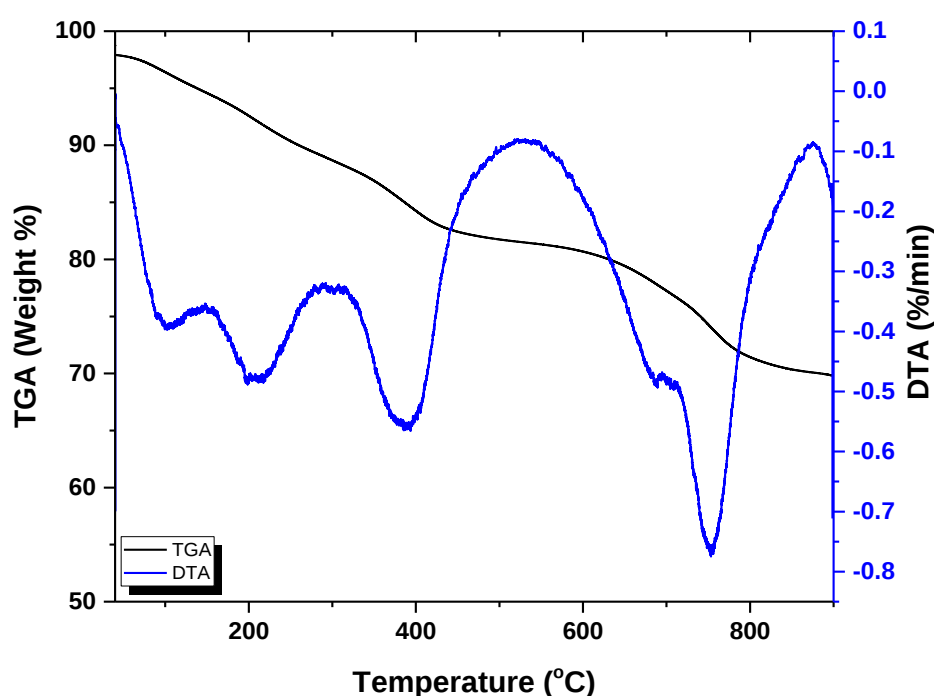


Figure 5.5: Thermal stability of the magnetite-oleic acid composite.

5.3.3 The TGA/DTA of magnetite-palmitic acid composite

The thermogram of magnetite-palmitic acid composite is shown in Fig. 5.6. The sample shows initial weight loss at temperature corresponding at 56.3 °C indicating absorbed moisture (Abboud *et al.*, 2015). It can be assumed that the surface of the magnetite-palmitic acid composite had no excess water molecules present after this stage. The weight loss at this stage was about 3.1 % (Baharuddin *et al.*, 2018). The thermogram of magnetite-palmitic acid composite also showed the second step weight loss over the temperature range of 56.3 to 382 °C with weight loss of 44.9 % indicating that palmitic acid molecule was directly bonded with the Fe₃O₄ nanoparticle (Morel *et al.*, 2013). Similar results have been obtained by (Qian *et al.*, 2008, Petcharoen and Sirivat, 2012). The third weight loss due to the conversion of magnetite (Fe₃O₄) to ferrous oxide (FeO) between 382 to 677 °C showed weight loss of 63.4 % (Zhang *et al.*, 2006, Petcharoen and Sirivat, 2012). Finally, from 677 °C upwards, there is no loss of weight loss the material becomes stable.

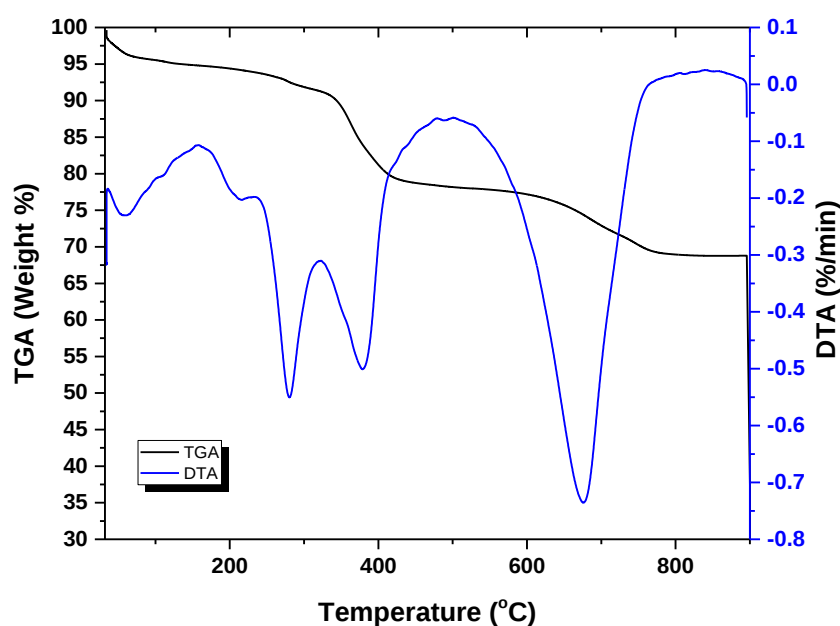


Figure 5.6: Thermal stability of the magnetite-palmitic acid composite.

5.4 X-RAY DIFFRACTION (XRD)

5.4.1 XRD of pure magnetite

The X-ray diffraction of pure magnetite is shown in Fig 5.7. The analysis shows six intense diffraction peaks at $2\theta = 30.17^\circ$, 35.46° , 43.38° , 53.69° , 57.23° and 77° with their corresponding indices at (220), (311), (400), (422), (511) and (440). The peaks matched well with the pattern of standard Fe_3O_4 (JCPDS card number: 00-019-0629) confirming that the material synthesized was pure magnetite (Arabi *et al.*, 2017, Zhao *et al.*, 2018). The pattern indicated magnetite has a crystalline structure (Castelló *et al.*, 2015, Baharuddin *et al.*, 2018).

The diffractogram also shows the absence of the diffraction peaks at (113) and (210) which are characteristic of goethite, maghemite and hematite. This shows there were no impurities on the sample (Muthukumaran and Philip, 2016, Klekotka *et al.*, 2018, Rajput *et al.*, 2016). The average crystalline particle size was calculated with the Debye–Scherrer formula from the half-maximum width of the (311) X-ray diffraction line and it was 19.7 nm.

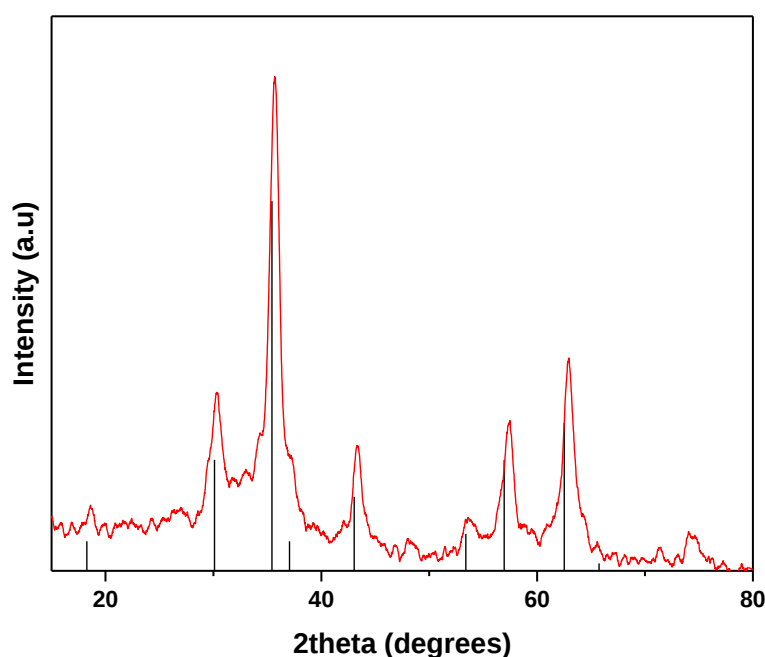


Figure 5.7: XRD diagram of pure magnetite nanoparticles.

5.4.2 XRD of magnetite-oleic acid composite

The XRD of magnetite-oleic acid composite is shown in Fig 5.8. The diffractogram shows that after encapsulation of magnetite nanoparticles with the hydrophobic oleic acid, peaks at $2\theta = 30.3^\circ$, 35.66° , 43.8° , 53.53° , 57.33° and 77.6° corresponding to (220), (311), (400), (422), (511) and (440) were also observed similar to that of pure magnetite nanoparticles indicating sample has crystalline structure. However, it was noted that the magnetite-oleic acid composite characteristics peaks became broad and the height of the peaks decreased drastically after coating. The shift to lower intensity after modification indicates that coating the iron oxide nanoparticle has control over the crystalline growth (Muthukumaran and Philip, 2016, Klekotka *et al.*, 2018). Also when the oleic acid molecule interact with the surface of the magnetite, microstrain may be induced on the particle resulting in broadening of peaks (Vasile *et al.*, 2012). The crystallite size obtained from Debye Scherrer equation was 17.1 nm.

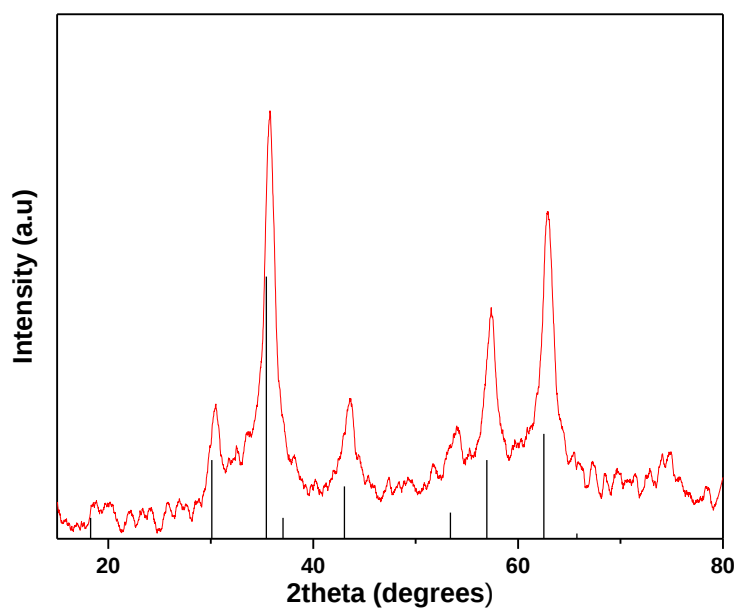


Figure 5.8: XRD of magnetite-oleic acid composite.

5.4.3 XRD of magnetite-palmitic acid composite

The XRD pattern of magnetite-palmitic acid composite is shown in Fig 5.9. The diffraction peaks confirm the crystalline structure of magnetite-palmitic acid composite. The diffractogram show a similar pattern with that of Fig 5.7, however slight decrease in intensity

was observed after coating. The peaks became broad for magnetite-palmitic acid composite as compared to pure magnetite nanoparticles. Surface O-H groups of the magnetite nanoparticles interact with the palmitic acid molecule. This will induce force/ strain on the particle and result to broadening of XRD peaks. The diffraction peaks were observed at $2\theta = 30.17^\circ$, 35.46° , 43.38° , 53.69° , 57.23° and 77° and are marked with their corresponding indices at (220), (311), (400), (422), (511) and (440) attributed to the presence of cube crystalline structure of inverse spinel (Dadwal and Joy, 2018). There is no evidence of other oxide formation, such as goethite (α -FeOOH) and hematite (α -Fe₂O₃). The average crystallite size was estimated from the full width at half maximum of the most intense (311) peak, using the Scherrer equation, $D = 0.89\lambda/\beta\cos\theta$ (D: average crystallite size, λ : wavelength of Cu K α radiation, β : full width at half maximum corrected for the broadening from the instrumental contribution, θ : Bragg angle). The crystallite size was calculated as 17.9 nm from (311) peak using the Debye-Scherrer equation.

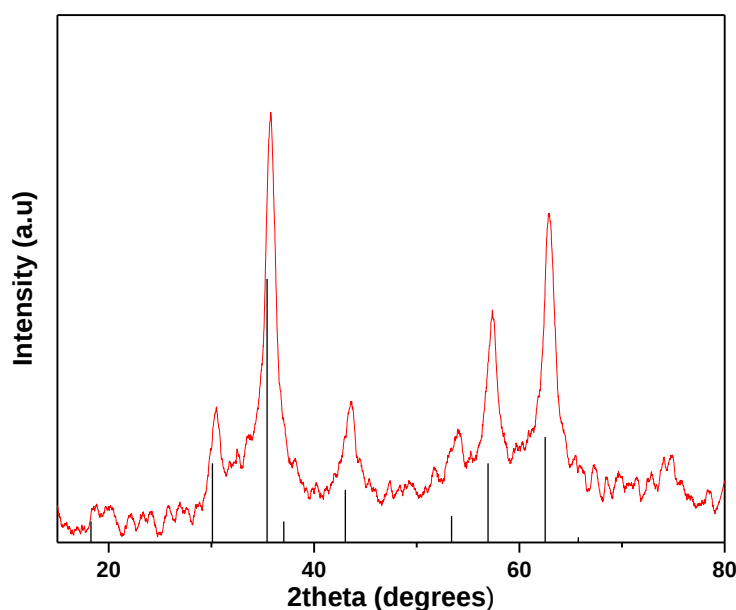


Figure 5.9: XRD of magnetite-palmitic acid composite.

5.5 TRANSMISSION ELECTRON SPECTROSCOPY (TEM)

5.5.1 TEM of pure magnetite nanoparticles

The transmission electron spectroscopy (TEM) of the pure magnetite nanoparticles is shown in Fig 5.10. From the figure, it can be observed the pure magnetite nanoparticles have a spherical shape. However a strong magnetic dipole-dipole interaction was shown by uncoated magnetite causing big clusters and bigger particle size (Shete *et al.*, 2015). The agglomeration in the nanometric size particles of the pure magnetite nanoparticles was due to the absence of surface capping agent (Taufiq *et al.*, 2017, Muthukumaran and Philip, 2016, Neto *et al.*, 2018). The statistical analysis for the Fe_3O_4 sample was performed through counting several particles, using ImageJ software and the average particles size was found to be 18.4 ± 0.5 nm.

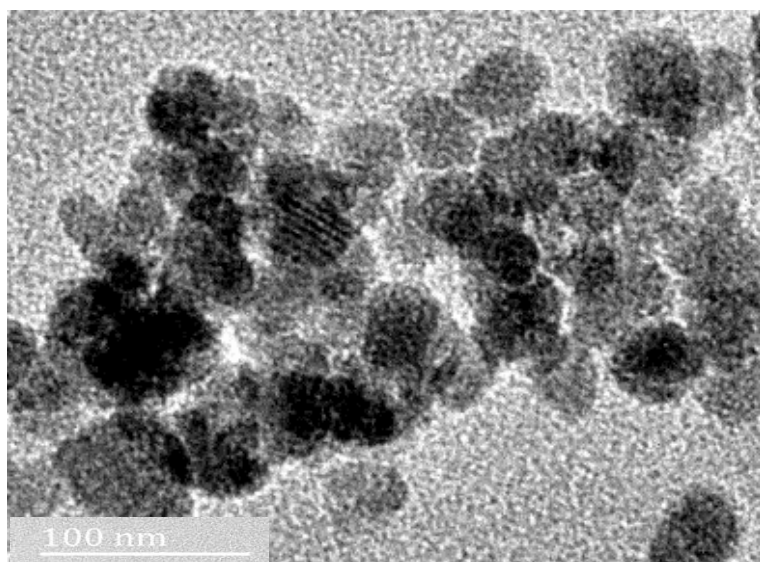


Figure 5.10: TEM images of pure magnetite nanoparticles.

5.5.2 TEM of magnetite-oleic acid composite

The TEM image of the magnetite-oleic acid composite is shown in Fig 5.11. The image shows the nanoparticles have a spherical shape and were better separated from one another as compared with the pure magnetite. This was due to the presence of the carboxylic acid surfactant on the surface of the nanoparticles. The average particle size obtained was 15.6 ± 0.5 nm. Also, after modification process a non-magnetic layer was formed on the magnetite surface resulting in decrease in particle size of the material. The particles had less degree of aggregation (Li *et al.*, 2013, Shete *et al.*, 2015). When compared the pure magnetite, the TEM image of the magnetite-oleic acid composite also show better isolation due to the strongly

held uniform monolayer coverage of oleic acid (Muthukumaran and Philip, 2016). These results are comparable with the XRD results which shows nanosized material.

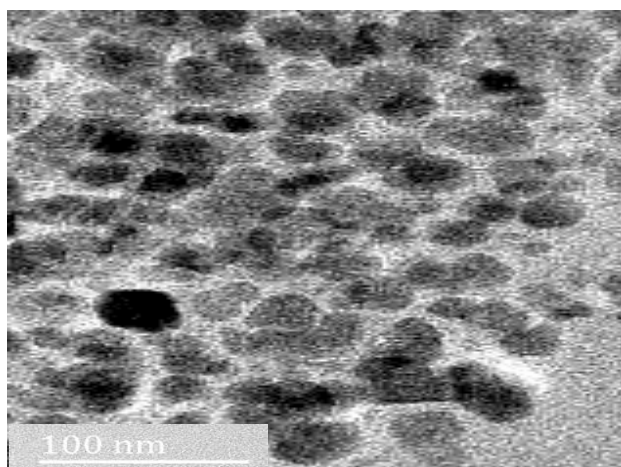


Figure 5.11: TEM images of magnetite-oleic acid composite.

5.5.3 TEM of magnetite-palmitic acid composite

The TEM image of the magnetite-palmitic acid composite is shown in Fig 5.12. The micrographs still show that the magnetite-palmitic acid composite was nanosized and spherical in shape. The micrographs of the magnetite-palmitic acid composite further showed better sample dispersibility compared to the pure magnetite nanoparticles, this was due to the capping of the magnetite surface by the hydrophobic acid. The average particle size was 16.5 ± 0.5 nm, this shows a slight decrease in the palmitic coated nanoparticles particle size when compared to the pure nanoparticles. The reduction in the particle size was due to the presence of the non-magnetic organic acid layer formed on the surface of the magnetite (Li *et al.*, 2013, Shete *et al.*, 2015). The TEM results are in good agreement with the crystalline size shown from the XRD analysis confirming the material was nanometric.

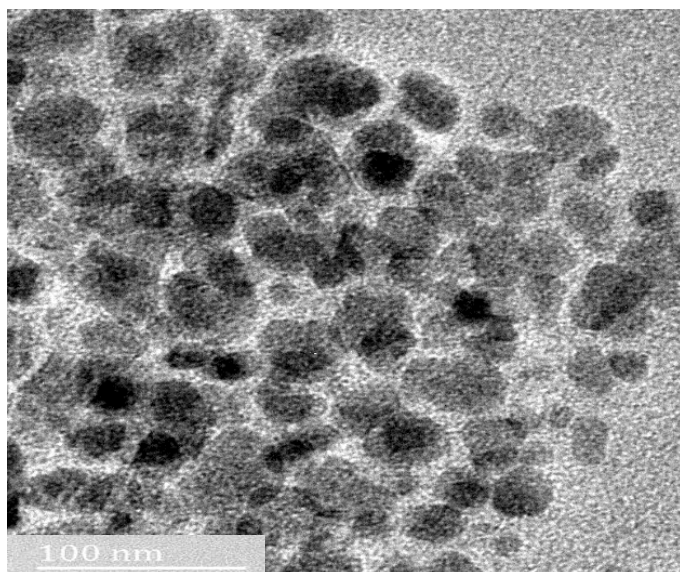


Figure 5.12: TEM images of magnetite-palmitic acid composite.

The crystallite size and the particle size studies of the magnetite-oleic acid composite and the magnetite-palmitic acid composite suggested that the samples were comparable. The only difference between the magnetite-organic acid composites is the difference in the chain length of the fatty acid molecules which shows that the coating layer plays a significant role in reducing the crystallite size (XRD) and particle size (TEM) of the material (Dey and Purkait, 2015). The magnetite-oleic acid composite showed smaller crystallite size than the magnetite-palmitic acid composite. This indicates that a stable dispersion of magnetite nanoparticles can be found using long-chain fatty acid compared to short-chain surfactant molecules hence the small crystallite size (Dadwal and Joy, 2018). The oleic acid molecule long alkyl chain (C-18) results in a strong chelating bidentate interaction between the -COO^- group and the Fe atom (Dey and Purkait, 2015, Klekotka *et al.*, 2018). Also, the smaller crystallite size of magnetite-oleic acid composite presents a barrier for mass transfer at the nanoparticle surface and thus limits the growth of the already formed nanoparticles. The carboxyl group of the first layer is oriented towards the nanoparticles surface while the oleate's long chain tail is oriented outwards. The tail of the second layer is parallel to the first layer while the carboxyl group orient itself outward from the surface. This bilayer structure as well as the reduction of the surface energy provides a barrier for the diffusion of the hydrolysed species needed for the particle's growth. The palmitic acid molecule possesses a shorter alkyl chain (C-16), hence coating with palmitic acid separates the particles and therefore diminishes interparticle

interaction causing an increased dipole-dipole interaction or increased particle size (Klekotka *et al.*, 2018). When comparing the TEM images of the magnetite-oleic acid composite with that of magnetite-palmitic acid composite, the difference in particles size due to the long alkyl chain of the stearic acid molecule, it will interpenetrate more into the alkyl chain attached to the neighboring particles as compared to the palmitic and myristic acid molecules (Dadwal and Joy, 2018).

5.6 SCANNING ELECTRON MICROSCOPY (SEM)

5.6.1 SEM of pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid composites

The surface morphology of the pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid composites is shown in Figure 5.13 (a)-(c). Surface of pure magnetite nanoparticles appears to have spherical structure. However due to strong inter-particles van der Waals and magnetic attraction among the bare Fe_3O_4 nanoparticles, some agglomeration was detected inside the sample. After modification with oleic and palmitic acid, Figure 5.13 (b)-(c) shows that the magnetite-oleic and magnetite-palmitic acid composite surface appears to be rough. This can be due to the combination of the coating agent layer on the surface of magnetite (Petcharoen and Sirivat, 2012). Also, the coating agent may form micelles around the magnetite surface and a small amount of the nuclei might be captured inside the micelle. It can be assumed that the lack of aggregation is probably because the carboxylic acid coating that weakens the magnetic interactions between particles (Petcharoen and Sirivat, 2012).

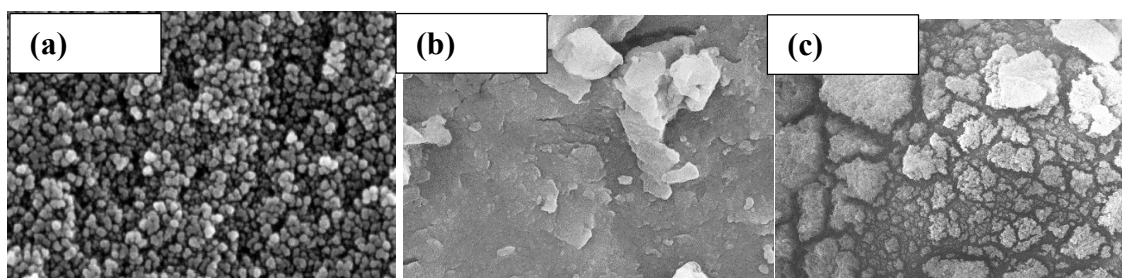


Figure 5.13: SEM images of (a) pure magnetite nanoparticles, (b) magnetite-oleic acid composite and (c) magnetite-palmitic acid composite.

5.7 ELECTRON DISPERSIVE SPECTROSCOPY (EDX)

5.7.1 EDX of pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid composites

The elemental analysis results of the samples obtained from EDX are shown in Fig.5.14. The EDX analysis confirm that the main constituent elements of pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid composites to be iron (Fe), carbon (C) and oxygen (O) (Muthukumaran and Philip, 2016). Fig. 5.14 shows peaks around 0.8, 6.3, and 6.8 keV associated to the binding energies of Fe (Wulandari *et al.*, 2018). The spectrum of pure magnetite nanoparticles contained two major peaks, which were assigned to Fe and O. This confirms that the material was pure magnetite. The spectrum of the pure magnetite nanoparticles also small peak C which attributed to the ethanol used during synthesis and ethanol used for washing the nanoparticles. The magnetite-oleic and magnetite-palmitic acid composite contained three major peaks assigned not only for Fe and O but also C. The carbon peak attributed observed for the two magnetite-organic acid composite confirmed the oleic and palmitic acid layer on the surface of the magnetite (Velusamy *et al.*, 2016). Figure 5.14 shows the EDX graphs for pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid composites. The results show that the % Fe content for magnetite-organic acid composites were lower than that of pure magnetite nanoparticles. This result can be attributed to the presence of the non-magnetic layer immobilized on the surface of the pure magnetite nanoparticles.

Table 5.1: Elemental analysis of pure magnetite, magnetite-oleic and magnetite-palmitic acid composite.

Sample	Fe	O	C
Pure magnetite	78.8	16.35	4.85
Magnetite-oleic acid composite	68.42	27.08	4.50
Magnetite-palmitic acid composite	63.96	17.96	18.54

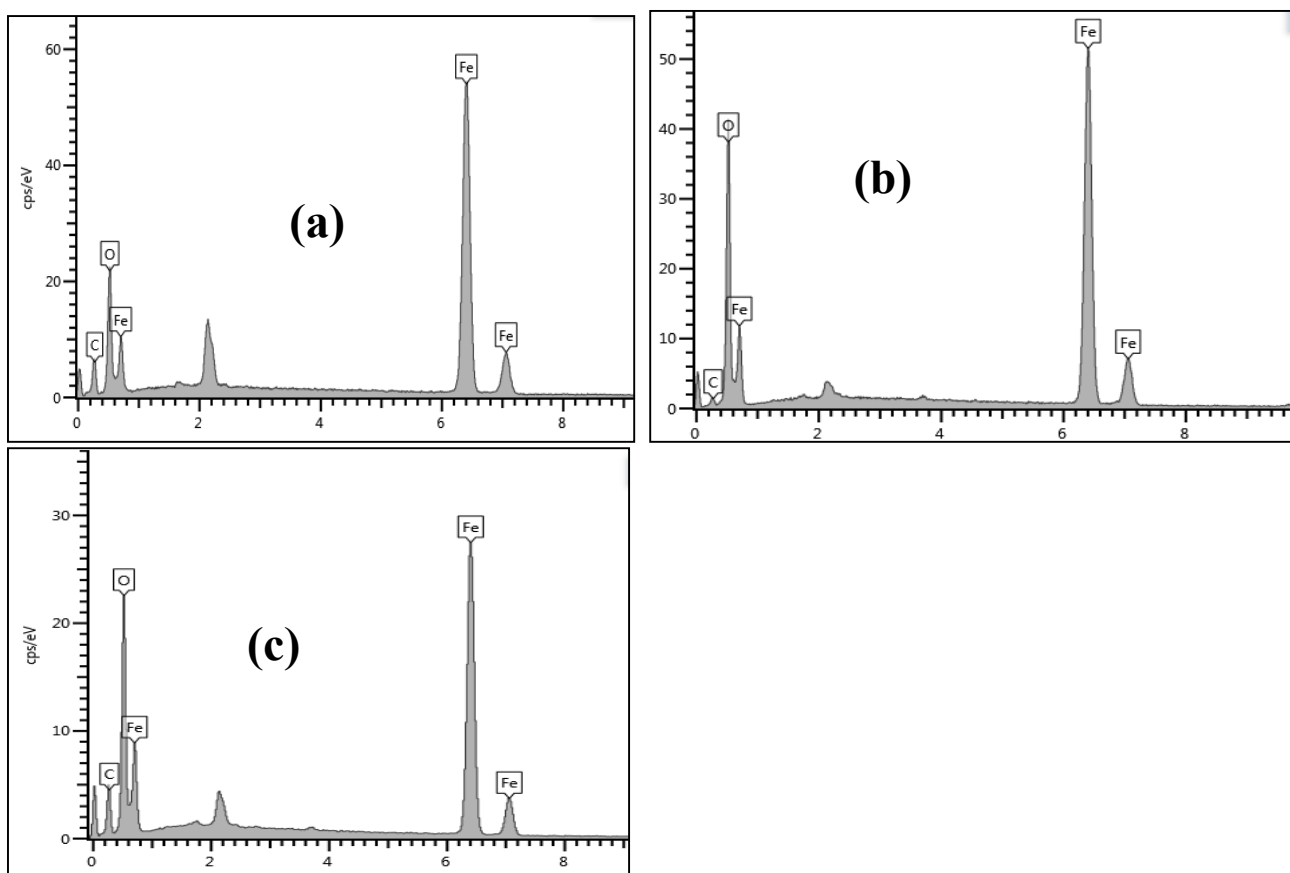


Figure 5.14: EDX of (a) pure magnetite, (b) magnetite-oleic acid composite and (c) magnetite-palmitic acid composite.

5.8 BRUNAUER-EMMETT-TELLER (BET) SURFACE AREA

5.8.1 BET of pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid composites

Adsorption-desorption isotherms using nitrogen and corresponding size distribution curves for pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid composite are shown in Fig 5.15. The BET surface areas for the samples were found to be 138.9, 46.6, 66.9, m^2/g , respectively. The pore volume and pore sizes were also found to be 0.32, 0.17, 0.23 cm^3/g , 9.11, 14.3, 13.9 nm, respectively. It can be observed from the result that the BET isotherms of the three samples shows a type IV shape according to the international union of pure and applied chemistry (IUPAC) classification indicating the materials were-uniform mesoporous solids (An *et al.*, 2017, Guivar *et al.*, 2017). In Fig 5.15, the isotherm curves of

the three samples shows magnetite had two hysteresis loops with increment in the relative pressure region between 0.2 to 0.6 and 0.6 to 1.0, magnetite-palmitic acid composite had two hysteresis loops between 0.2 to 0.6 and 0.7 to 1.0 and magnetite-oleic acid composite had hysteresis loop between 0.6 to 1.0. This may indicate the presence of interparticle porosity probably due to the agglomeration of nanoparticles resulting in a broad pore size of mesopores and micropores (Hou *et al.*, 2017). The isotherm curves also show that after coating the pure magnetite with the two-organic carboxylic acid (oleic and palmitic acid) a decrease in the BET surface area was observed with a decrease in nitrogen adsorption. The reduction of the BET surface area was caused by the functionalization of the magnetite surface with hydrophobic carboxylic acid (oleic and palmitic acids), causing a strong bond of the organic molecule onto the surface iron atoms specific surface area since the exposed area is covered by the carboxylic molecules resulting from functionalization. Similar results were observed by (Connie and Ariya, 2015, Guivar *et al.*, 2017).

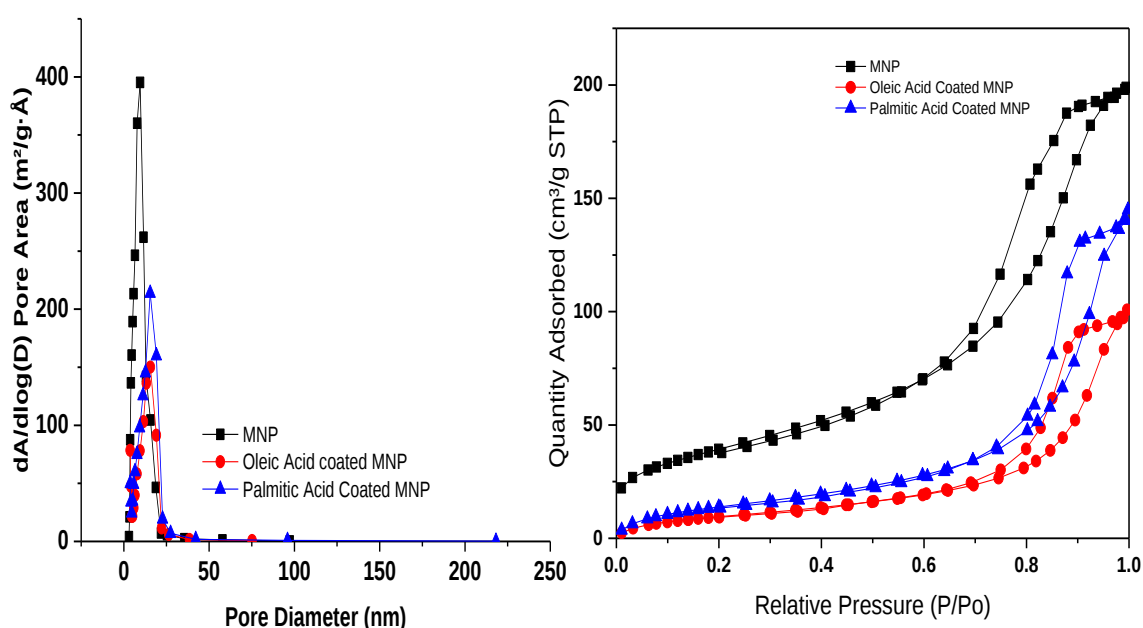


Figure 5.15: N₂ adsorption–desorption isotherms of pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid composite.

5.9 VIBRATING SAMPLE MAGNETOMETER (VSM)

5.9.1 VSM of pure magnetite nanoparticles

The plot of the vibrating sample magnetometer indicating pure magnetite nanoparticles is shown in Fig 5.16. The properties of magnetization on uncoated magnetite samples as a function of the field were measured at room temperature (25 °C). The magnetic curves observed in Fig 5.16 indicate that the magnetite showed no hysteresis in the magnetization and the particles showed superparamagnetic behaviour (Guo *et al.*, 2010). The superparamagnetic behaviour resulting from the magnetite cores in the sample is an advantage in adsorption applications (Dadwal and Joy, 2018). The saturation magnetization (M_s), determined by using the law of approach to saturation for uncoated, magnetite and the coercivity (H_c) as shown from the hysteresis loop, was 62.9 emu/g. The saturation magnetization of the pure magnetite shows that it was smaller than that of its bulk value Fe_3O_4 (92 emu/g) and 115–150 Oe (Oshtrakh *et al.*, 2014, Aliakbari *et al.*, 2015, Marín *et al.*, 2018). The small saturation of magnetization of pure magnetite may be due to the decrease in particle sizes, the disordered surface spin canting at the magnetite surface and change in degree of inversion (Aliakbari *et al.*, 2015, Lobato *et al.*, 2017).

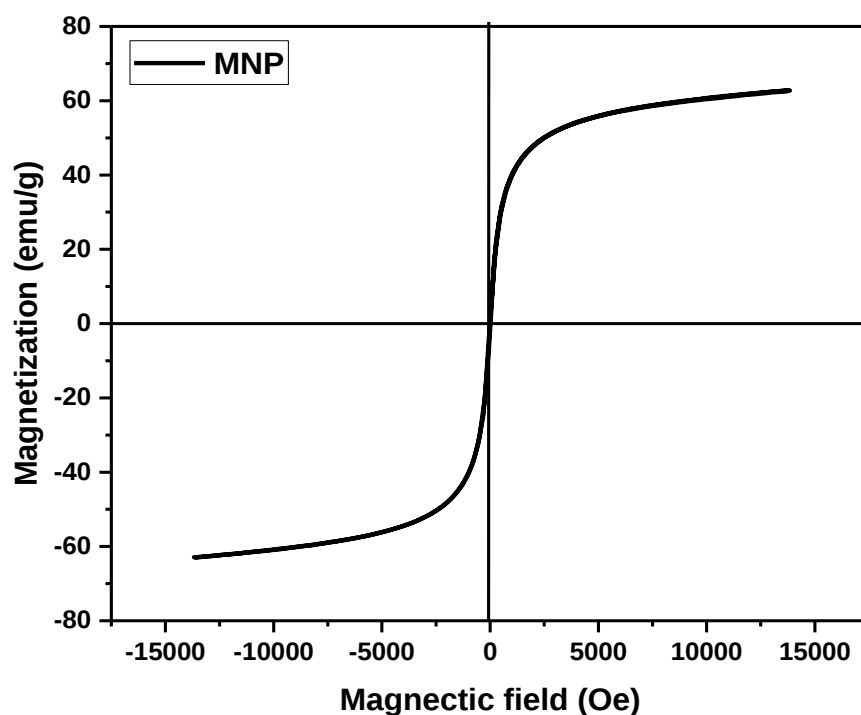


Figure 5.16: Magnetization curve of pure magnetite nanoparticles.

5.9.2 VSM of magnetite-oleic acid composite

The VSM of magnetite-oleic acid composite is presented in Fig 5.17. The saturation magnetization (M_s) of the magnetite-oleic acid composite was 59 emu/g. The saturation magnetization, (M_s) of the pure magnetite was reduced after the modification by hydrophobic oleic acid. Similar results on the reduction of the saturation magnetization of magnetite when the resultant particle size reduces were also reported by (Anbarasu *et al.*, 2015, Viante *et al.*, 2018). The degree of reduction can be attributed to that magnetite have a disordered surface spin layer, and when the size of the resultant particle size was decreasing, the ratio of disordered layer to the radius of the MNPs is significant (Anbarasu *et al.*, 2015). Additionally, the existence of diamagnetic shell that coated on the surface of the magnetite can also result in lower M_s values (Viante *et al.*, 2018). In this case, the oleic stabilizing agent layer protect the magnetite from oxidation reaction, and then decreases the magnetic dipole–dipole interaction between the magnetite particles (Jiang *et al.*, 2017).

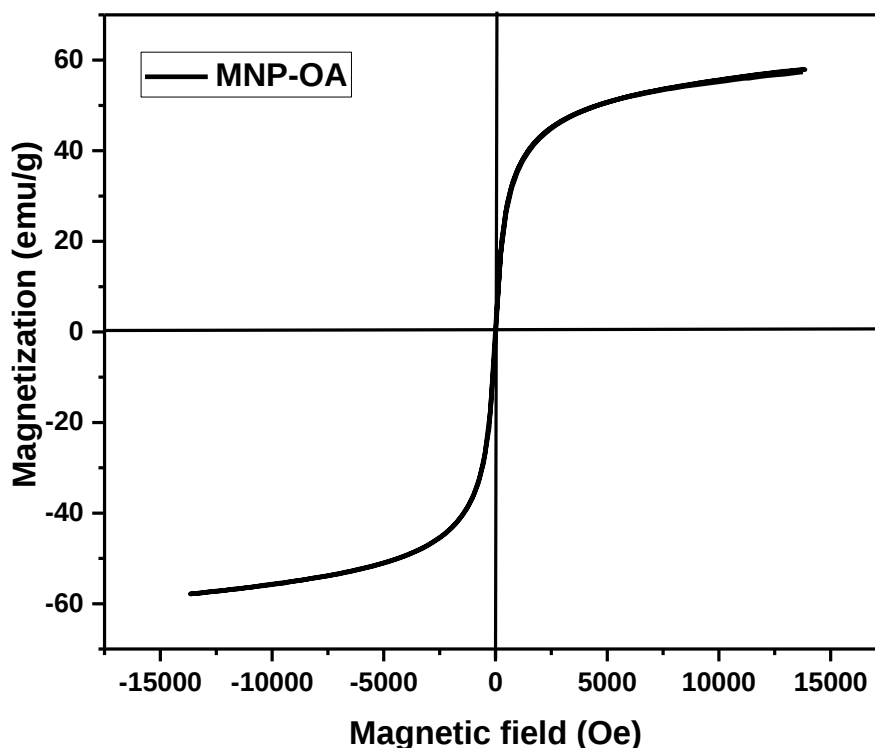


Figure 5.17: Magnetization curve of magnetite-oleic acid composite.

5.9.3 VSM of magnetite-palmitic acid composite

The VSM of magnetite-palmitic acid composite is presented in Fig 5.18. The magnetization curve of the magnetite-palmitic acid composite measured at room temperature shows no hysteresis loop and the saturation magnetization (M_s) value indicated that the synthesized composite showed superparamagnetic properties (Aliakbari *et al.*, 2015). The superparamagnetism ensure an excellent dispersibility once the applied magnetic field is removed and also prevent nanoparticles from irreversible aggregation. The saturation magnetization (M_s) value was 51 emu/g, however it was noted that after coating with palmitic acid, the magnetization of magnetite-palmitic acid composite decreased compared with the pure magnetite nanoparticles in Fig 5.18. The decrease in magnetization after encapsulation was due to the presence of non-magnetic palmitic acid layer immobilized on its surface of the magnetite which resulted in the reduction of magnetic interaction between the oleic acid and magnetite. (Patil *et al.*, 2014, Lobato *et al.*, 2017).

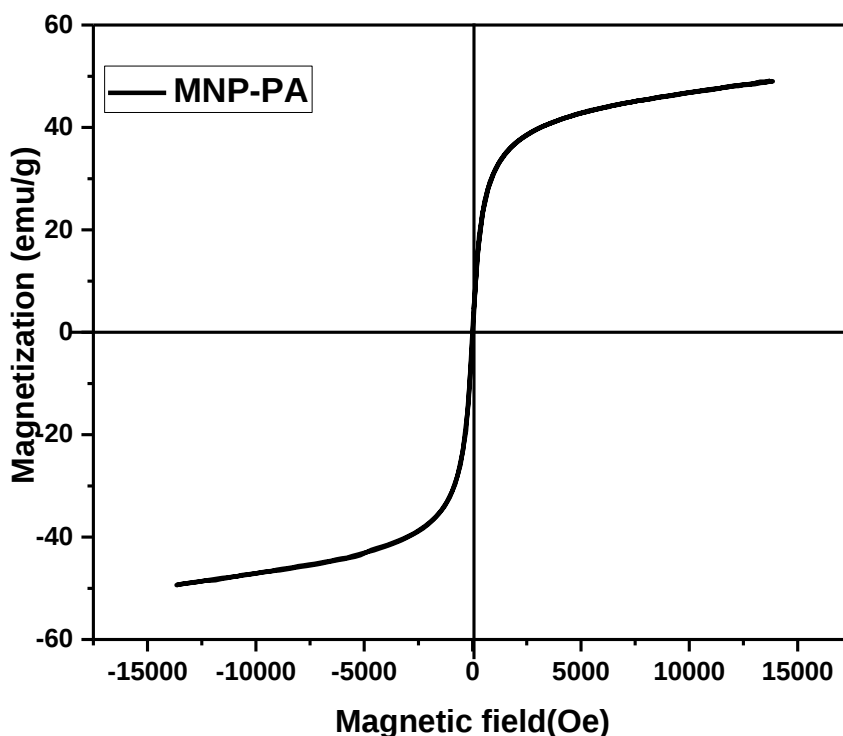


Figure 5.18: Magnetization curve of magnetite-palmitic acid composite.

5.10 POINT ZERO CHARGE (pH_{pzc})

The pH at point zero charge (pH_{pzc}) is important in adsorption studies. The pH of point zero charge can be described as the measure of the pH at which the amount of negative charges on adsorbent surface just equals the amount of positive charges, that is the pH at which the adsorbent surface has net electrical neutrality (Ofomaja, 2010, Rao *et al.*, 2014). The adsorbent surface is negatively charged at $\text{pH} > \text{pH}_{\text{pzc}}$, neutral at $\text{pH} = \text{pH}_{\text{pzc}}$ and net positive charge at $\text{pH} < \text{pH}_{\text{pzc}}$ (Ofomaja, 2010, Rao *et al.*, 2014, Baig *et al.*, 2015).

The pH_{pzc} of the pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid composite were observed to be different and the values are presented in Table 5.2. Figs. 5.19 and 5.20 also shows the plots of pH_{pzc} for pure magnetite, magnetite-oleic and magnetite-palmitic acid composite.

Table 5.2: pH_{pzc} values of pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid composite.

	Pure magnetite	Magnetite-oleic acid composite	Magnetite-palmitic acid composite
pH _{pzc}	6.9	6.4	6.1

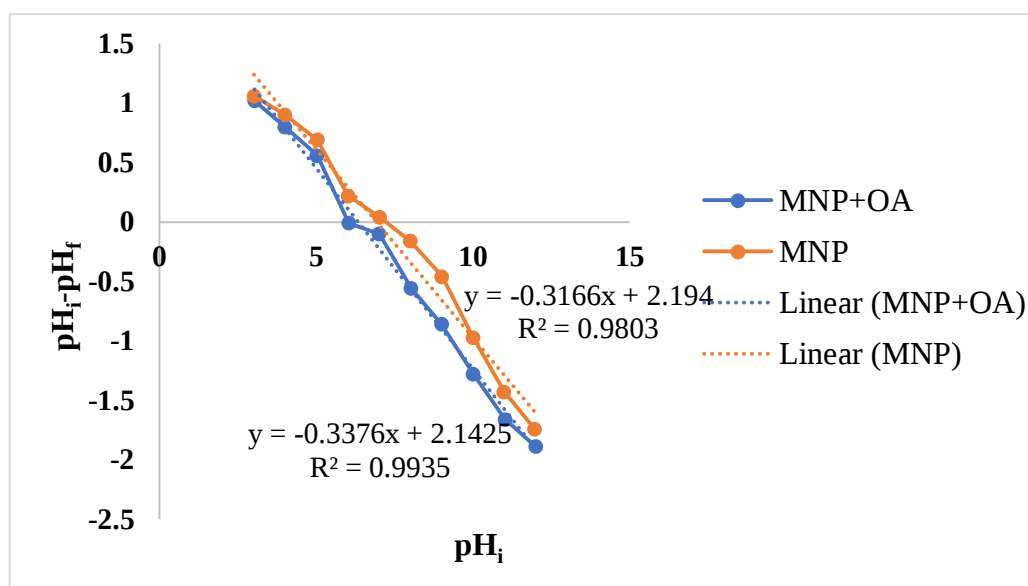


Figure 5.19: Point zero charge of pure magnetite nanoparticles and magnetite-oleic acid composite.

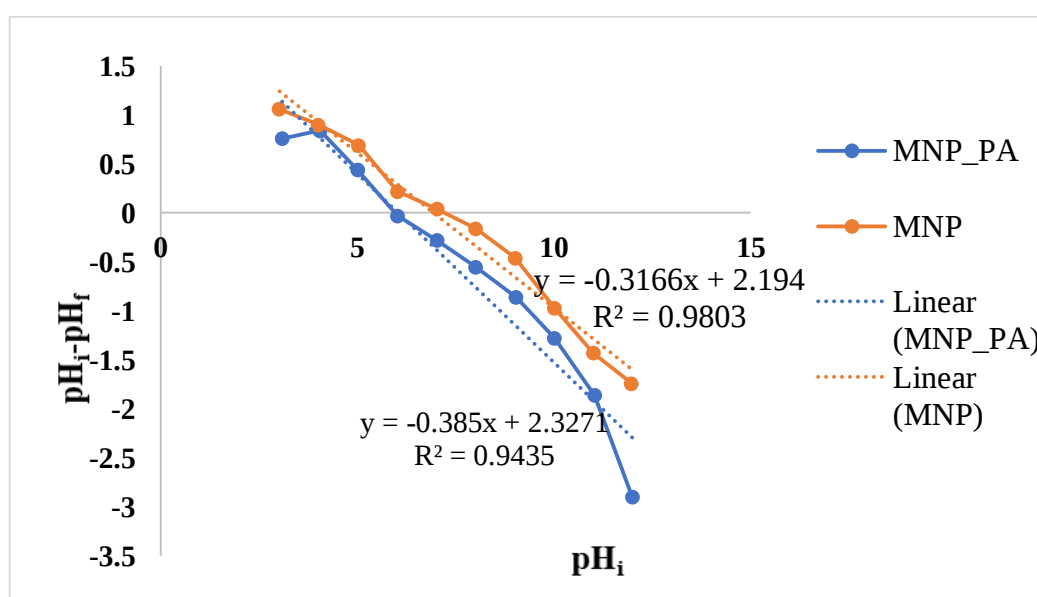
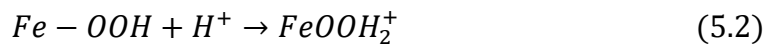
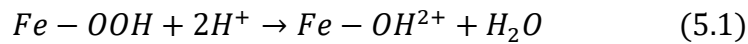
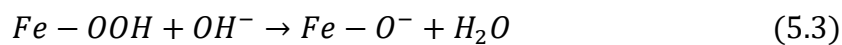


Figure 5.20: Point zero charge of pure magnetite and magnetite-palmitic acid composite.

As shown in Table 5.2 the pH_{pzc} of pure magnetite nanoparticles was found to be 6.9. Under acid condition iron oxides will accept protons to form positively charged species as shown in the Eq. (5.1- 5.2).



As the solution pH increases the amount of H^+ ions in solution reduces thereby reducing the amount of H^+ ions that will interact with the iron oxide, this then reduces the charge of positive charge on the magnetite nanoparticles. At high solution pH (alkaline condition) OH^- predominates in solution and can abstract H^+ from the Fe-OH producing a negatively charged iron oxide specie (Fe-O^-) as shown in Eq. (5.3).



Therefore, the pH_{pzc} of magnetite was observed at solution pH close to neutral (6.9), which is similar to what observed by other authors (Kim *et al.*, 2016).

Decrease in pH_{pzc} from 6.9 for the pure magnetite nanoparticles adsorbent to 6.4 for magnetite-oleic acid composite and 6.1 for magnetite-palmitic acid composite was due the charging acid-base interaction mechanism of metal oxide nanoparticles. The charge on the metal oxides in the aqueous solution was due to adsorption of H^+ or OH^- ions through the protonation and deprotonation mechanism (Bhosale *et al.*, 2015). The presence of the carboxylic group from the organic acid on the magnetite surface after modification process has been shown to result in decrease in pH_{pzc} (Nigam *et al.*, 2011). When the oleic and palmitic acid was introduced into magnetite colloid solution, the oleic and palmitic molecules became attached to the magnetite surface due to the carboxylic acids having a high affinity for metallic oxides. The bond of Fe-OH at the surface of the magnetite interacts with the carboxylic acid group of the oleic and palmitic acid molecule via an acid-base reaction, giving Fe-O-C species with the elimination of H_2O (Kim *et al.*, 2018). Therefore, the amount of available Fe-OH for acid

base reaction is reduced on the magnetite-organic acid composite which results in reduced pH_{pzc} .

5.11 CONCLUSION

In summary, pure magnetite nanoparticles, magnetite-oleic and magnetite-palmitic acid composites were successfully synthesized and characterized with different techniques. The three adsorbents were examined in terms of functional group, thermal stability, structural, morphology, BET surface area as well as their magnetic properties.

Based on the results obtained, the pure magnetite showed characteristics bands of Fe-O confirming the presence of the iron oxide. For the magnetite-organic acid composites, the interaction between the functional groups of magnetite and organic acid was confirmed by the bands that represents the asymmetric and symmetric carboxylic ion (COO^-) at 1400 to 1600 cm^{-1} . The results also indicate that the C = O stretching at 1700 shifted to lower region between 1400 and 1600 cm^{-1} confirming the interaction between organic acid and magnetite. This indicates that the magnetite surface and the stabilizing agent are bonded as the esterification happens between the hydroxyl groups on the magnetite surface and the (COO^-) carboxyl group from the acid molecule. The TGA analysis shows that the three adsorbents were stable low 200 °C, however incorporation of oleic and palmitic acid induces some interaction on the nanoparticles. The XRD confirmed the structure of the pure magnetite, magnetite-oleic and magnetite-palmitic acid composites. The average particle size of the pure magnetite, magnetite-oleic and magnetite-palmitic acid composites were in the range 15-20 nm. The broadening of the magnetite-oleic and magnetite-palmitic acid composites peaks when compared with uncoated nanoparticles peaks were due to the interaction between surface O-H groups of the magnetite nanoparticles and the organic acid molecules. There is no evidence of other oxides formation in the XRD pattern of the nanoparticles. From TEM measurement, it was observed that the image shows the nanoparticles have a spherical shape with average size of 18.4 ± 0.5 , 15.6 ± 0.5 and 16.5 ± 0.5 nm for pure magnetite, magnetite-oleic and magnetite-palmitic acid composites, respectively. The decrease in particle size of the material was due to a non-magnetic layer formed on the magnetite surface and increase dispersion caused by organic acid coating. Comparing the pure magnetite and the magnetite-organic acid composite, the modified nanoparticles were better separated and had less degree of aggregation due to the presence of the carboxylic acid surfactant on the surface of the magnetite. The BET isotherms of the three samples shows a type IV shape indicating the

materials were-uniform mesoporous solids. The results also show that the BET surface areas of the pure magnetite decreased after coating with the two-organic carboxylic acid (oleic and palmitic acid). This may be due to functionalization of the surface with hydrophobic carboxylic acid (oleic and palmitic acids), causing a strong bond of the organic molecule onto the surface iron atoms specific surface area since the exposed area is covered by the carboxylic molecules resulting from functionalization. The magnetic properties of the three samples also shows the materials were superparamagnetic with saturation mass value of 62.9, 59.0, 51.0 emu/g for pure magnetite nanoparticles magnetite-oleic and magnetite-palmitic acid composites. The size of magnetization mass of the three samples were lower than that for bulk particles 92 emu/g, reflecting the ultrafine nature of the sample. The pH_{pzc} results also showed a decrease due to modification of the magnetite. Decrease in pH_{pzc} from 6.9 for the pure magnetite nanoparticles adsorbent to 6.4 for magnetite-oleic acid composite and 6.1 for magnetite-palmitic acid composite was due the charging acid-base interaction mechanism of metal oxide nanoparticles.

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CHAPATER 6

6. RESULTS AND DISCUSSION (PART 2)

6.1 INTRODUCTION

The chapter presents and discusses the effects of adsorption parameters such as effect of solution pH, adsorbent dose and kinetics of BTX uptake at different initial concentrations and the kinetics data were also modelled using the pseudo first and second order models.

6.2 OPTIMISATION OF KINETIC PARAMETERS

6.2.1 Effect of solution pH

The effect of solution pH is a key parameter in controlling adsorption process as it influences the properties of both adsorbent and adsorbate in aqueous solution (Ofomaja *et.al.*, 2009). In the present study the effect of solution pH on the adsorption of benzene, toluene and xylene using pure magnetite, oleic and palmitic acid coated magnetite nanoparticles was studied in the pH range 3 to 12 and the results are presented in Figures 6.1 to 6.9.

The adsorption of benzene at different pH onto pure magnetite, magnetite-palmitic and magnetite-oleic acid composite is shown in Figure 6.1. From Fig 6.1 it was observed that the adsorption capacity of benzene for all samples increased from pH 3, reaching a maximum at pH 7. Although oleic acid coated magnetite nanoparticles had the least capacity at pH 3 but had the highest capacity at pH of 7. Above pH of 7, the adsorption capacities of the different adsorbent were found to decrease with an increase of pH. The oleic acid coated magnetite nanoparticles had the highest adsorption capacity of 77.1 mg/g, palmitic coated magnetite nanoparticles had an adsorption capacity of 64.8 mg/g and pure magnetite had an adsorption capacity of 59.5 mg/g. Therefore, the optimum pH for all three adsorbents was at pH 7.

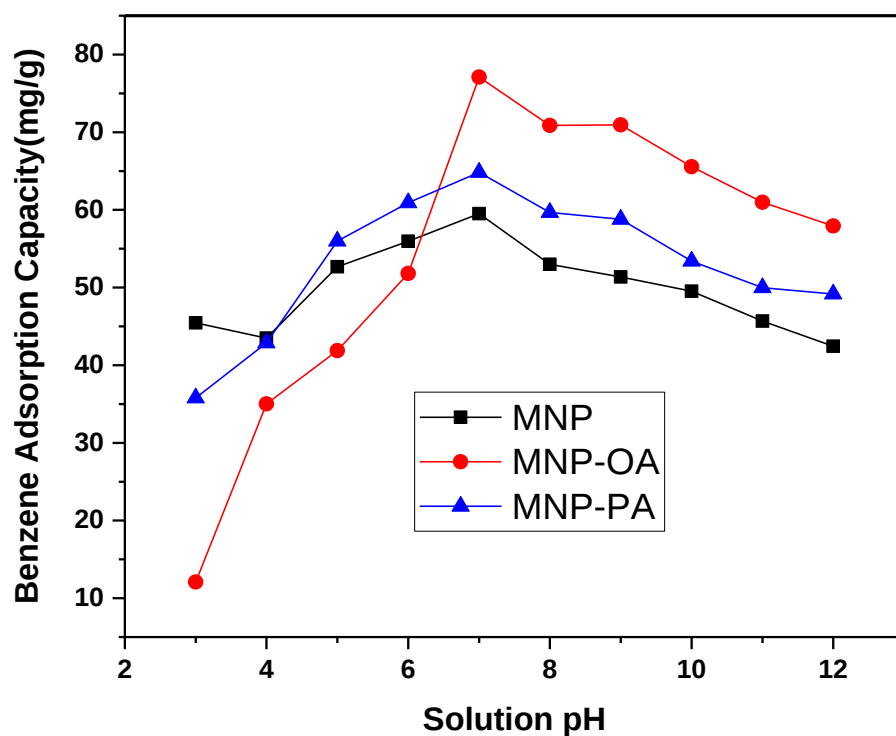


Figure 6.1: Effects of initial solution pH on benzene uptake on MNP, MNP-PA and MNP-OA composites.

The adsorption of toluene at different pH onto pure magnetite, magnetite-palmitic and magnetite-oleic acid composites is shown in Figure 6.2. From Fig 6.2 it was observed that the adsorption capacity of toluene for all samples increased from pH 3, reaching a maximum at pH 8. Both the magnetite-palmitic and magnetite-oleic acid composites had the least

adsorption capacity at pH 3 however oleic acid had the highest capacity at pH of 8. Above a pH of 8, the adsorption capacities of the different adsorbent were found to decrease with increase of pH. The magnetite-oleic acid composite had the highest adsorption capacity of 73.3 mg/g, magnetite-palmitic acid composite had an adsorption capacity of 66.8 mg/g and pure magnetite had an adsorption capacity of 57.5 mg/g. Therefore, the optimum pH for all three adsorbents was at pH 8.

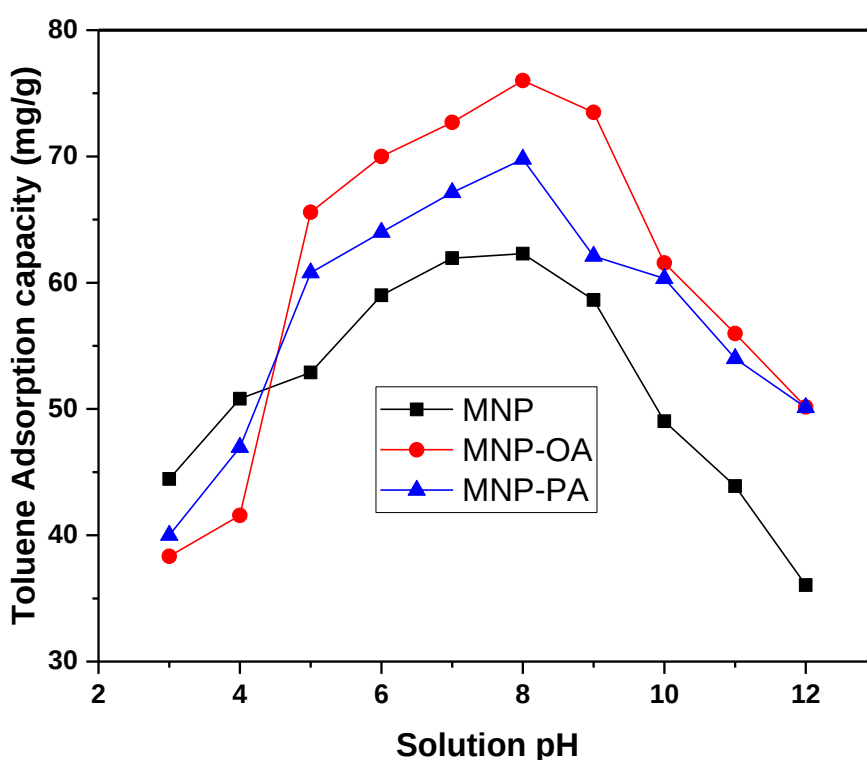


Figure 6.2: Effects of initial solution pH on toluene MNP, MNP-PA and MNP-OA composites.

The adsorption of xylene at different pH onto pure magnetite, magnetite-palmitic and magnetite-oleic acid composites is shown in Figure 6.3. From Fig 6.3 it was observed that the adsorption capacity of xylene for magnetite-palmitic and magnetite-oleic acid composites samples increased from pH 3, reaching a maximum at pH 8. However, for that of pure magnetite the adsorption capacity increased from pH 3 to pH. 6. Magnetite-palmitic acid composite had the least capacity at pH 3. The magnetite-oleic acid composite had the highest

capacity at pH of 8. Above pH of 8, the adsorption capacities of the different adsorbents were found to decrease an with increase in pH. The magnetite-oleic acid composite had the highest adsorption capacity of 84.99 mg/g, magnetite-palmitic acid composite had an adsorption capacity of 75.7 mg/g and pure magnetite had an adsorption capacity of 66.2 mg/g. Therefore, the optimum pH for oleic and magnetite-palmitic acid composite was at pH 8 and for the pure magnetite nanoparticles was at pH 6.

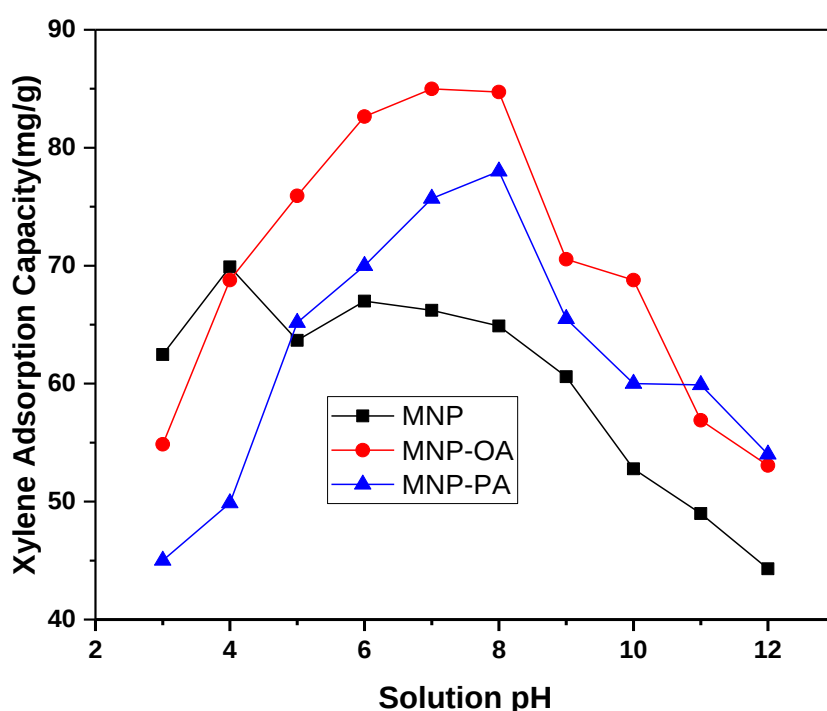


Figure 6.3: Effects of initial solution pH on xylene uptake on MNP, MNP-PA and MNP-OA composites.

The results show that coating the magnetite with oleic and palmitic acid increased its affinity for BTX adsorption. The variation in adsorption with change in pH may be explained by the following mechanism. As the solution pH increases the amount of H^+ ions in solution reduces thereby reducing the amount of H^+ ions that will interact with the iron oxide therefore allowing for the interaction between pollutant and adsorbent. This will explain the increase in adsorption capacity with increasing pH from 3 to between 6 and 8. The adsorption of BTX onto the surface of the magnetite and magnetite-organic acid composite can arise from the interaction between Fe^{2+} and Fe^{3+} and the π electrons groups of BTX. This interaction can be

explained by acid–base chemistry, where the delocalized π electrons of the aromatic ring of BTX are capable of sharing electrons (basic character) through σ bonding with the unfilled 3d metal orbital of the iron cations (acidic character). Electron donation from the phenyl ring of each BTX compound to surface iron atoms of magnetite has been suggested (Joseph *et al.*, 2000; Sasaki and Tanaka, 2011). This π -electron interaction depends on the available surface-active sites on the adsorbent, structure, orientation as well as the configuration of the adsorbate which could potentially activate side chain interactions (Joseph *et al.*, 2000). The reduction in adsorption capacity at high pH can be explained by using the pH_{pzc} of the adsorbents and the presence of the OH^- in the solution. The pH_{pzc} of the three adsorbents were 6.9, 6.4 and 6.1 mg/g for pure magnetite, oleic and palmitic acid coated magnetite nanoparticles, respectively. Therefore, at solution pH above the pH_{pzc} of the adsorbents, their surfaces will become negative thereby repelling the π electron system in the rings of the pollutants. This will result in the reduction in approach of the pollutants to the adsorbent surface and there a reduction in adsorption capacity.

It was observed that xylene had the highest BTX adsorption capacity, followed by the toluene and benzene. The reason for this trend can be attributed to the increasing order of hydrophobicity ($\text{Log } K_{\text{ow}}$) (B, $2.13 < \text{T}$, $2.69 < \text{X}$, 2.77), molecular weight (B, $78 \text{ g/mol} < \text{T}$, $92 \text{ g/mol} < \text{X}$, 106 g/mol), descending order of water solubility (B, $790 \text{ mg/L} > \text{T}$, 530 mg/L X, $>150.5 \text{ mg/L}$) and ascending order of boiling point (B, $80.1^\circ\text{C} < \text{T}$, $110.7^\circ\text{C} < \text{X}$, 138°C) of BTX compounds (Bandura *et al.*, 2017).

6.2.2 Adsorbent dose

The effect of varying adsorbent dose on the uptake of BTX is shown in Figures 6.4 to

6.6. Figs 6.4 to 6.6 show plots of percentage removal and adsorption capacity versus mass of pure magnetite, magnetite-palmitic and magnetite-oleic acid composite respectively.

The figures all show that the percentage BTX removal increased as the adsorbent mass increased from 0.05 to 1.5 g, while the adsorbent capacity of BTX decreased as the adsorbent mass increased. It was observed that the percentage BTX removal from aqueous solution using 1.5 g of the adsorbent was highest for the pure magnetite nanoparticles at 75.1% for benzene, 77.8% for toluene and 79.3 % for xylene. For the magnetite-palmitic acid composite the percentage removal was 81.1 % for benzene, 85.8 % for toluene and 86.7 % for xylene. For

magnetite-oleic acid composite was 86.4 % for benzene, 88.1 % for toluene and 88.2 % for xylene. The adsorbent capacity of the pure magnetite on the other hand, reduced from 59.51 to 2.52 mg/g for benzene, 63.0 to 2.5 mg/g toluene and 69.6 to 2.9 mg/g xylene, from 64.83 to 3.0 mg/g benzene, 69.1 to 2.9 mg/g toluene and 75.7 to 2.9 mg/g xylene for the magnetite-palmitic acid composite and from 77.1 to 3.4 mg/g for benzene, 80.7 to 4.1 mg/g for toluene and 78.493 to 3.2 mg/g for xylene in the magnetite-oleic acid composite. The decrease in adsorption capacity was due to increase in number of adsorbent particles with constant BTX concentration. While the increase in BTX percentage removal was attributed to an increase in number of adsorbent sites. The observed result suggests that the optimum adsorbent dose for the three adsorbents for the adsorption process was 0.1 g/dm^3 . The results also show that the three adsorbents enhanced its adsorptive capability towards BTX.

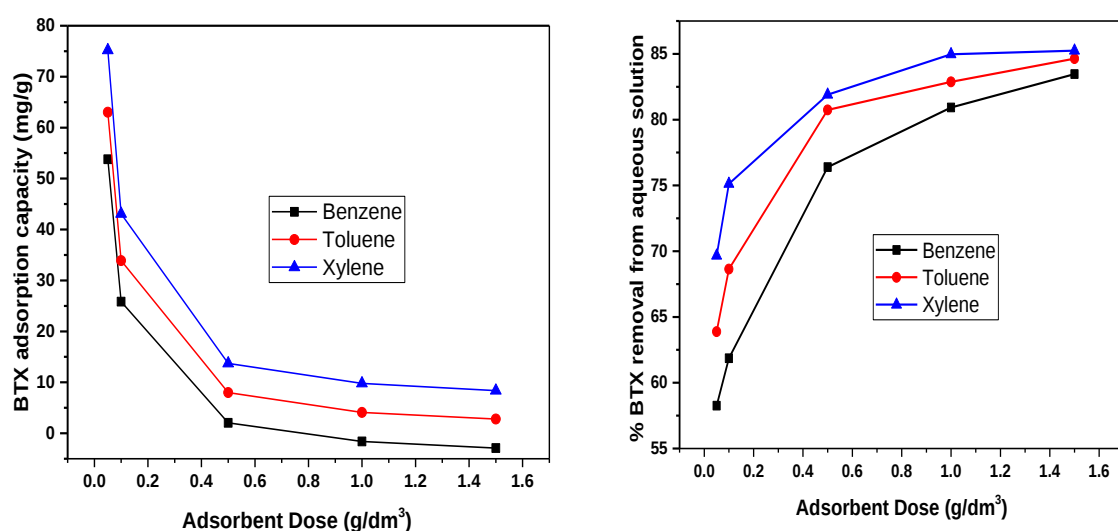


Figure 6.4: The effect of adsorbent dose on the uptake of BTX onto MNP

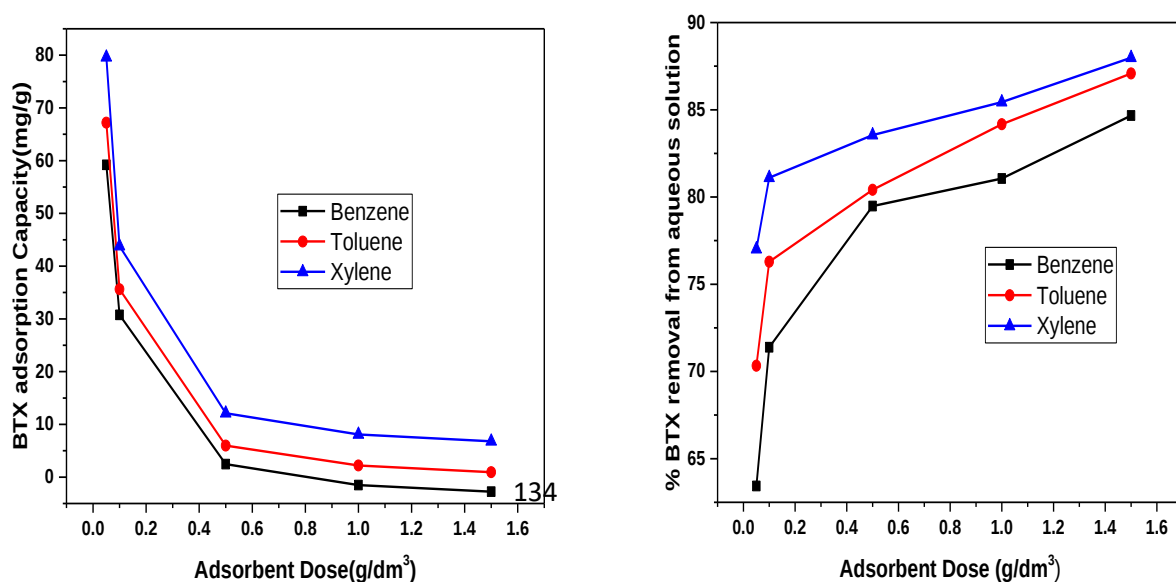


Figure 6.5: The effect of adsorbent dose on the uptake of BTX onto MNP-PA composite.

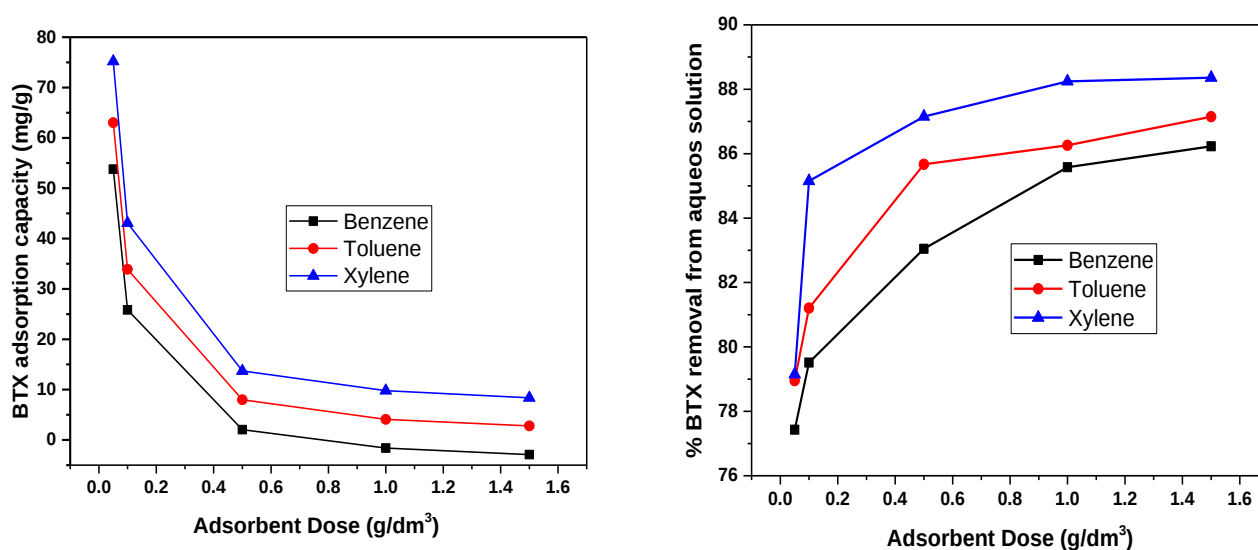


Figure 6.6: The effect of adsorbent dose on the uptake of BTX onto MNP-OA.

6.3 KINETIC STUDIES

Adsorption kinetics involves the profile of uptake of pollutants from aqueous solution with time. The adsorption process is divided into three parts, (1) the movement of pollutant molecules from the bulk solution to the external surface of the adsorbents (external mass transfer), (2) diffusion of pollutant molecules across the thin liquid film on the adsorbent surface (film diffusion) and (3) the diffusion of the pollutant molecule into the internal structure of the adsorbent. Step one is not usually rate determining since the solution is properly stirred, therefore rate determining state of adsorption process could be either film or particle diffusion.

6.3.1 Effect of adsorption time on kinetics

The effect of time on the uptake of benzene, toluene and xylene onto MNP, MNP-PA and MNP-OA composites are shown in Figs. 6.7 to 6.9. The plots can be divided into two sections, (1) an initial rapid uptake of the pollutants and (2) the final almost constant section of pollutant uptake. The uptake-time profile for all adsorbents and for all the pollutants were similar with the rapid section of the plot between 0 and 3 min of contact time. These results suggest that the pollutants were rapidly adsorbed in the first 3 min of contact and slowly saturated as time increased. Figs 6.7 shows the uptake time profile for benzene, toluene and xylene onto MNP. Although the initial rapid uptake time were similar, the percentage removal of benzene, toluene and xylene at 3 min were 35.07, 43.49, 53.02 %. This indicates that xylene had a faster kinetics than benzene and toluene. Similar trends were observed for MNP-PA and MNP-OA. Between 3 and 120 min of contact the change in adsorption capacity varied only slightly indicating that the adsorption sites were almost saturated. Therefore, the optimum time for the adsorption process was taken to be 120 min. Similar trends were also observed for MNP-PA and MNP-OA.

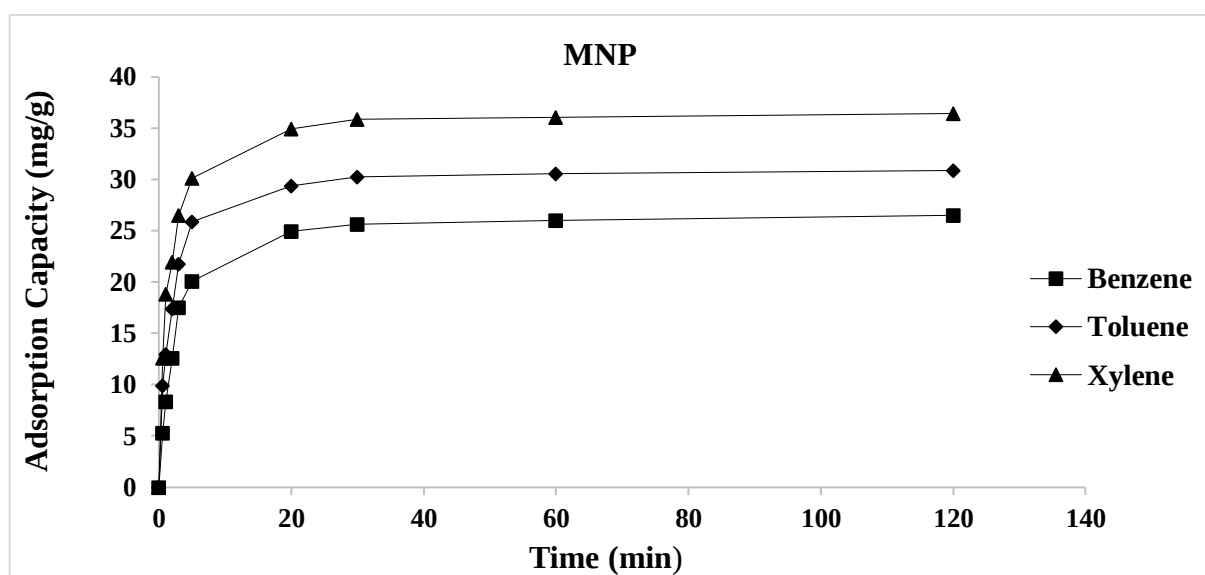


Figure 6.7: The effect of time on the uptake of BTX onto MNP.

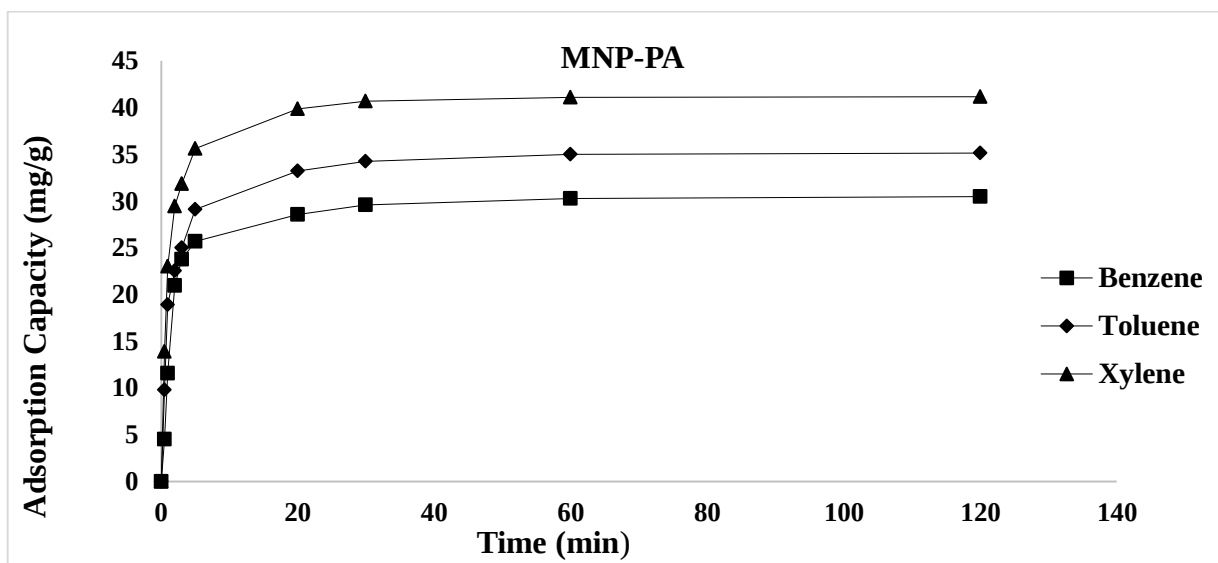


Figure 6.8: The effect of time on the Uptake of BTX onto MNP-PA.

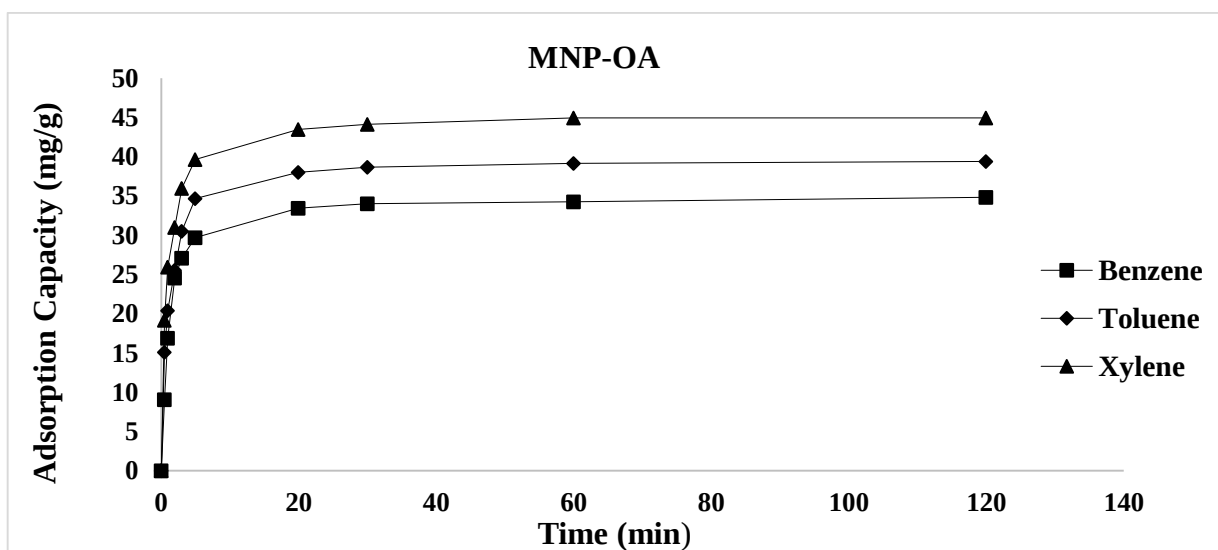


Figure 6.9: The effect of time on the uptake of BTX onto MNP-OA.

6.3.2 Effect of concentration on the uptake of Benzene, Toluene and Xylene

The effect of initial concentration on the uptake of BTX onto MNP, MNP-PA and MNP-OA was performed by varying the initial concentration of BTX between 100 to 350 mg/dm³ and

determining the kinetic uptake for each of the adsorbents. Fig 6.10 to 6.18 show the uptake of BTX onto MNP, MNP-PA and MNP-OA. The graphs in Figs. 6.10 to 6.12 shows the effect of initial concentration on the uptake of BTX onto MNP. The figures reveal that the initial rapid uptake of BTX onto MNP occurred in the first 3 min of contact. The result also shows that as initial concentration of BTX increased from 100 to 350 mg/dm³, the adsorption capacity at 120 min for benzene increased from 26.89 to 63.66 mg/g, for toluene from 30.89 to 69.34 mg/g and for xylene from 36.44 to 68.10 mg/g. An increase in adsorption capacity with increasing initial concentration suggest that the adsorption process is driven by the concentration driving force (Ofomaja *et al.*, 2013). There as the initial concentration is increased BTX molecules are forced to the surface of the adsorbent by concentration difference.

The plots of the effect of initial concentration on BTX adsorption onto MNP-PA are shown in Figs. 6.13 to 6.15. The figures reveal that the BTX uptake increased as initial concentration of BTX was increased from 100 to 350 mg/dm³, the adsorption capacity at 120 min for benzene increased from 30.49 to 66.93 mg/g, for toluene from 35.15 to 71.89 mg/g and for xylene from 41.15 to 83.18 mg/g. Concentration driving force was also observed to influence the adsorption process and its influence was greater than for MNP as seen from the higher adsorption capacities although the surface area of MNP is larger than that of MNP-PA. The stronger influence of concentration driving force on the MNP-PA adsorbent can be attributed to presence of the long carbon chain of the carboxylic acid increasing the affinity of BTX for MNP-PA surface.

The initial concentration-time profile for the adsorption of BTX onto MNP-OA shown in Figs. 6.16 to 6.18. The plots show an increase in adsorption capacity of BTX as the initial concentration of BTX in solution has increased from 100 to 350 mg/dm³, the adsorption capacity at 120 min for benzene increased from 34.88 to 72.48 mg/g, for toluene from 39.36 to 73.90 mg/g and for xylene from 44.91 to 88.36 mg/g. The result suggests that the stronger influence of concentration driving force was involved in the driving process. This influence cannot be attributed to the surface area of the MNP-OA particles but can be attributed to the higher carbon content of the oleic acid molecule which increases the affinity of the surface of the BTX.

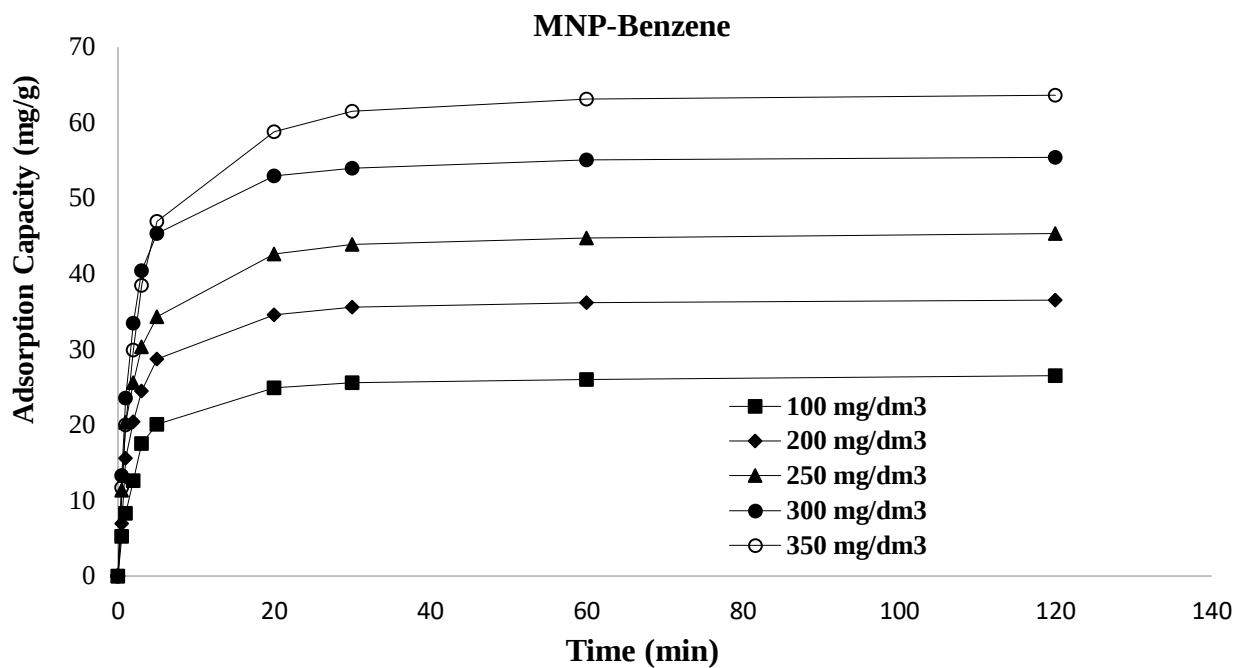


Figure 6. 10: Adsorption kinetics of Benzene on MNP. Initial pH: 7, adsorbate dose: 0.1 g/dm³, solution volume: 10 mL, agitation speed: 300 rpm, temperature: 299 K.

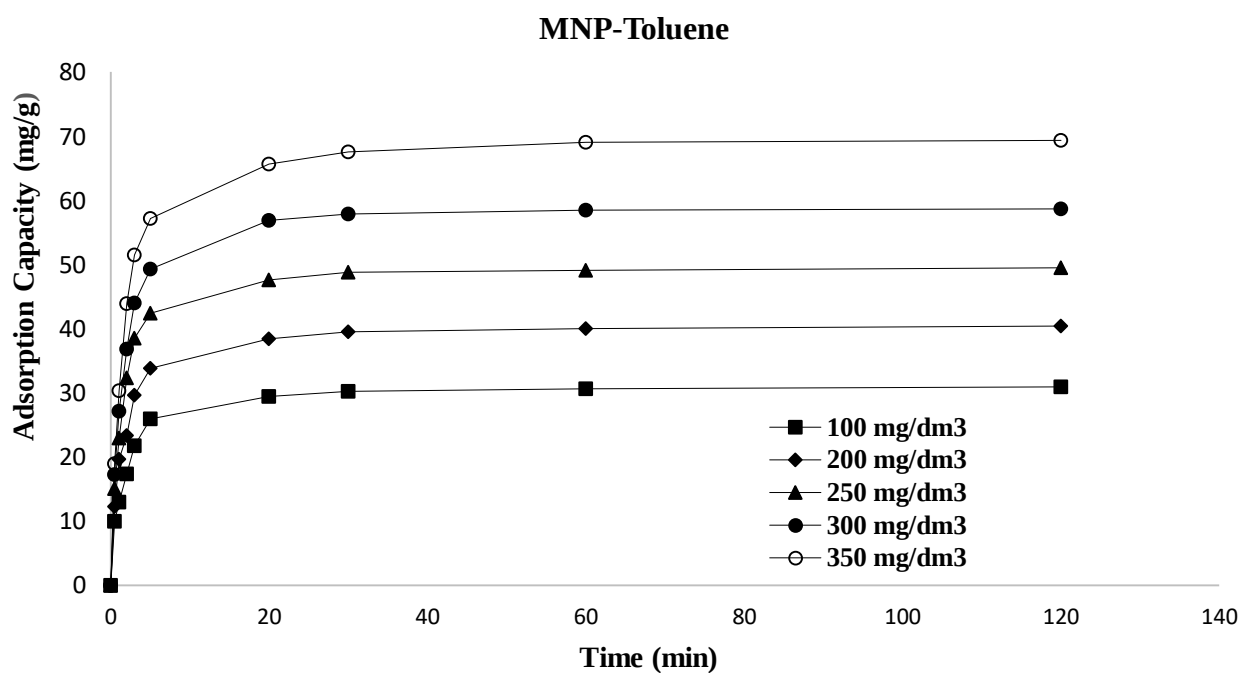


Figure 6. 11: Adsorption kinetics of Toluene on MNP. Initial pH: 8, adsorbate dose: 0.1 g/dm³, solution volume: 10 mL, agitation speed: 300 rpm, temperature: 299 K.

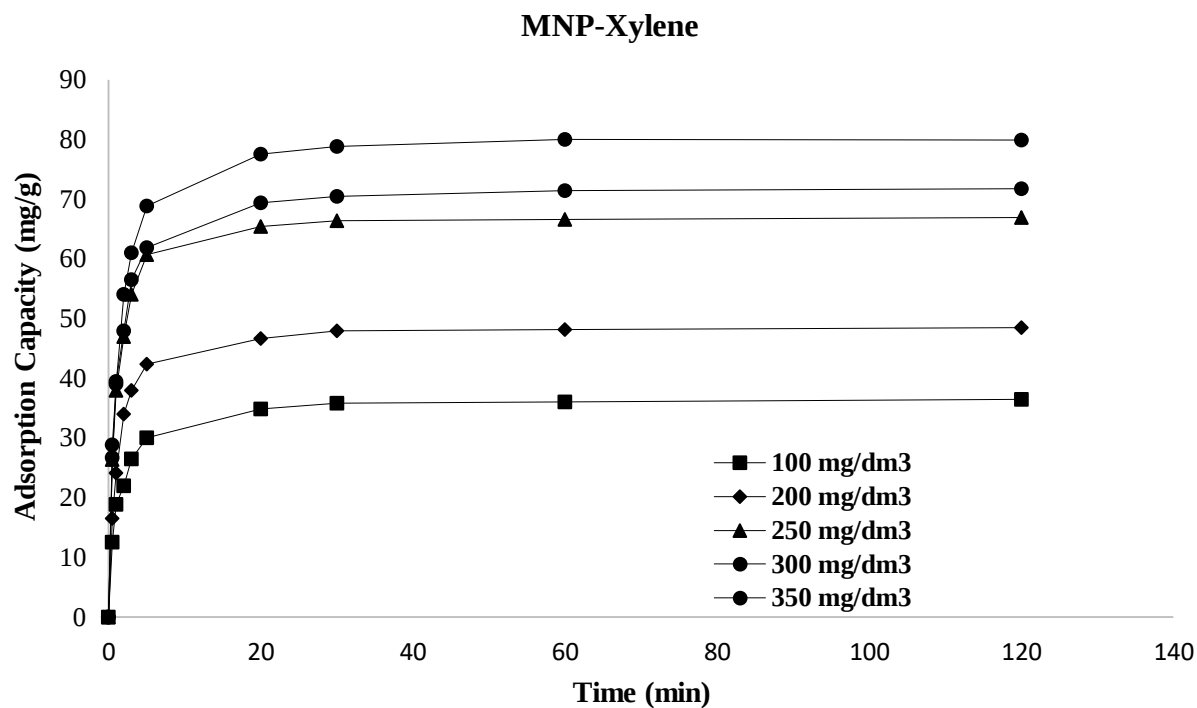


Figure 6. 12: Adsorption kinetics of Xylene on MNP. Initial pH: 8, adsorbate dose: 0.1 g/dm³, solution volume: 10 mL, agitation speed: 300 rpm, temperature: 299 K.

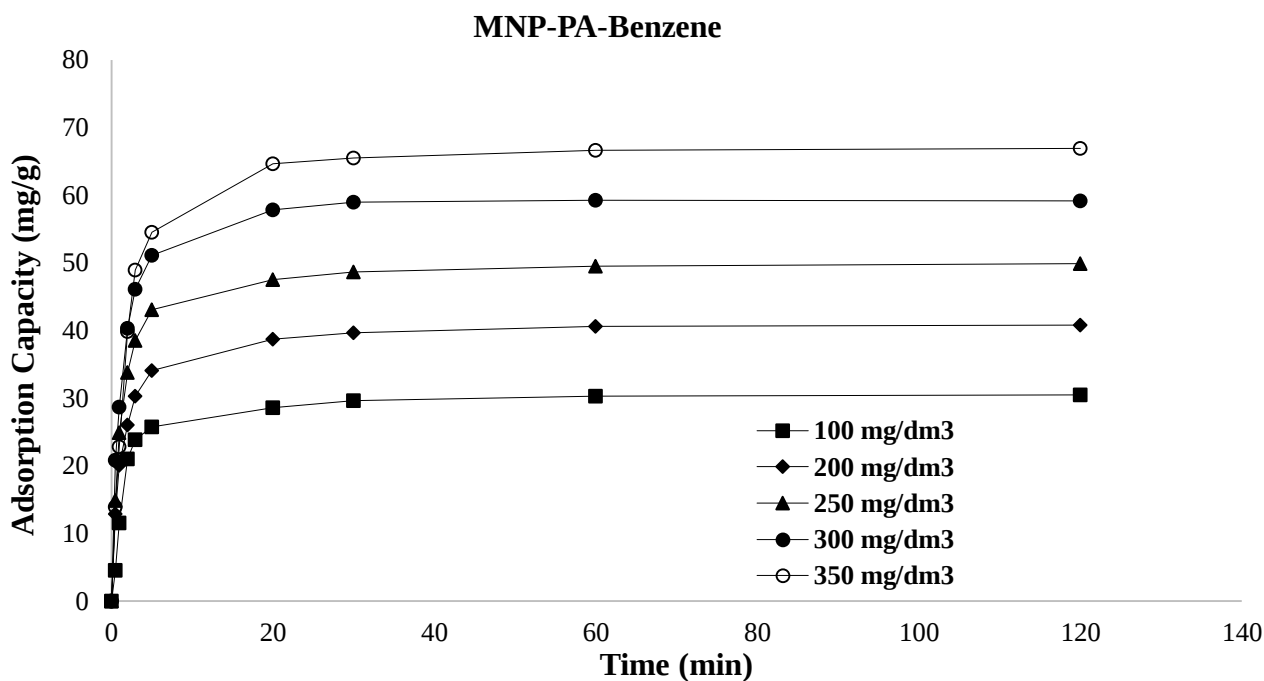


Figure 6. 13: Adsorption kinetics of Benzene on MNP-PA. Initial pH: 7, adsorbate dose: 0.1 g/dm³, solution volume: 10 mL, agitation speed: 300 rpm, temperature: 299 K.

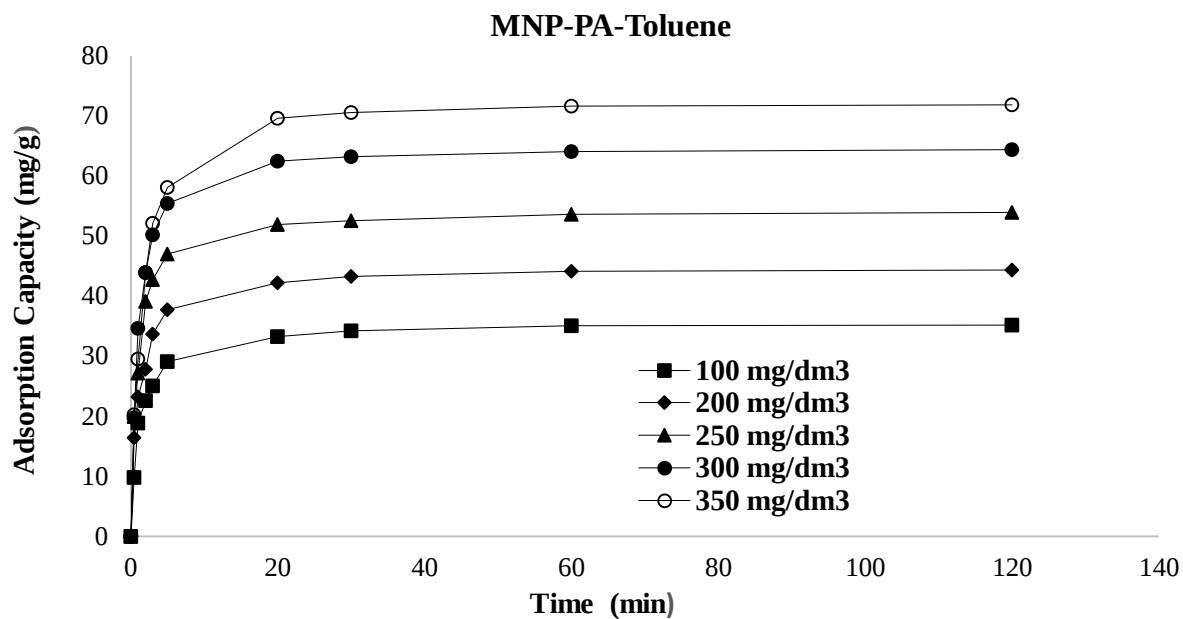


Figure 6. 14: Adsorption kinetics of Toluene on MNP-PA. Initial pH: 8, adsorbate dose: 0.1 g/dm³, solution volume: 10 mL, agitation speed: 300 rpm, temperature: 299 K.

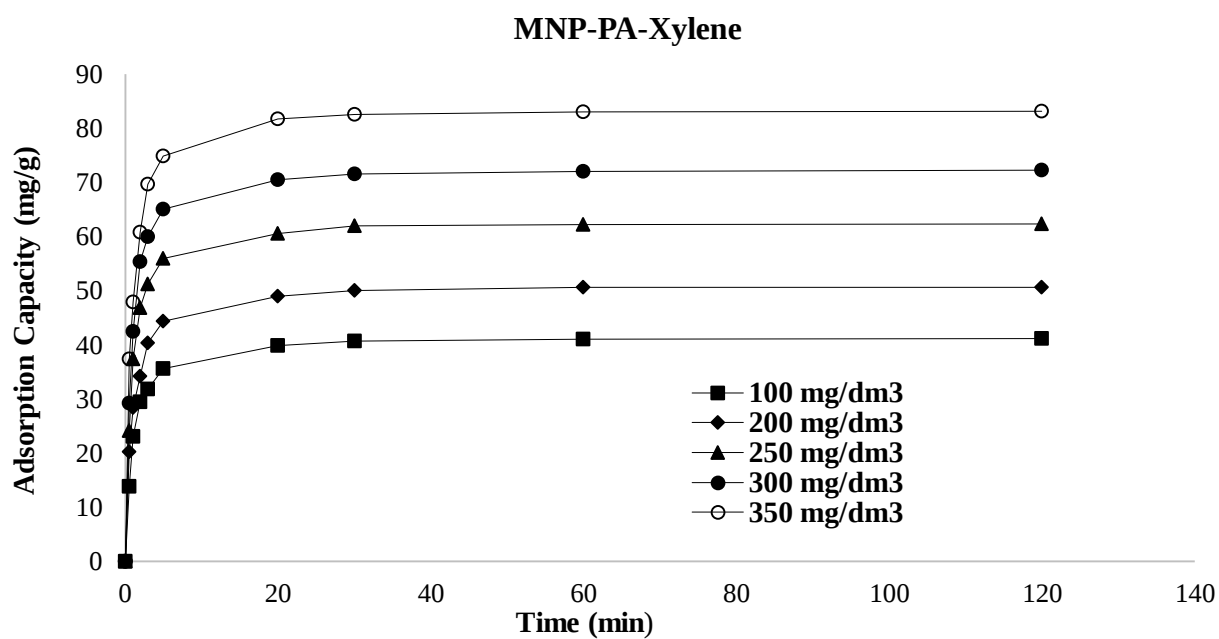


Figure 6. 15: Adsorption kinetics of Xylene on MNP-PA. Initial pH: 8, adsorbate dose: 0.1 g/dm³, solution volume: 10 mL, agitation speed: 300 rpm, temperature: 299 K.

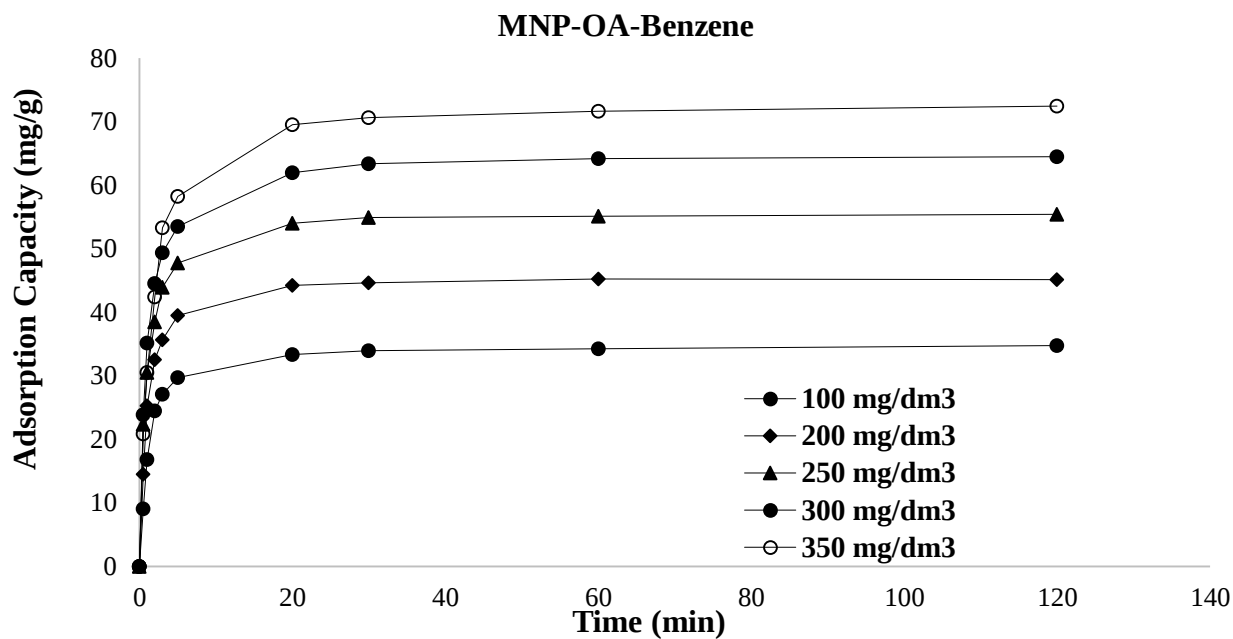


Figure 6. 16: Adsorption kinetics of Benzene on MNP-OA. Initial pH: 7, adsorbate dose: 0.1 g/dm³, solution volume: 10 mL, agitation speed: 300 rpm, temperature: 299 K

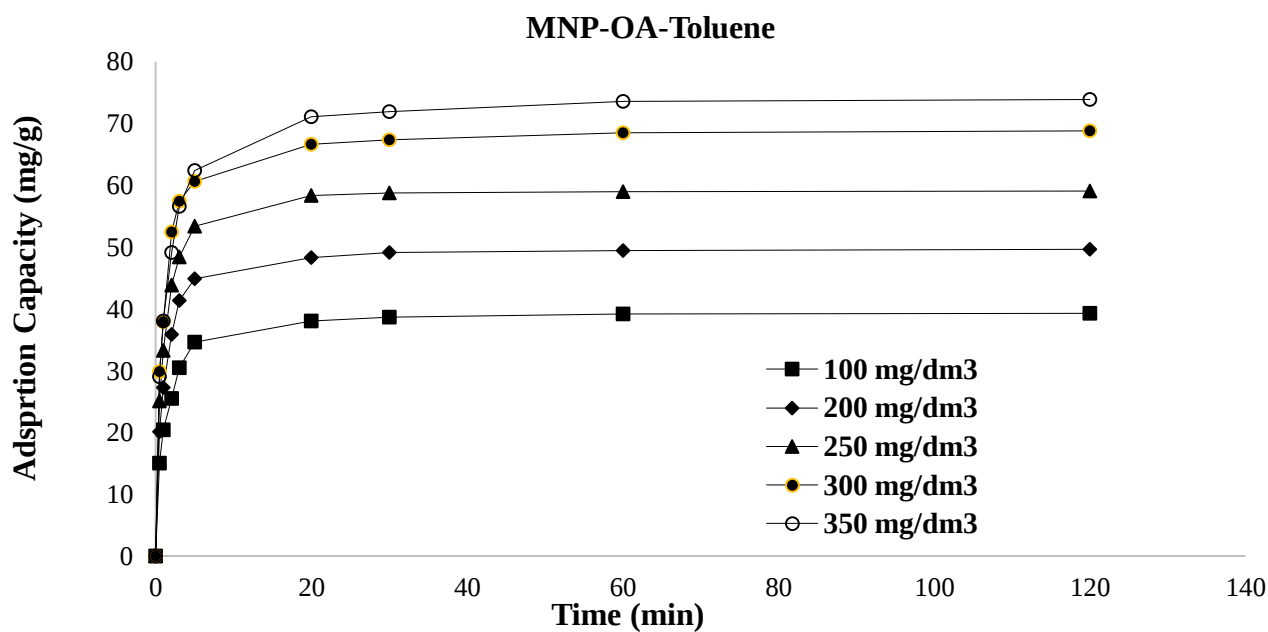


Figure 6. 17: Adsorption kinetics of Toluene on MNP-OA. Initial pH: 8, adsorbate dose: 0.1 g/dm³, solution volume: 10 mL, agitation speed: 300 rpm, temperature: 299 K.

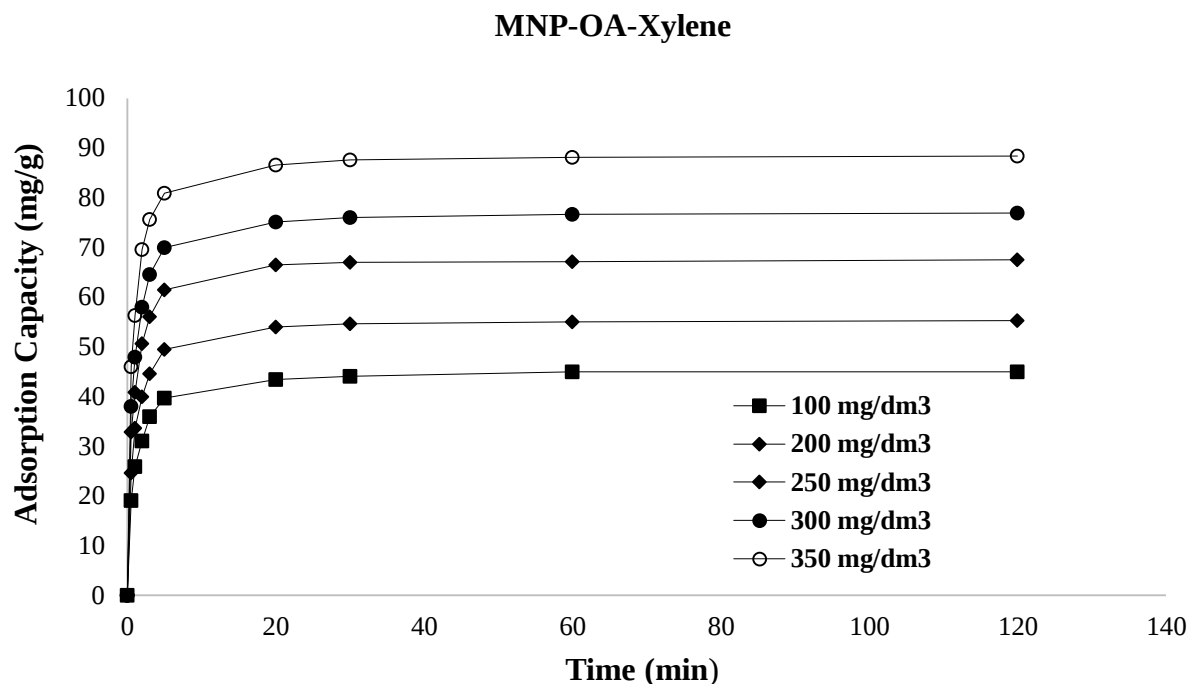


Figure 6. 18: Adsorption kinetics of Xylene on MNP-OA. Initial pH: 8, adsorbate dose: 0.1 g/dm³, solution volume: 10 mL, agitation speed: 300 rpm, temperature: 299 K.

6.4 KINETIC MODELLING

The kinetics of BTX adsorption onto MNP, MNP-PA and MNP-OA were modelled using the pseudo-first and pseudo-second kinetic models. The pseudo-first-order kinetic model can be used to follow adsorption kinetics which proceeds by diffusion through a boundary layer. On the other hand, adsorption processes that proceeds by surface chemisorption is described by the pseudo-second-order model. The expression of the pseudo-first and pseudo-second kinetic models have been described on section 2.7.1 in chapter 2.

6.4.1. Kinetic modelling for MNP

The effect of concentration on BTX onto MNP was modelled using the pseudo-first and pseudo second kinetic models and the fit of the models determined using the coefficient of correlation, r^2 and the % variable. The values for the kinetics parameters and results for error measurements are shown in Tables 6.1 to 6.2. The results in Table 6.1 to 6.2 reveals that the r^2 values for the pseudo-second-order models for MNP adsorbent and for all pollutants were higher than those of the pseudo-first-order model. The MNP the r^2 values for benzene with pseudo-first-order model lies between 0.9734 to 0.9938, while for pseudo-second-order is

between 0.995 to 0.9989. On the other hand, the % variable error was between 0.651 to 7.248 for pseudo-first-order and 0.4625 to 0.923 for pseudo-second-order. Higher values of r^2 signifies better fit of the model to the experimental data while lower values of percentage error also signify better fit of the model. For toluene the r^2 values were 0.9866 to 0.9998 for pseudo-first-order and 0.9946 to 0.9990 for pseudo second order model. On the other hand, the % variable error was between 2.559 to 6.1696 for pseudo-first-order and 0.444 to 0.885 for pseudo-second-order. For xylene the r^2 values were 0.9632 to 0.9863 for pseudo-first-order and 0.9952 to 0.9988 for pseudo-second-order. On the other hand, the % variable error was between 4.404 to 17.029 for pseudo-first-order model and 0.424 to 0.972 for pseudo-second-order model.

The fit of the kinetic models to the experimental data were also tested by plotting the predicted capacities at various times along with the experimental data against time as shown in Fig. 6.19. Fig. 6.19 shows kinetics plot of BTX at 100 mg/dm³ onto MNP along with the predicted pseudo-first and pseudo-second-order at different time period. From the Figure it is observed that the predicted capacities for the pseudo-second-order kinetics were much closer to the experimental data than those of the predicted values of the pseudo-first-order kinetics for BTX. It can also be seen from Tables 6.1 to 6.2 that the predicted capacities of the pseudo-second-order model at all concentrations were closer to the experimental data than the pseudo-first-order model. Therefore, we can conclude that the adsorption of benzene, toluene and xylene onto MNP follows the pseudo-second-order kinetics.

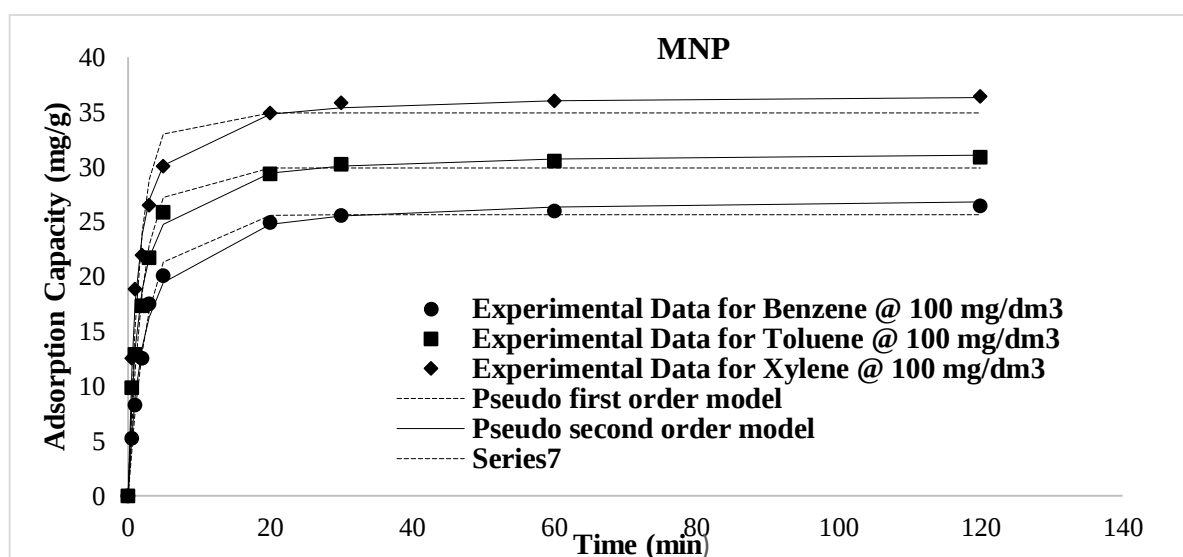


Figure 6.19: Comparison of predicted equilibrium capacities of kinetic models with experimental data for BTX adsorption on MNP.

The pseudo-second-order model assumes that the mechanism of uptake involves valence forces through sharing or exchange of electrons between MNP and BTX molecules (Ho and Ofomaja, 2006). Table 6.1 shows the pseudo-first-order rate constant for BTX adsorption onto MNP. The adsorption capacities for BTX on MNP were observed to increase with increasing concentration of BTX. The adsorption capacity values were in the range of 26.63 to 61.49 mg/g for benzene, 29.90 to 57.00 mg/g for toluene and 34.98 to 77.31 mg/g for xylene. The pseudo- first order rate constant for BTX adsorption onto MNP did not follow any particular trend. This may be due to the fact that the model does not describe accurately the adsorption kinetics.

Table 6.2 shows the pseudo-second-order rate constant for BTX adsorption onto MNP. The adsorption capacities were observed to increase with increasing concentration of BTX from 100 to 350 mg/dm³. From the results it will be observed that the trend in adsorption capacities were benzene < toluene < xylene. This trend is in line with the trend in increasing order of hydrophobicity, molecular weight, descending order of water solubility and ascending order of boiling point of BTX compounds (Bandura *et al.*, 2017).

The pseudo-second-order rate constant, k_2 was observed to reduce from 0.0182 to 0.0069 g/mg min for benzene, 0.0328 to 0.0114 g/mg min for toluene and 0.0254 to 0.0124 for xylene. The values for rate constant were in the order of benzene < toluene < xylene. The initial sorption rate, h was observed to increase with increasing concentration for 100 to 350 mg/dm³. The values of h were in the range of 13.505 to 29.666 mg/g min for benzene, 23.484 to 56.645 mg/g min for toluene and 34.099 to 81.859 mg/g min for xylene. The h determines the rate at which the pollutant molecules accumulates on the surface of the adsorbent at initial state of the adsorption. The trend in the result shows that as BTX concentration is increased the rate at which BTX molecules accumulate on the surface at the initial stage of adsorption increases. The h rate for xylene was much higher than toluene and benzene due to the increasing order of hydrophobicity, molecular weight, descending order of water solubility and ascending order of boiling point of BTX compounds (Bandura *et al.*, 2017). Although the h rate increased with increasing BTX concentration, the pseudo second order rate constant decreased with BTX concentration this could be as a result of interaction between adsorbate molecules at high concentrations as they accumulate on the adsorbent surface.

Table 6.1: Pseudo-first-order kinetic data for BTX adsorption onto MNP.

Kinetic model	100 mg/dm ³	200 mg/dm ³	250 mg/dm ³	300 mg/dm ³	350 mg/dm ³
MNP BENZENE					
Pseudo-first-order					
Exp. q (mg/g)	26.48	36.49	45.30	55.41	63.66
Model q (mg/g)	26.63	35.29	43.38	53.66	61.49
k_1 (g/mg min)	0.3678	0.4276	0.4523	0.4900	0.3310
r^2	0.9938	0.9864	0.9734	0.9912	0.9929
%Variable Error	0.651	2.583	7.248	3.765	4.296
MNP TOLUENE					
Pseudo-first-order					
Exp. q (mg/g)	30.89	40.37	49.48	58.63	69.34
Model q (mg/g)	29.90	38.89	43.99	57.00	57.00
k_1 (g/mg min)	0.4835	0.5346	0.5875	0.5483	0.563
r^2	0.9998	0.9770	0.9898	0.9866	0.9866
%Variable Error	2.559	4.884	3.312	6.1693	6.1169
MNP XYLENE					
Pseudo-first-order					
Exp. q (mg/g)	36.44	48.47	66.99	71.80	79.89
Model q (mg/g)	34.89	46.87	64.74	68.82	77.31
k_1 (g/mg min)	0.5843	0.6680	0.7776	0.7134	0.6381
r^2	0.9632	0.9863	0.9787	0.9736	0.9790
%Variable Error	6.682	4.104	11.749	17.029	17.029

Table 6.2: Pseudo-second-order kinetic data for BTX adsorption onto MNP

Kinetic model	100 mg/dm ³	200 mg/dm ³	250 mg/dm ³	300 mg/dm ³	350 mg/dm ³
MNP BENZENE					
Pseudo-second-order					
Exp. q (mg/g)	26.48	36.49	45.30	55.41	63.66
Model q (mg/g)	26.44	37.31	45.67	56.63	65.57
k_2 (g/mg min)	0.0182	0.0167	0.0149	0.0129	0.0069
h (mg/g min)	13.505	23.247	31.078	41.370	29.666
r^2	0.9956	0.9964	0.9964	0.9978	0.9989
Variable Error	0.4625	0.691	0.674	0.923	0.685
MNP TOLUENE					
Pseudo-second-order					
Exp. q (mg/g)	30.89	40.37	49.48	58.63	69.34
Model q (mg/g)	31.41	40.87	50.51	59.99	70.49
k_2 (g/mg min)	0.0238	0.0204	0.0179	0.0140	0.0114
h (mg/g min)	23.481	34.075	45.668	50.383	56.645
r^2	0.9946	0.9958	0.9978	0.9990	0.9987
Variable Error	0.688	0.885	0.719	0.444	0.849
MNP XYLENE					
Pseudo-second-order					
Exp. q (mg/g)	36.44	48.47	66.99	71.80	79.89
Model q (mg/g)	36.64	49.31	67.99	72.39	81.25
k_2 (g/mg min)	0.0254	0.0212	0.0185	0.0157	0.0124
h (mg/g min)	34.099	51.547	85.519	82.273	81.859
r^2	0.9952	0.9986	0.9983	0.9986	0.9988
Variable Error	0.791	0.424	0.952	0.894	0.972

6.4.2 Kinetic modelling for MNP-PA

The effect of concentration on BTX onto MNP-PA was modelled using the pseudo-first and pseudo-second kinetic models and the fit of the models determined using the coefficient of correlation, r^2 and the % variable. The values for the kinetics parameters and results for error measurements are shown in Tables 6.3 to 6.4. The results in Table 6.3 to 6.4 shows that the r^2 values for the pseudo-second-order models for MNP-PA adsorbents and for all pollutants were higher than those of the pseudo-first-order model. The MNP-PA the r^2 values for benzene with pseudo-first-order model was between 0.9791 to 0.9987, while for pseudo-second-order were between 0.9731 to 0.9996. On the other hand, the % variable error was between 1.733 to 8.804 for pseudo-first-order and 0.0904 to 5.604 for pseudo-second-order. Higher values of r^2 signifies better fit of the model to the experimental data while lower values of percentage error also signify better fit of the model. For toluene the r^2 values were 0.9672 to 0.9866 for pseudo-first-order and 0.9946 to 0.9989 for pseudo second order model. On the other hand, the % variable error was between 4.725 to 9.459 for pseudo-first-order and 0.756 to 1.254 for pseudo- second order. For xylene the r^2 values were 0.9696 to 0.9825 for pseudo-first-order and 0.9978 to 0.9991 for pseudo-second-order. On the other hand, the % variable error was between 4.478 to 22.257 for pseudo-first-order model and 0.345 to 1.692 for pseudo-second-order model.

The fit of the kinetic models to the experimental data were also tested by plotting the predicted capacities at various times along with the experimental data against time as shown in Fig. 6.20. Fig. 6.20 shows kinetics plot of BTX at 100 mg/dm³ onto MNP-PA along with the predicted pseudo-first and pseudo-second-order at different time period. From the Figure it is observed that the predicted capacities for the pseudo-second-order kinetics were much closer to the experimental data than those of the predicted values of the pseudo-first-order kinetics for BTX. It can also be seen from Tables 6.3 to 6.4 that the predicted capacities of the pseudo-second-order model at all concentrations were closer to the experimental data than the pseudo-first-order model. Thus, we can conclude that the adsorption of BTX onto MNP-PA follows the pseudo-second-order kinetics.

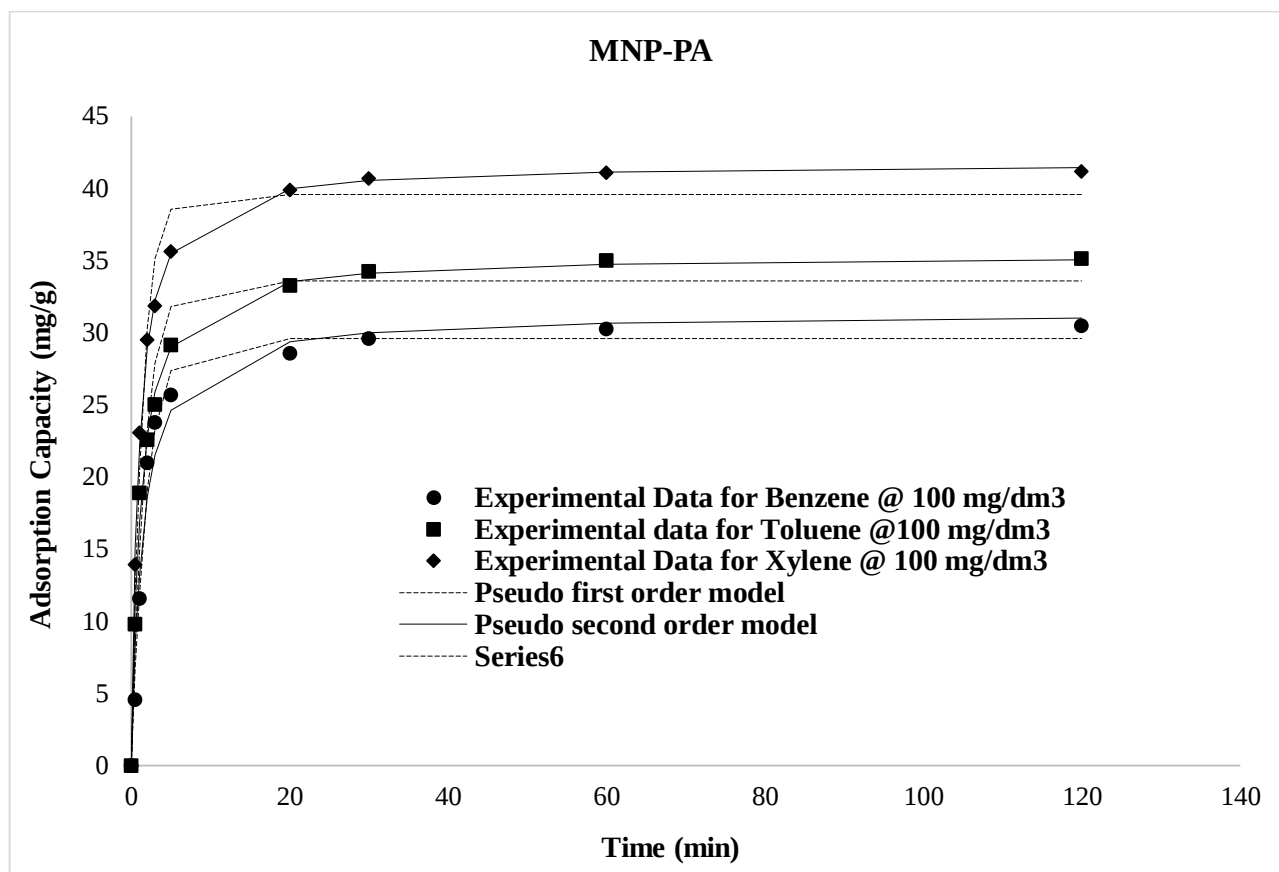


Figure 6.20: Comparison of predicted equilibrium capacities of kinetic models with experimental data for BTX adsorption on MNP-PA.

The pseudo-second-order model assumes that the mechanism of uptake involves valences forces through sharing or exchange of electrons between MNP-PA and BTX molecules (Ho and Ofomaja, 2006). Table 6.3 shows the pseudo-first-order rate constant for BTX adsorption onto MNP-PA. The adsorption capacities for BTX on MNP-PA were observed to increase with increasing concentration of BTX. The adsorption capacity values were in the range of 29.59 to 65.49 mg/g for benzene, 33.56 to 69.82 mg/g for toluene and 39.58 to 80.15 mg/g for xylene. The pseudo-first-order rate constant for BTX adsorption onto MNP-PA did not follow any particular trend. This may be due to the fact that the model does not describe accurately the adsorption kinetics.

Table 6.4 shows the pseudo-second-order rate constant for BTX adsorption onto MNP-PA. The adsorption capacities were observed to increase with increasing concentration of BTX from 100 to 350 mg/dm³. From the results it will be observed that the trend in adsorption capacities were benzene < toluene < xylene. This trend is in line with the trend in

hydrophobicity, boiling point and solubility (Bandura *et al.*, 2017). The pseudo-second-order rate constant, k_2 was observed to reduce from 0.0232 to 0.0091 g/mg min for benzene, 0.0258 to 0.0100 g/mg min for toluene and 0.0272 to 0.0172 g/mg min for xylene. The values for rate constant were in the order of benzene < toluene < xylene. The initial sorption rate, h was observed to increase with increasing concentration for 100 to 350 mg/dm³. The values of h were in the range of 22.831 to 43.741 mg/g min for benzene, 32.295 to 54.435 mg/g min for toluene and 47.343 to 119.01 mg/g min for xylene. The h determines the rate at which the pollutant molecules accumulate on the surface of the adsorbent at initial state of the adsorption. The trend in the result show that as BTX concentration is increased the rate at which BTX molecules accumulate on the surface at the initial stage of adsorption increases. The h rate for xylene was much higher than toluene and benzene because of hydrophobicity, boiling point and solubility (Bandura *et al.*, 2017). Although the h rate increased with increasing BTX concentration, the pseudo second order rate constant decreased with BTX concentration this could be as a result of interaction between adsorbate molecules at high concentrations as they accumulate on the adsorbent surface.

Table 6.2: Pseudo-first-order kinetic data for BTX adsorption onto MNP-PA

Kinetic model	100 mg/dm ³	200 mg/dm ³	250 mg/dm ³	300 mg/dm ³	350 mg/dm ³
MNP-PA BENZENE					
Pseudo-first-order					
Exp. q (mg/g)	30.49	40.80	49.83	59.17	66.93
Model q (mg/g)	29.59	39.06	48.01	57.54	65.49
k_l (g/mg min)	0.5158	0.5886	0.6303	0.6332	0.4397
r^2	0.9878	0.9791	0.9887	0.9827	0.9958
%Variable Error	1.733	4.430	3.656	7.845	8.804
MNP-PA TOLUENE					
Pseudo-first-order					
Exp. q (mg/g)	35.15	44.32	53.90	64.39	71.89
Model q (mg/g)	33.56	42.36	51.79	62.11	69.82
k_l (g/mg min)	0.5920	0.5458	0.7222	0.6639	0.4906
r^2	0.9702	0.9672	0.9835	0.9837	0.9866
%Variable Error	4.725	7.882	5.970	8.720	9.459
Exp. q (mg/g)	35.15	44.32	53.90	64.39	71.89
MNP-PA XYLENE					
Pseudo-first-order					
Exp. q (mg/g)	41.15	50.69	62.38	72.29	83.18
Model q (mg/g)	39.58	48.65	60.09	39.58	80.15
k_l (g/mg min)	0.7273	0.7501	0.8636	0.7272	0.8838
r^2	0.9789	0.9696	0.9825	0.9789	0.9729
%Variable Error	4.478	9.434	8.299	4.749	22.257

Table 6 4: Pseudo-second-order kinetic data for BTX adsorption onto MNP-PA

Kinetic model	100 mg/dm ³	200 mg/dm ³	250 mg/dm ³	300 mg/dm ³	350 mg/dm ³
MNP-PA BENZENE					
Pseudo-second-order					
Exp. q (mg/g)	30.49	40.80	49.83	59.17	66.93
Model q (mg/g)	31.37	41.12	50.57	60.50	69.33
k_2 (g/mg min)	0.0232	0.0222	0.0192	0.0165	0.0091
h (mg/g min)	22.831	37.537	49.101	60.394	43.741
r^2	0.9731	0.9996	0.9978	0.987	0.9917
Variable Error	3.824	0.0904	0.704	0.590	5.604
MNP-PA TOLUENE					
Pseudo-second-order					
Exp. q (mg/g)	35.15	44.32	53.90	64.39	71.89
Model q (mg/g)	35.38	44.50	54.49	65.43	73.78
k_2 (g/mg min)	0.0258	0.0233	0.0209	0.0157	0.0100
h (mg/g min)	32.295	46.140	62.055	67.213	54.435
r^2	0.9946	0.9964	0.9979	0.9976	0.9989
Variable Error	0.848	0.862	0.756	1.254	0.808
MNP-PA XYLENE					
Pseudo-second-order					
Exp. q (mg/g)	41.15	50.69	62.38	72.29	83.18
Model q (mg/g)	41.72	51.13	63.27	73.31	84.19
k_2 (g/mg min)	0.0272	0.0237	0.0217	0.0193	0.0172
h (mg/g min)	47.343	61.958	86.867	103.725	119.01
r^2	0.9984	0.9978	0.9988	0.9991	0.9979
Variable Error	0.345	0.697	0.559	0.582	1.692

6.4.3 Kinetic modelling for MNP-OA

The effect of concentration on BTX onto MNP-OA was modelled using the pseudo-first and pseudo-second kinetic models and the fit of the models determined using the coefficient of correlation, r^2 and the % variable. The values for the kinetics parameters and results for error measurements are presented in Tables 6.5 to 6.6. The results in Table 6.5 to 6.6 indicates that the r^2 values for the pseudo-second-order models for MNP-OA adsorbents and for all pollutants were higher than those of the pseudo-first-order model. For MNP-OA the r^2 values for benzene with pseudo-first-order model was between 0.9673 to 0.9911, while for pseudo-second order lies between 0.9932 to 0.9990. On the other hand, the % variable error was between 1.144 to 16.471 for pseudo-first-order and 0.401 to 1.377 for pseudo-second-order. Higher values of r^2 signifies better fit of the model to the experimental data while lower values of percentage error also signify better fit of the model. For toluene the r^2 values were 0.9666 to 0.9928 for pseudo-first-order and 0.9964 to 0.9988 for pseudo-second-order model. On the other hand, the % variable error was between 5.196 to 21.972 for pseudo-first-order and 0.495 to 1.494 for pseudo-second-order. For xylene the r^2 values were 0.9653 to 0.9691 for pseudo-first-order and 0.9975 to 0.9984 for pseudo-second-order. On the other hand, the % variable error was between 8.184 to 27.101 for pseudo-first-order model and 0.598 to 1.442 for pseudo-second-order model.

The fit of the kinetic models to the experimental data were also tested by plotting the predicted capacities at various times along with the experimental data against time as shown in Fig. 6.21. Fig. 6.21 shows kinetics plot of BTX at 100 mg/dm³ onto MNP-OA along with the predicted pseudo-first and pseudo-second-order at different time period. From the Figure it is observed that the predicted capacities for the pseudo-second-order kinetics were much closer to the experimental data than those of the predicted values of the pseudo-first-order kinetics for BTX. It can also be seen from Tables 6.5 to 6.6 that the predicted capacities of the pseudo-second-order model at all concentrations were closer to the experimental data than the pseudo-first-order model. Therefore, we can conclude that the adsorption of BTX onto MNP-OA follows the pseudo-second-order kinetics.

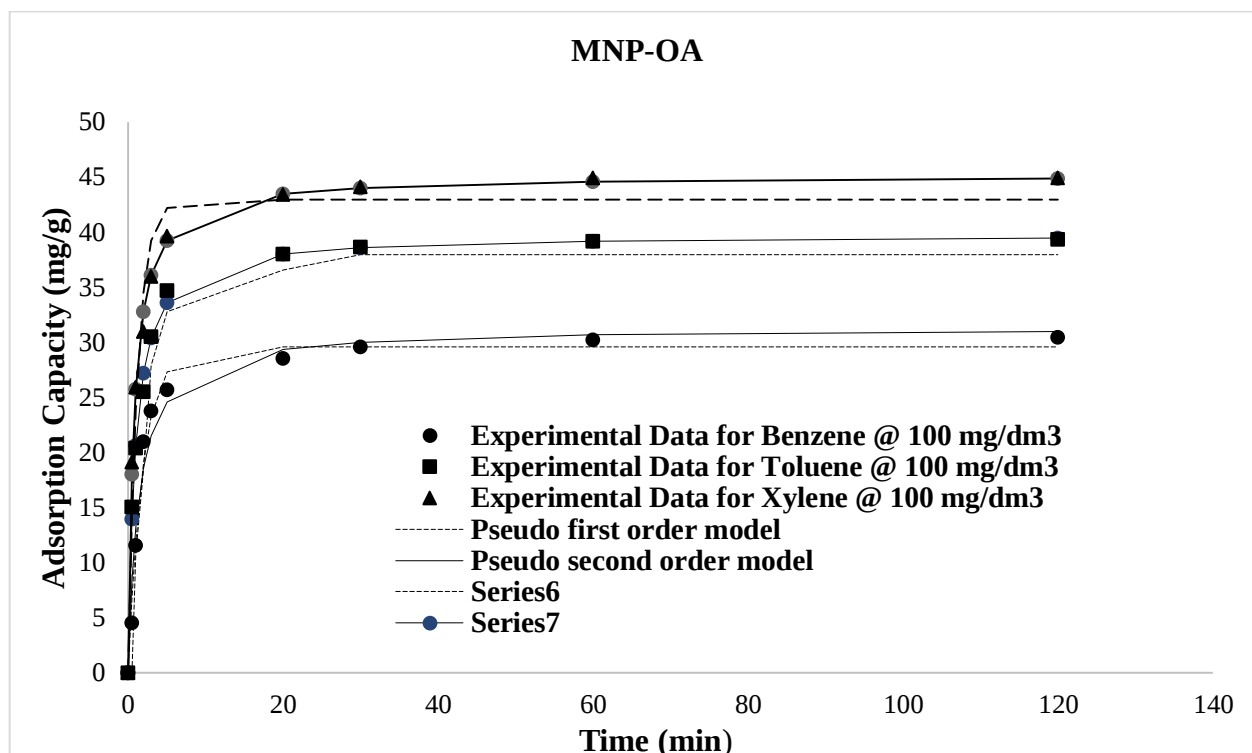


Figure 6.21: Comparison of predicted equilibrium capacities of kinetic models with experimental data for BTX adsorption on MNP-OA.

The pseudo-second-order model assumes that the mechanism of uptake involves valences forces through sharing or exchange of electrons between MNP-OA and BTX molecules (Ho and Ofomaja, 2006). Table 6.5 shows the pseudo-first-order rate constant for BTX adsorption onto MNP-OA. The adsorption capacities for BTX on MNP-OA were observed to increase with increasing concentration of BTX. The adsorption capacity values were in the range of 33.55 to 70.00 mg/g for benzene, 39.81 to 74.12 mg/g for toluene and 45.14 to 88.69 mg/g for xylene. The pseudo-first-order rate constant for BTX adsorption onto MNP-OA did not follow any particular trend. This may be since the model does not describe accurately the adsorption kinetics.

Table 6.6 shows the pseudo-second-order rate constant for BTX adsorption onto MNP-OA. The adsorption capacities were observed to increase with increasing concentration of BTX from 100 to 350 mg/dm³. From the results it will be observed that the trend in adsorption capacities were benzene < toluene < xylene. This trend is in line with the trend in hydrophobicity, boiling point and solubility (Bandura *et al.*, 2017). The pseudo-second-order rate constant, k_2 was observed to reduce from 0.0264 to 0.0102 g/mg min for benzene, 0.0271

to 0.0148 g/mg min for toluene and 0.0294 to 0.0218 g/mg min for xylene. The values for rate constant were in the order of benzene < toluene < xylene. The initial sorption rate, h was observed to increase with increasing concentration for 100 to 350 mg/dm³. The values of h were in the range of 33.102 to 55.463 mg/g min for benzene, 42.949 to 81.308 mg/g min for toluene and 59.606 to 171.477 mg/g min for xylene. The h value determines the rate at which the pollutant molecules accumulate on the surface of the adsorbent at initial state of the adsorption. The trend in the result shows that as BTX concentration is increased the rate at which BTX molecules accumulate on the surface at the initial stage of adsorption increases. The h rate for xylene was much higher than toluene and benzene because of hydrophobicity, boiling point and solubility (Bandura *et al.*, 2017). Although the h rate increased with increasing BTX concentration, the pseudo second order rate constant decreased with BTX concentration this could be because of the interaction between adsorbate molecules at high concentrations as they accumulate on the adsorbent surface.

Table 6.5: Pseudo-first-order kinetic data for BTX adsorption onto MNP-OA

Kinetic model	100 mg/dm ³	200 mg/dm ³	250 mg/dm ³	300 mg/dm ³	350 mg/dm ³
MNP-OA BENZENE					
Pseudo-first-order					
Exp. q (mg/g)	34.79	45.15	55.39	64.49	72.48
Model q (mg/g)	33.55	43.72	53.14	61.38	70.00
k_1 (g/mg min)	0.6207	0.7190	0.7588	0.7195	0.4945
r^2	0.9911	0.9841	0.9695	0.9673	0.9846
%Variable Error	1.144	4.184	11.284	16.471	10.873
MNP-OA TOLUENE					
Pseudo-first-order					
Exp. q (mg/g)	39.36	49.72	59.15	68.82	73.90
Model q (mg/g)	37.97	48.08	57.25	65.92	70.51
k_1 (g/mg min)	0.6661	0.7996	0.8360	0.8810	0.6856
r^2	0.9730	0.9828	0.9786	0.9782	0.9666
%Variable Error	5.196	5.196	9.352	12.219	21.972
MNP-OA XYLENE					
Pseudo-first-order					
Exp. q (mg/g)	44.91	55.32	67.45	76.87	88.36
Model q (mg/g)	42.94	52.79	64.67	73.39	84.46
k_1 (g/mg min)	0.8164	0.9157	0.9943	1.0548	1.1615
r^2	0.9654	0.9653	0.9664	0.9668	0.9691
%Variable Error	8.184	12.333	17.6132	22.290	27.101

Table 6.6: Pseudo-second-order kinetic data for BTX adsorption onto MNP-OA

Kinetic model	100 mg/dm ³	200 mg/dm ³	250 mg/dm ³	300 mg/dm ³	350 mg/dm ³
MNP-OA BENZENE					
Pseudo-second-order					
Exp. q (mg/g)	34.79	45.15	55.39	64.49	72.48
Model q (mg/g)	35.41	46.08	55.91	64.72	73.74
k_2 (g/mg min)	0.0264	0.0242	0.0218	0.0174	0.0102
h (mg/g min)	33.1021	51.3855	68.1452	72.8830	55.4634
r^2	0.9932	0.9970	0.9989	0.9990	0.9980
Variable Error	1.094	0.785	0.401	0.512	1.377
MNP-OA TOLUENE					
Pseudo-second-order					
Exp. q (mg/g)	39.36	49.72	59.15	68.82	73.90
Model q (mg/g)	39.81	50.49	60.15	69.32	74.12
k_2 (g/mg min)	0.0271	0.0256	0.0226	0.0205	0.0148
h (mg/g min)	42.9491	65.2605	81.7673	98.5079	81.3079
r^2	0.9964	0.9979	0.9988	0.9973	0.9977
Variable Error	0.687	0.624	0.495	1.473	1.494
MNP-OA XYLENE					
Pseudo-second-order					
Exp. q (mg/g)	44.91	55.32	67.45	76.87	88.36
Model q (mg/g)	45.14	55.55	62.94	77.13	88.69
k_2 (g/mg min)	0.0294	0.0268	0.0242	0.0226	0.0218
h (mg/g min)	59.9060	82.6995	111.7034	134.4482	171.4770
r^2	0.9975	0.9983	0.9976	0.9981	0.9984
Variable Error	0.598	0.643	1.267	1.221	1.442

The comparison of the pseudo-second-order model adsorption capacities of different adsorbents as reported in literature are shown in Table 6.7. The results show that the prepared MNP, MNP-PA and MNP-OA adsorption capacities for BTX were higher and were in line with those reported in literature. Among the ones reported in literature, only the Carbon 119 showed higher adsorption capacities. Therefore, we can conclude that the material produced were effective for BTX removal from aqueous solution.

Table 6.7: Pseudo second order capacities of different adsorbents

Materials				References
	Benzene	Toluene	Xylene	
Claytone-40	13.280	15.664	16.986	Nourmoradi <i>et al.</i> , 2012
PEG-Montmorillonite	6.250	6.450	8.493	Vidal and Volzone 2009
Thermally modified diatomite	0.312	0.276	0.637	Aivalioti <i>et al.</i> 2010
Purolite-macronet® MN-202	62.496	73.712	66.880	Fabiola <i>et al.</i> , 2014
Carbone CD-500	50.778	58.970	67.942	Fabiola <i>et al.</i> , 2014
Carbon 119	117.180	128.996	138.008	De Souza 2012
Smectite organoclay	2.040	1.270	3.830	Calvalho <i>et al.</i> , 2012
Mesoporous carbon (OMC)	2.476	3.156	3.975	Konggidinata <i>et al.</i> , 2017
Hydrophobic Zr metal	23.200	23.300	38.200	Amador <i>et al.</i> , 2018
Na-P1 zeolite	0.0176	0.0201	0.079	Bandura <i>et al.</i> , 2017
MNP	63.655	69.340	68.100	This study
MNP-PA	66.925	71.885	83.175	This study
MNP-OA	72.480	71.885	88.360	This study

6.4.4 Desorption and Reuse

Desorption is the extraction of an adsorbed substance from a surface. It is the reverse process of adsorption mechanism, whereby the adsorbed molecules are released back into solution. Desorption and reusability studies of an adsorbent are key attributes for industrial applicability. The possibility of recycling the exhausted adsorbent material is of importance in order to reduce cost of operation and increase the amount of times the adsorbent can be used. Methanol and water are commonly used in the recovery of adsorbed benzene, toluene and xylene. The water used as desorbing agent helps to determine how stable the benzene, toluene and xylene pollutants will be if the adsorbent can be regenerated in the same medium as used in adsorption while the methanol is used for making the medium slightly hydrophobic or non-polar. Desorption of benzene toluene and xylene was carried out using two desorbing agents, 0.5 M of CH₃OH and H₂O. The percentage efficiency of benzene, toluene and xylene desorption was calculated following (Eq. 6.1)

$$\text{Desorption (\%)} = \frac{\text{amount desorbed}}{\text{amount adsorbed}} \times 100 \quad (6.1)$$

The desorption studies using water as a desorbing agent for MNP, MNP-PA and MNP-OA show that the amount desorbed was not the same for the three adsorbents. The desorption trend of benzene, toluene and xylene followed the order MNP > MNP-PA > MNP-OA. The trend observed can be explained by the difference in water solubility of the organic pollutants. In this case the xylene being more soluble in water than the toluene and benzene would be strongly leached as compared to benzene and toluene (Bandura *et al.*, 2017). The trend can also be explained in terms of type and number of bonds formed. From Figs 6.22-6.24 it can be observed that MNP-PA and MNP-OA composites had less desorption percent as compared to MNP. This can be attributed to the fact that magnetite-organic acid composites have more bonding interactions such as the pi-pi and hydrophobic interactions than the magnetite. Comparing the two magnetite-organic acid composites desorption percentages, the MNP-OA percentage was lower than that of MNP-PA due to the fact that MNP-OA has longer hydrocarbon chain length chains hence will result in stronger hydrophobic interactions. The desorption studies using 50 % methanol for all the three pollutants show that the percentage desorption was not the same for the three adsorbents. The percentage desorption trend of the three pollutants (BTX) followed the order MNP > MNP-PA > MNP-OA and is

the same in each adsorbent. The pollutant trend followed the order of benzene > toluene > xylene. The adsorption mechanism of benzene, toluene and xylene onto the three adsorbents can be explained in relation to acid–base chemistry. This mechanism is based on the electron donating ability of the phenyl ring in each benzene, toluene and xylene compound to the d-orbitals of iron in magnetite. Methyl substitution on a benzene ring is capable of donating electrons into the ring system thereby activating the ring towards acid-base reactions. Therefore, toluene with one methyl substituent on the benzene ring is activated to acid base reaction stronger than benzene. The more methyl substituents on the ring the more activated is the ring towards acid-base reactions. For this reason, xylene will form stronger bonds with each of the adsorbents than toluene or benzene (Joseph *et al.*, 2000; Sasaki and Tanaka, 2011). Figs.6.23-6.24 shows that magnetite-organic acid composites had lower percentage decomposition as compared with the pure magnetite. This can be attributed to the stronger bonds formed between toluene and xylene and the modified magnetic adsorbents. Compared to the magnetite which only have one pi-pi interaction hence the decrease. Comparing the MNP-PA and the MNP-PA, the MNP-OA percentage had lower percentage desorption as compared with MNP-PA. The reason for this is that MNP-OA has longer hydrocarbon chain attached to the adsorbent surface which increases its hydrophobic interactions.

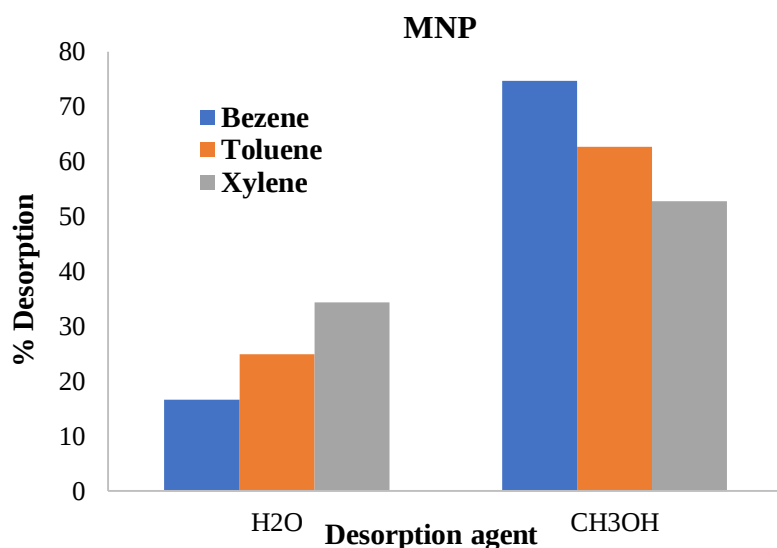


Figure 6.22: Desorption efficiency of BTX using different solvents for MNP

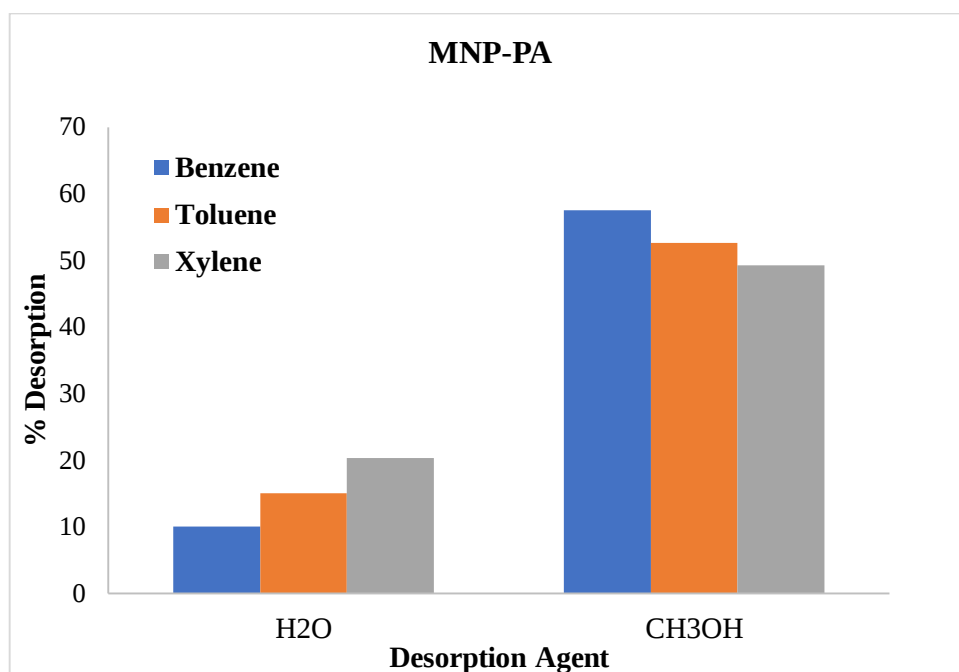


Figure 6. 23: Desorption efficiency of BTX using different solvents for MNP-PA

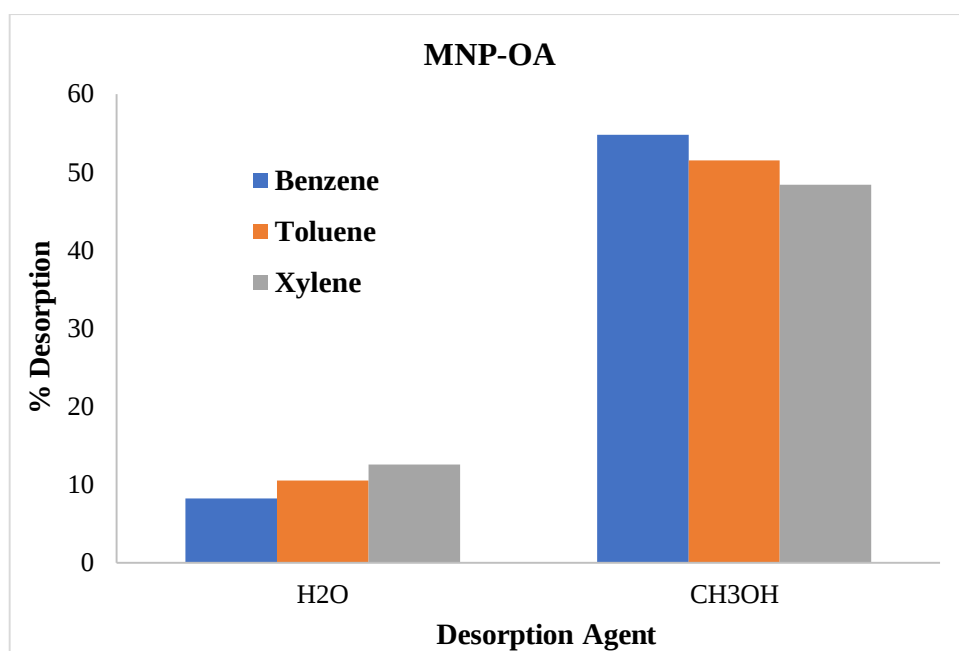


Figure 6.24: Desorption efficiency of BX using different solvents for MNP-OA

6.4.5: Reusability of MNP, MNP-PA and MNP-OA for BTX adsorption

The recycling of MNP, MNP-PA and MNP-OA adsorbents on benzene, toluene and xylene adsorption capacity was studied to evaluate the reusability of the adsorbents. which is an important practical application of the materials. Figs.6.25-6.27 show the results of the five adsorption/desorption cycles of benzene, toluene and xylene. The percentage adsorption and percentage desorption show similar trends for all the three adsorbents. The figures show that the adsorption capacity of the three adsorbents increased in the order benzene < toluene < xylene while the desorption percentage decreases in the order benzene > toluene > xylene for all cycles.

The plots reveal that the adsorption capacities of benzene, toluene and xylene onto MNP, MNP-PA and MNP-OA reduced with the increasing number of cycles. For example, benzene desorption percentage decreased with the number of cycles for all the three adsorbents. The decrease in adsorption capacities were lower for MNP (36.48-25.68 mg/g) for benzene, (40.37-30.99 mg/g) for toluene (48.47-40.45 mg/g) for xylene. On the other hand, for the MNP-PA they were between (40.80-27.66 mg/g) for benzene, (44.32-37.09 mg/g) for toluene (50.69-43.62 mg/g) for xylene and finally for MNP-OA lies between (45.14-34.22 mg/g) for benzene, (49.72-39.09 mg/g) for toluene (55.32-47.62 mg/g) for xylene.

The higher reduction in adsorption capacities of MNP-PA and MNP-OA composites can be attributed to loss and of adsorbent mass deactivation of active sites. The percentage desorption after each of the five cycles were also calculated and plotted in Figs. 6.25-6.27. The results show that the percentage desorption was higher for MNP and it lies between (74.68-64.88 %) for benzene, (70.47-54.88 %) for toluene (65.22-50.68 %) for xylene. On the other hand, for the MNP-PA it was between (70.47-58.88 %) for Benzene, (68.87-52.88 %) for Toluene (63.19-48.68 %) for xylene and finally for MNP-OA was between (67.13-55.28 %) for benzene, (63.25-49.99 %) for toluene and (58.83-45.66) for xylene. The trend show that the desorption percentage decreased from benzene, toluene and xylene for all the cycles and also decreased from MNP, MNP-PA and MNP-OA for all the adsorbent. The magnetite-organic acid composite had lower desorption percentage than the pure magnetite. This trend observed can be attributed to the additional interactions that occur between the benzene, toluene and xylene and the magnetite-organic composites surface such as pi-pi and hydrophobic interactions. Comparing the MNP-PA and the MNP-OA percentage desorption, the MNP-OA had lesser percentage desorption due to the fact that the material is more hydrophobic and had

longer carbon chains. Therefore, we can conclude that all the prepared adsorbents were therefore favourable for benzene, toluene and xylene adsorption and can be applied in at least five cycles therefore increasing their cost effectiveness of the adsorbent

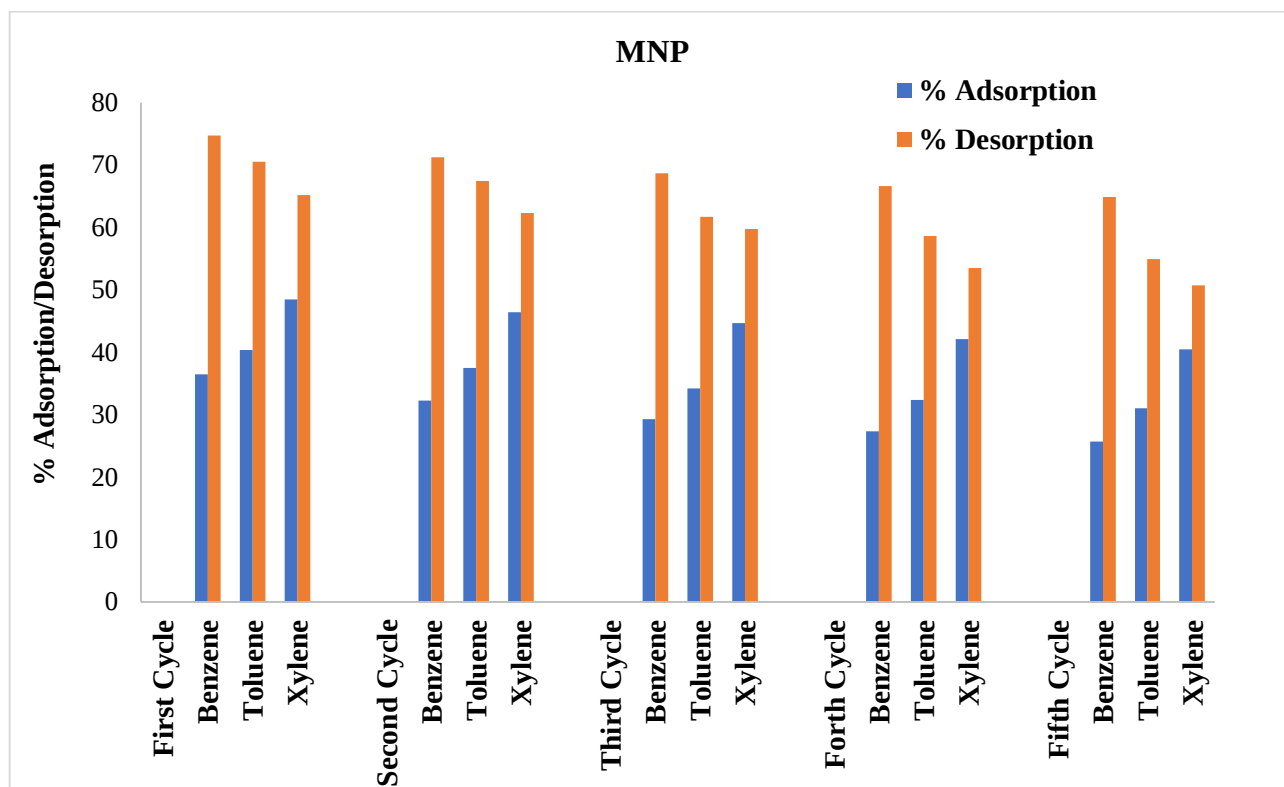


Figure: 6.25: Reusability of MNP for Benzene, Toluene and Xylene adsorption.

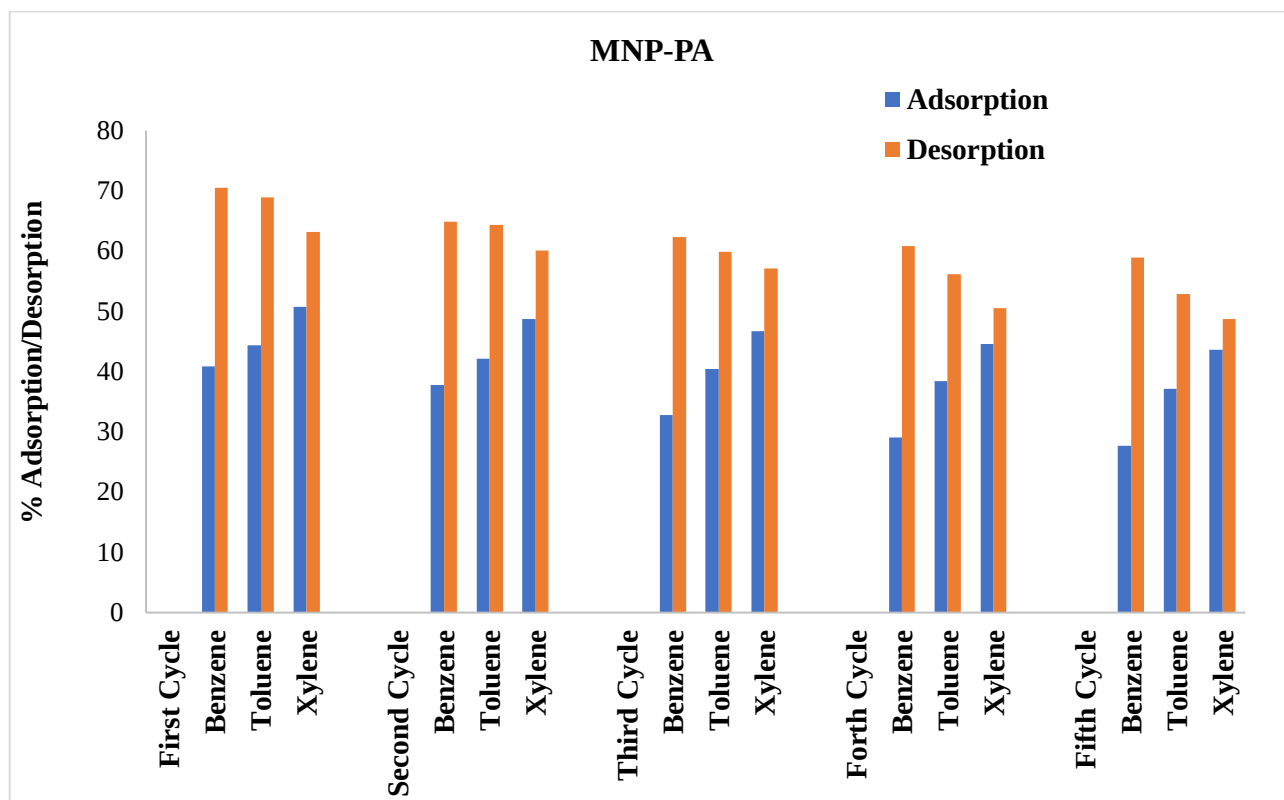


Figure 6.26: Reusability of MNP-PA for Benzene, Toluene and Xylene adsorption

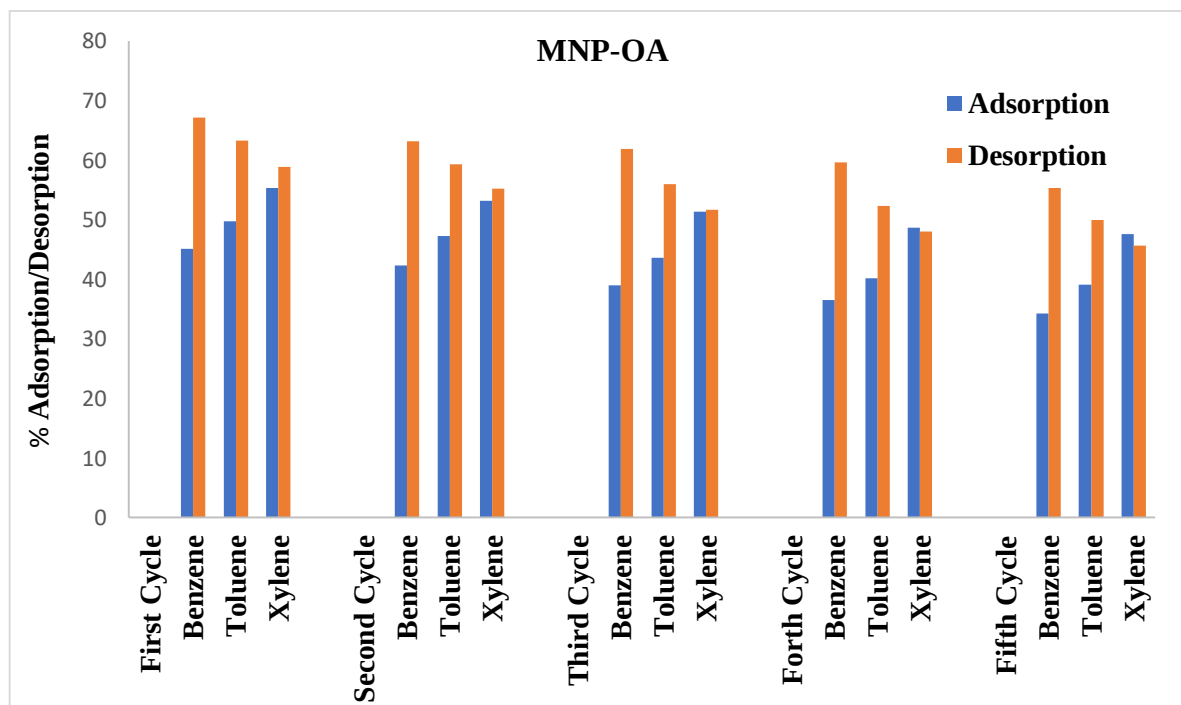


Figure 6.27: Reusability of MNP-OA for Benzene, Toluene and Xylene adsorption

6.5 CONCLUSION

The optimum pH for the adsorption of benzene, toluene and xylene onto pure magnetite nanoparticles, magnetite-oleic acid and magnetite-palmitic acid composites determined to be at pH 7 for benzene, and pH 8 for toluene and xylene. This pH value is close to the pH_{pzc} for the pure magnetite, magnetite-oleic acid, and magnetite-palmitic acid composite. The optimum adsorbent dosage was determined as 0.1 g/dm^3 for all three adsorbents. The adsorption capacity of pure magnetite, magnetite-palmitic and magnetite-oleic acids composites increased with an increase in BTX concentration. The adsorption kinetics show a good fit with the pseudo-second-order model for all three adsorbents. The r^2 values were close to one and the % variable errors were very small. The theoretical and experimental uptakes are also in good agreement. The desorption studies of MNP-MNP-PA and MNP-OA for the uptake of benzene, toluene and xylene was carried out using two desorbing agents, 50 % methanol and water. The desorption percentage plots using methanol and water desorbing agent indicated that benzene, toluene and xylene adsorbent had different desorption percentages. The desorption trend of BTX was found to be in the order $MNP > MNP-PA > MNP-OA$ when using both the water and methanol desorbing agent. The reusability of the three materials was observed to decrease with increase in the number of cycles, this can be attributed decrease in the number of some of the active sites or decrease in adsorbent mass. Therefore, we can conclude that the produced adsorbents can reduce cost.

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7 CONCLUSION AND RECOMMENDATIONS

7.1 CONCLUSION

Several researchers have investigated the ability of magnetite-organic acid composite (magnetite-oleic and magnetite-palmitic acid) to remove pollutants from aqueous solution. The main achievement of this study was to develop a one-step microwave synthesis method optimized using Response Surface Methodology approach for the preparation of magnetite-organic composite and its application in pollutant removal from aqueous solution.

For both magnetite-oleic and magnetite-palmitic acid composites the effect of five sorbent preparation variables $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution (mL), microwave power (W), NH_4OH volume (mL), reaction time (min), and volume of acid (oleic and palmitic) (mL) on the resulting % Fe, conductivity (S/cm), and adsorption capacity (mg/g) was studied. The study showed that the most significant synthesis variables that control reaction responses for both magnetite-oleic and magnetite-palmitic acid composites were the volume of oleic and palmitic acid, microwave power and $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution since they had higher F-values. The CCD estimated optimum preparation conditions for the synthesis of the magnetite-oleic acid composite were: 0.5 mL of $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution, 200 W microwave power, 5 min microwave irradiation reaction time and 0.8 mL volume NH_4OH and 0.2 of oleic acid solution. On the other hand, that of the magnetite-palmitic acid composite were: 0.5 mL of $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution, 200 W microwave power, 15 min microwave irradiation reaction time and 0.8 mL volume NH_4OH and 0.2mL of palmitic acid solution. For the magnetite-oleic acid composite, Fe content was 78.3 %, conductivity was 1561.9 S/cm, benzene adsorption capacity was 82.2 mg/g, toluene adsorption capacity was 84.1 mg/g and xylene adsorption capacity were 85.3 mg/g xylene. For palmitic-oleic acid composite were Fe content was 75.6 %, conductivity was 1325.66 S/cm, benzene adsorption capacity was 60.55 mg/g, toluene adsorption capacity was 64.47 mg/g and xylene adsorption capacity were 63.06 mg/g. The plots of predicted versus actual values for % Fe content, Conductivity (S/cm) and BTX adsorption capacity (mg/g) indicate that the predicted and actual value were closely distributed near the straight line indicating that the models well fitted the experimental data and all predictive models can be used to navigate the design space defined by CCD. This study successfully applied response surface

methodology, for the first time to substantiate the adsorption mechanism of an adsorption process.

The optimum synthesized magnetite-organic were successfully characterized. The immobilization of oleic and palmitic acid molecules on the surface of the magnetite was confirmed by Fourier transform infrared spectroscopy. The asymmetric and symmetric carboxylic ion (COO^-) bands were observed at 1400 to 1600 cm^{-1} for oleic and palmitic acid coated magnetite, respectively. This indicates that the magnetite surface and the stabilizing agent are bonded as the esterification happens between the hydroxyl groups on the magnetite surface and the (COO^-) carboxyl group from the acid molecule. The Energy-dispersive X-ray spectroscopy confirms that the main constituent elements of pure magnetite, magnetite-oleic, and magnetite-palmitic acid composite were iron, carbon, and oxygen. The vibrating-sample magnetometer indicates all three materials had superparamagnetic property. X-ray analysis shows the materials were nanosized and matched well with JCPDS card number: (00-019-0629). No impurities were observed in the sample. It was observed that modifying the magnetite with oleic and palmitic acid reduced the XRD peaks height indicating that surface modification has control over the crystallinity of the material. Monodisperse magnetite nanoparticles of 19.7 pure magnetite, 17.1 magnetite-oleic acids, and 17.9 nm magnetite-palmitic acid were prepared. The study also shows that the TEM images of three adsorbents were spherical in shape. Due to the long chain carboxylic acids present on the magnetite surface, the magnetite-coated organic composite was better separated than the pure magnetite. Their particles average sizes were 18.4 ± 0.5 for pure magnetite, 15.6 ± 0.5 nm magnetite-oleic acid and 16.5 ± 0.5 nm magnetite palmitic acid composite. The slight difference in particle size in the magnetite-oleic acid composite with that of the magnetite-palmitic acid composite can be attributed to the long alkyl chain of the oleic acid molecule since it will interpenetrate more into the alkyl chain attached to the neighboring particles as compared to the palmitic acid molecules. The results also show that the crystallite size and the particle size studies of the magnetite-oleic acid composite and the magnetite-palmitic acid composite suggested that the samples were comparable. The only difference between the magnetite-coated magnetite composites is the difference in the chain length of the fatty acid molecules which shows that the coating layer plays a significant role in reducing the crystallite size (XRD) and particle size (TEM) of the material. The study also reports on the BET isotherms of the three materials. The adsorption-desorption isotherms were well described by a type IV characteristic related to uniform mesoporous materials.

The pH_{pzc} showed a decrease due to modification of the magnetite using oleic and palmitic acids. The pH_{pzc} were 6.9 for the pure magnetite, 6.4 for magnetite-oleic acid composite and 6.1 for magnetite-palmitic acid composite.

BTX compounds removal from aqueous solutions was successfully achieved using the three adsorbents. The optimum pH for the adsorption of BTX onto pure magnetite, magnetite-palmitic and magnetite-oleic acid was determined to be pH 7 for benzene, pH 8 for toluene and xylene. The effect of solution pH increases the amount of H^+ ions in solution reduces thereby reducing the amount of H^+ ions that will interact with the iron oxide, therefore, allowing for the interaction between pollutant and adsorbent. Among the three adsorbents, the magnetite-oleic acid composite was the most effective adsorbent. Xylenes had the highest adsorption capacity, followed by the toluene and benzene. The reason for this trend can be attributed to the increasing order of hydrophobicity, molecular weight, descending order of water solubility and ascending order of boiling point. The optimum adsorbent dose for the three adsorbents for the adsorption process was 0.1 g/dm^3 .

The shapes of the effect of time on the uptake of BTX onto pure magnetite, magnetite-palmitic and magnetite-oleic acid composites are all similar and are divided into two kinetics profiles. An initial rapid uptake-time between 0 and 3 min and a slower rate from 3 min till equilibrium is reached at 120 min. The adsorption capacity of pure magnetite, magnetite-palmitic and magnetite-oleic acid composites increases with an increase in BTX concentration ($100\text{--}350 \text{ mg/dm}^3$) signifying that the adsorption process is driven by concentration driving force. The pseudo-first-order and pseudo-second-order models best described the kinetic models. The adsorption kinetics reveals that the r^2 values for the pseudo-second-order models for all the adsorbent and for all pollutants were higher than those of the pseudo-first order model.

For the pseudo-first-order rate constant for BTX adsorption onto the three adsorbents. The adsorption capacities for BTX on adsorbents were observed to increase with increasing concentration of BTX. The pseudo-first-order rate constant for BTX adsorption onto the three adsorbents did not follow any trend. This may be since the model does not describe accurately the adsorption kinetics.

For the pseudo-second-order rate constant for BTX adsorption onto the three adsorbents had a similar trend as the pseudo-first-order model, showing that adsorption capacities to increase with an increase in the concentration of BTX from 100 to 350 mg/dm^3 . The pseudo-second-

order model, however, show a trend in adsorption capacities in the order of benzene < toluene < xylene. This trend is in line with the trend in hydrophobicity, boiling point, and solubility.

The pseudo-second-order rate constant, k_2 was observed to reduce for all three pollutants. The values for rate constant followed also the order of benzene < toluene < xylene. The result also shows that the initial sorption rate, h was observed to increase with increasing concentration for 100 to 350 mg/dm³. For example, the values of h for MNP were in the range of 13.505 to 29.666 mg/g min for benzene, 23.484 to 56.645 mg/g min for toluene and 34.099 to 81.859 mg/g min for xylene. The h rate for xylene was much higher than toluene and benzene. Although the h rate increased with increasing benzene, toluene and xylene concentration, the pseudo-second-order rate constant decreased with benzene, toluene and xylene concentration this could be because of interaction between adsorbate molecules at high concentrations as they accumulate on the adsorbent surface.

Desorption studies further confirmed the adsorption mechanism of all the three adsorbates on the MNP, MNP-PA and MNP-OA surface was not the same. The trend observed can be explained in terms of water solubility. benzene < toluene < xylene. The xylene will be leached out faster than the toluene and Benzene. The desorption of all the adsorbents used, show similar trend when 50% methanol was used as desorbing agent. The percentage efficiency of benzene, toluene and xylene decreased from MNP > MNP-PA > MNP-OA. The trend of the pollutants followed the order benzene > toluene > xylene. and show that xylene had less desorption compared to benzene and toluene. This can be attributed to that xylene aromatic ring is more electron-rich than that of toluene and benzene compounds as a result, the electron donating substituent group of xylene supplies electrons to the aromatic ring in turn provides electron density to unoccupied 3d orbitals of iron cations which display Lewis acid character. All adsorbents were reused five times with less reduction in adsorption capacity after the cycles. The material can be easily regenerated to cut economical costs.

7.2 RECOMMENDATIONS

Based on the findings of this research, more work may be done out to continue the generation of knowledge and scientific development in wastewater treatment. The organic acid coated magnetite composite used were successful in the remediation of benzene, toluene and xylene from water and may be efficient in the removal of other pollutants including chloro-benzene and nitro-benzene. One-step microwave synthesis method was successfully used in the

preparation of the materials. The use of other synthesis methods for example co-precipitation, thermal decomposition, sol-gel, and microemulsion could, therefore, be investigated to synthesize the magnetite-organic acid composite and to determine the effect of different-sized Fe_3O_4 nanoparticles. The adsorption studies of benzene, toluene and xylene using magnetite-organic acid of shorter chain length such as myristic, decanoic and lauric acid can also be explored. Adsorption modelling, for example, thermodynamic studies using Langmuir-Freundlich isotherm, Hill and Redlich-Peterson and sips can also be investigated.