VUT

COMPETITIVE BIOSORPTION OF A MIXTURE OF CATIONIC DYES FROM A MULTICOMPONENT SOLUTION USING MODIFIED PINE CONE POWDER

by

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Declaration of Candidate

I, Silindile Lucia Ngema, declare that unless indicated, this dissertation is my own and that it has not been submitted for a degree at another University or Institution.

_____ On this _____ day of _____ 2012

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DEDICATION

I dedicate this work to my parents my late mother Jabulisiwe Ngema, my father Vusi Mchunu, my sublings Mphumelelo and Thula Ngema, my husband Mthunzi Lushozi and my children Thingolethu and Mmangaliso Lushozi.

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PRESENTATIONS AND PUBLICATIONS

The work presented in this dissertation has been presented at the Water Institute of South Africa (WISA) 2011 and at the South African Chemical Institute (SACI) young chemist symposium, Oral presentation, *Preliminary results on the graft polymerization of polyacrylic acid onto pine cone and its application as biosorbents for wastewater purification*. The Water Institute of South Africa (WISA) Conference 2012 in Cape Town, Oral presentation, *Removal of dyes from wastewater by acrylic acid grafted pine cone: effect of temoerature on grafted and adsorption performance.* To be presented at the Analytical Chemistry for the Environmental, Health, and Water, SEANAC Conference in Mozambique Maputo 2012, Poster presentation, *Methyl violet and Methylene blue removal from aqueous solution by acrylic acid grafted pine cone: effect of Fentons modification.*

Publications

1. A.E Ofomaja, S.L Ngema and E.B Naidoo. The grafting of acrylic acid onto natural biosorbents: Effect of plant components and initiator concentration on grafting efficiency and biosorption performance. Journal of Carbohydrate Polymers. dx.doi.org/10.1016/j.carbpol.2012.05.024.

ABSTRACT

The biosorption of methyl violet and methylene blue onto modified pine cone powder was studied. Single and binary component systems studies were carried out for the biosorption of methyl violet and methylene blue onto raw, Fenton treated and acrylic acid grafted pine cone powder. Various experimental parameters were studied including initial dye concentration (200-900 mg/dm^3), contact time, solution pH (4-12), mass of adsorbent (0.05-0.30g) and temperature (25-45 °C). Pseudo-first order and pseudo-second order equations were used to analyze the kinetic data. It was found that the data follow the pseudo -second order kinetic model for all temperature studied. The experimental data were analyzed using Langmuir and Freudlich isotherm model. The biosorption of methyl violet and methylene blue showed a better fit to Langmuir isotherm which properly describes the experimental data and that the sample surfaces are homogeneous. Various thermodynamic parameters, such as Gibbs energy (ΔG^*), enthalpy change (ΔH^*) and entropy change (ΔS^*), were calculated which indicated the present system was spontaneous and exothermic process for methyl violet and methylene blue. It was found that enthalpy and entropy of acrylic acid grafted pine cone was higher as compared to raw and Fenton's reagent for methyl violet and methylene blue.

Raw, Fenton treated and acrylic acid pine cone powder were characterized with Fourier transform infrared spectroscopy (FTIR), Ultraviolet-visible spectroscopy (UV-VIS), Thermogravimetic analysis (TGA/DTA), X-ray Diffraction (XRD) and Brauner, Emmett and Teller (BET). The following parameters were used to determine the surface properties of the grafted pine cone: change in H^+ concentration and oxidation reduction potential (ORP), surface negative charge, bulk density and acid number measurements. The FTIR analysis confirmed the presence of the organic compounds on the raw, Fenton treated and acrylic acid grafted pine cone powder. The UV/VIS determined the percentage removal of dyes from aqueous solution in single and binary component systems by comparing the raw, Fenton treated and Acrylic acid grafted pine cone powder. Thermo gravimetric analysis confirmed the reactions which occur at the molecular level of the raw, Raw + $KMnO_4$ and Fenton treated + $KMnO_4$ pine cone powder materials.

The second order derivative spectroscopy (SODS) was a suitable method for the analysis of the study of cationic dyes in binary solution. To determine the unknown concentrations of methyl violet and methylene blue dyes in binary solution using SODS, maximum wavelengths 561.8 nm and 623.1 nm were obtained. It was found that the percentage removal was higher for acrylic acid grafted pine cone than Fenton's treated and raw pine cone and treated samples adsorbed more methyl violet that methylene blue.

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LIST OF ABREVIATION

Abbreviation	Explanation
BET	Brauner, Emmett and Teller
XRD	X-ray diffraction
UV/Vis	Ultaviolet-Visible
FTIR	Fourier transform infrared
TGA	Thermogravimetric Analysis
DTA	Derivative thermogravimetric
MV	Methyl violet
MB	Methylene blue
$CH_2CHCOOH$	Acrylic acid
HCL	Hydrogen chloride
NaOH	Sodium hydroxide
Fe^{2+}/H_2O_2	Iron (II) and Hydrogen peroxide
MnO_2	Manganese oxide
$KMnO_4$	Potassium permanganate
H^+	Hydrogen ion
Na_2CO_3	Sodium carbonate
KOH	Potassium Hydroxide
ORP	Oxidation reduction potential
Fe^{3+}	Iron(III)
OH	Hydroxyl
HNO_3	Nitric acid
ΔH^+	change in Hydrogen ion concentration
ΔpH	change in solution pH
°C	Degrees celcius
K	K
%	Percentage
Hr	Hour
min	Minute

nm	Nanometer
µm	Micrometer
m_o	initial mass
m_1	mass after first wash and drying
m_2	final mass
cm	centimetre
r^2	correlation coefficient
x^2	chi-square
mg/g	milligrams per grams
g	gram
mol/ dm^3	mols per decimeter cube
$m^2 g^{-1}$	meter square per gram
mg g^{-1}	milligram per gram
mgL^{-1}	milligram per liter
$mmol/dm^3$	millimol per decimeter
X	adsorption capacity at equilibrium (mg g.1);
X	adsorption capacity at time t (mg g.1);
K	rate constant of pseudo-first order adsorption (min.1);
t	reaction time (min);
qm	adsorption capacity at equilibrium (mg g.1);
qt	adsorption capacity at time t (mg g.1)
k_2	pseudo-second order rate constant
q_e	equilibrium adsorption capacity
r_2	linear correlation
h	initial adsorption rate
r_a	the sorption rate
r_d	the desorption rate
exp	experimental
i.e.	that is
e.g.	example
Fig	Figure

CHAPTER ONE

INTRODUCTION AND PROBLEM STATEMENT

1.1 INTRODUCTION

Cationic dyes are of great importance in the manufacturing industries such as textile, paper, and pulp. Their application for leather finishing, food colouring, laboratory indicators, colourants for natural and synthetic plastics and in medicine makes them largely produced in industry. These synthetic dyes contain large organic rings in their structure which makes them both carcinogenic and mutagenic in nature. Several methods are available for the treatments of dyes in industrial wastewater. Among these methods (chemical coagulation/flocculation, ozonation, oxidation, ion exchange, irradiation, precipitation), adsorption has become more popular in recent years because of its efficiency and cost effective. Several adsorbents have been developed to remove dyes from aqueous solution e.g. activated carbon, rice husk and bagasse fly ash (Vadiyelan *et al.*, 2005; Mall *et al.*, 2006).

Pine cone is also one of the adsorbent widely used to treat industrial wastewater since it possess impressive biosorption capacities for the removal of heavy metal ions and dye (Özer and Turabik, 2009). Pine cone has some limitations such as low binding capabilities, and low filtration. These methods include Fenton's reagent, which is a powerful oxidant, and chemical grafting or graft copolymerization, which results in addition of functional monomers onto the pine cone powder surface.

This research examines the use of raw pine, acrylic acid modified pine and Fenton treated pine cone for the removal of methyl violet and methylene blue from aqueous solution in a single and multi-component solution. Fenton's treatment was performed using Fenton's reagent solution (Fe^{2+}/H_2O_2) in a 50% ratio. Parameters such as change in oxidation/reduction potential, solution pH and MnO_2 deposited were measured to determine the effect of Fenton's oxidation on the initiation process. Acrylic acid modified pine cone was prepared by chemical grafting of acrylic acid monomers onto Fenton treated pine cone at 50, 70, 80, 90 °C using various potassium permanganate ($KMnO_4$) concentration (0.0005-0.020 mol/ dm^3) as a radical intiator. $KMnO_4$ has been used because it's a strong oxidant, efficient and it is eco-friendly. The efficiency of $KMnO_4$ as a radical initiator was measured by change of oxidation reduction potential (ORP) and the change in H^+ concentration. Acrylic acid solution was mixed with the activated pine cone to initiate the polymerization reaction.

The efficiency of the grafting process was followed by monitoring the total monomer conversion, the percentage grafting, and the rate of homopolymer formation and rate of graft polymerization.

The product of grafting was applied to remove methyl violet and methylene blue in solution, which adsorbed more methylene blue than methyl violet and has the highest percentage grafting comparing to Fenton treated and raw pine cone powder. In the single component solutions methyl violet showed a high adsorption at pH 10 while methylene blue showed a high adsorption at pH 12. Acrylic acid grafted pine cone adsorbed more methylene blue than methyl violet followed by Fenton treated and raw pine cone powder. In a multi-component system (mixed solution) 1:1 ratio, methyl violet was more efficiently removed from solution than methylene blue due to higher selectivity of the biosorbents for methyl violet than for methylene blue. To measure the use of raw, Fenton treated and acrylic acid grafted pine cone to remove methyl violet and methylene blue from aqueous solution, the effect of dye concentration, solution pH, mass of adsorbent and temperature have been evaluated.

1.2 PROBLEM STATEMENT

South Africa has a large and growing textile industry and there is a need to develop simple and cost effective methods to remove spent dyes from effluent streams before discharge into receiving water bodies. Most biosorption studies have been performed on single component dye systems; therefore, the efficacy of the application of biosorbents to real textile industry waste has not been reported. Serious attempts have not been made in determining an effective method of overcoming the interferences caused by overlapping of spectra in multi-component analysis of dyes. Derivative spectrophotometry has been successfully applied in pharmaceutical and environmental analysis for the determination of drugs in multi-component systems (Rojas and Ojeda, 2009; Benamor and Aguerssif, 2008). The problems associated with spectra overlap, has not yet been extensively applied to biosorption processes in the analysis of dye from binary solutions.

1.3 OBJECTIVES

The aim of this research is to study the mechanisms of removal of cationic dyes and analyze the multi-component cationic dye systems present in wastewater by using pine cone powder before it is discharged to the environment.

1.3.1 Specific Objectives

The objectives of this study were:

1. To treat the surface of pine cone powder to reduce lignin using Fenton's reagent.
2. To modify and optimize modification of pine cone powder with acrylic acid.
3. To apply the modified and optimized pine cone powder for dye removal using single and binary dye component systems.
4. To apply derivative spectrophotometry to resolve the problems of overlapping spectra in the multi-component system.
5. To determine the kinetics and the thermodynamics of the dye biosorption in single and bi- component systems.

1.4 VALUE OF RESEARCH

The Vaal river is used widely by a large number of industries in the Vaal Triangle in Gauteng, South Africa. Deposition of industrial effluents into the Vaal river is very common leading to pollution of the Vaal river. This research will produce a simple technique for the removal of such pollutants before effluents are discharged into the Vaal river.

The research will also provide simple techniques for analysis of a multicomponent dye solution. This research will benefit the environment and community of the Vaal in Gauteng, South Africa by producing a cost effective way of minimizing the effluent from industries before it is discharged into the rivers.

1.5 OUTLINE OF THE DISSERTATION

This research is outlined as follows:

Chapter one: This chapter gives a brief summary of this thesis on the research work conducted.

Chapter two: Brief introduction of dye pollutants in water, the effect of dye to the environment, methods of their removal, and adsorption as an alternative method for removal

of dye pollutant was discussed. Selective biosorbent used by other researches, the application of pine cone as a biosorbent and the grafting method used for biosorbent modification were also discussed.

Chapter three: The experimental procedure which is divided into three sections is described. The first section describes the sample preparation. Section two involved the grafting procedure and parameter. Section three involved the application of the application of the raw and the grafted pine cone powder for the dye removal from aqueous water using single and binary component systems.

Chapter four: This chapter is divided into six part which covers the results and discussion for:

4.1. Fenton's reagent measurements which include surface properties such as bulk density, BET, and acid number for the raw, Fenton treated and acrylic acid grafted samples.

4.2. Grafting with acrylic acid onto raw and Fenton treated pine cone samples.

4.3. Optimization of adsorption parameter which includes optimization of solution pH, optimization of adsorbent mass and percentage removal of each cationic dye.

4.4. Adsorption kinetics data calculation with includes pseudo-first and pseudo-second order equation.

4.5 Equilibrium biosorption measurements which includes Langmuir and Freundlich isotherm and thermodynamic studies.

4.6 The simultaneous analysis of cationic dyes in single and multi component dyes solutions.

Chapter five: from the results obtained, conclusions are drawn with respect to the initial objectives of this thesis.

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CHAPTER TWO

DYES, GENERAL OVERVIEW

2.1 INTRODUCTION

Dyes are natural or synthetic organic colourants which are used in the manufacture of textile, paper, leather and carpets. There are many different structural dyes available such as, acidic, basic, disperse, azo, diazo, anthroquinone based and metal complex dyes. It is estimated that more than 100,000 dyes are commercially available with over $7x10^5$ tonnes of dyestuff produced annually (Meyer, 1981; Zollinger, 1987). Textile industries are found in most countries and wastewater from these industries are characterized by components high in colour and organics (Ofomaja and Ho, 2007). This causes considerable environmental pollution problems. When effluents containing colours from these industries are discharged into surface or ground water, it reduces light required for photosynthesis and this causes toxic effects to aquatic life.

Dye molecules comprise of two key components; (i) the chromophores, responsible for producing the colour, and (ii) the auxochromes, which does not only supplement the chromophore but also render the molecule soluble in water and give enhanced affinity toward the fibers (Gupta and Sushas 2009). Dyes contain complex aromatic molecular structures which make them stable and non-biodegradable (Gao *et al*., 2010). The presence of these dyes in water can also lead to bioaccumulation in living aquaticorganisms, and is suspected to cause health problems in animals, plants and humans since they are known to be carcinogenic and mutagenic (Özcan *et al.*, 2004; Qiao *et al.*, 2009;).

2.2 CLASSIFICATION OF DYES

Dyes may be classified according to chemical structure or by their usage or application method.

2.2.1 *Chemical classification* is the classification of dyes by their chemical structure. Dyes are identified by groups that has characteristic properties, for example, azo dyes (-N=N-) (strong, good all-round properties, cost-effective) and anthraquinone dyes ($C_{14}H_8O_2$) (weak, expensive) (Gregory, 1990).

2.2.2 *Usage Classification* is the classification of dyes by its use or method of application e.g., dispersed dyes which have low solubility in aqueous solution and must be dispersed when applied.

However, Mishra, and Tripathy, (1993) and Fu *et al., (*2001) suggested that dyes may also be classified as anionic dyes, acid and reactive dyes; cationic:basic dyes; non-ionic:disperse dyes. Nevertheless, a review by Aksu (2005) reported that the chromophores in anionic and non-ionic dyes are mostly azo groups or anthraquinone types.

2.3 TYPES OF DYES

2.3.1 Cationic (Basic) Dyes.

Cationic (basic) dyes are water-soluble dyes applied to paper, polyacrylonitrile (e.g. Dralon), modified nylons, and modified polyesters (Christie, 2007 and Hunger, 2003). The authors reported that the original use of this group of dyes was for silk, wool, and tannin-mordanted cotton when brightness of shade is more important than fastness to light and washing. These water-soluble dyes yield coloured cations in solution and for this reason they are frequently referred to as cationic dyes. The principal chemical classes hemicyanine, acridine, diazahenicyanine, triarylmethane, thiazine and oxazine.

2.3.2 Acid Dyes.

These water-soluble anionic dyes carry the organic sulphonic acid group. However, their commercially available forms are usually sodium salts which exhibit good water solubility (Özer and Turabik, 2009). Acid dyes are applied to nylon, wool, silk, and modified acrylics. They are also used to some extent for paper, leather, ink-jet printing, food, and cosmetics. The principal chemical classes of these dyes are azo (including premetallized), anthraquinone, azine, triphenylmethane, xanthene, nitro and nitroso.

2.3.3 Reactive Dyes.

Reactive dyes form a covalent bond with the fiber and contain chromophoric groups such as azo,anthraquinone, triarylmethane, phthalocyanine, formazan, oxazine, etc. Their chemical structures are simpler, the absorption spectra show narrower absorption bands, and the dyeing are brighter making them advantageous over direct dye. Reactive dyes are generally used for cotton and other cellulosics, but are also used to a small extent on wool and nylon.

2.3.4 Disperse Dyes.

These are substantially water-insoluble nonionic dyes for application to hydrophobic fibers from aqueous dispersion. They are used mainly on polyester and to some extent on nylon, cellulose, cellulose acetate, and acrylic fibers. They generally contain azo, anthraquinone, styryl, nitro, and benzodifuranone groups.

2.3.5 Anionic-Direct Dyes.

These are water-soluble anionic dyes, when applied from aqueous solution in the presence of electrolytes have high affinity for cellulosic fibers. Their principal use is in the dyeing of cotton and rayon, paper, leather, and to some extent to nylon. Generally, most of the dyes in this class are polyazo compounds, along with some stilbenes, phthalocyanines, and oxazines.

2.3.6 Vat Dyes.

These types of dyes are water-insoluble with the principal chemical class containing anthraquinone and indigoid. Vat dyes are mainly used for cotton, mainly to cellulosic fibers as soluble leuco salts, for rayon and wool.

2.3.7 Sulfur Dyes.

These dyes have intermediate structures and form a relatively small group of dyes important from an economic point of view with sodium sulfide as the reducing agent. The low cost and good wash fastness properties of the dyeing make this class important from environmental viewpoint. Sulphur dyes are used for cotton.

2.3.8 Solvent Dyes.

Solvent dyes are water soluble and nonpolar or slightly polar, i.e., lacking polar solubilizing groups such as sulfonic acid, carboxylic acid, or quaternary ammonium. They are used for plastics, gasoline, lubricants, oils, and waxes. The principal chemical classes are predominantly azo and anthraquinone, but phthalocyanine and triarylmethane are also used.

Gupta and Suhas (2009), reported that there are some other classes of dyes such as azoic having azo groups used for cotton and other cellulosic materials; fluorescent brighteners having stilbene, pyrazoles, coumarin and naphthalimides used for soaps and detergents, fibers, oils, paints, and plastics and mordant having azo and anthraquinone used for wool, leather, natural fibers after pretreating withmetals and anodized aluminium.

Table 2.1 Classification of Dyes by Use or Application Method (Hunger, 2003)

Class	Principal Substrate	Method of application	Chemical types
Acid	Nylon, wool, silk, paper, inks, and leather	Usually from neutral to acidic dyebaths	Azo(including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso
Azoic components and compositions	Cotton, rayon, cellulose acetate and polyester	Fiber impregnated with coupling component and treated with a solution of stabilized diazonium salt	Azo
Basic	Paper, polyacrylonitrile, modified nylon, polyester and inks	Applied from acidic dyebaths	Cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triarylmethane, azo, azine, xanthene, acridine, oxazine, and anthraquinone
Direct	Cotton, rayon, paper, leather and nylon	Applied from neutral or slightly alkaline baths containing additional electrolyte	Azo, phthalocyanine, stilbene, and oxazine
Disperse	Polyester, polyamide, acetate, acrylic and plastics	Fine aqueous dispersions often applied by high temperature/ pressure or lower temperature carrier methods; dye may be padded on cloth and baked on or thermofixed	Azo, anthraquinone, styryl, nitro, and benzodifuranone
Fluorescent brighteners	Soaps and detergents, all fibers, oils, paints, and plastics	From solution, dispersion or suspension in a mass	Stilbene, pyrazoles, coumarin, and naphthalimides

Food, drug, And cosmetic	Foods, drugs, and cosmetics		Azo, anthraquinone, carotenoid and triarylmethane
Mordant	Wool, leather, and anodized aluminium	Applied in conjunction with Cr Salts	Azo and anthraquinone
Oxidation Bases	Hair, fur, and cotton	Aromatic amines and phenols oxidized on the substrate	Aniline black and indeterminate structures
Reactive	Cotton, wool, silk, and nylon	Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)	Azo, anthraquinone, phthalocyanine, formazan, oxazine, and basic
Solvent	Cotton and rayon	Aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur-containing products on fiber	Indeterminate structures
Vat	Cotton, rayon, and wool	Water-insoluble dyes solubilized by reducing with sodium hydrogensulfite, then exhausted on fiber and reoxidized	Anthraquinone (including polycyclic quinones) and indigoids

2.4 DYES IN AQUATIC

Dyes and pigments are discharged into wastewaters from various industrial effluent streams, mainly from the dye manufacturing and textile finishing (Turabik, 2008). The presence of dyes in effluent reduces photosynthesis by blocking the passage of light through water. The presence of very low concentrations of dyes in effluent is highly visible and undesirable (Robinson, *et al*., 2001).

2.5 MANUFACTURING OF DYES

The reactions in the production of intermediates and dyes are carried out in bomb-shaped reaction vessels made from cast iron, stainless steel, or steel lined with rubber, glass (enamel), brick, or carbon blocks. These vessels have capacities of 2.40 m^3 and are equipped with mechanical agitators, thermometers, or temperature recorders, condensers, pH probes, etc., depending on the nature of the operation. Jackets or coils are used for heating and cooling by circulation of high-boiling fluids (e.g. hot oil or Dowtherm), steam, or hot water to raise the temperature, and air, cold water, or chilled brine to lower it. Unjacketed vessels are often used for reactions in aqueous solutions in which heating is affected by direct introduction of steam, and cooling by addition of ice or by heat exchangers. The reaction vessels normally span two or more floors in a plant to facilitate ease of operation. Products are transferred from one piece of equipment to another by gravity flow, pumping, or blowing with air or inert gas. Solid products are separated from liquids in centrifuges, in filter boxes, on continuous belt filters, or in various designs of plate-and-frame or recessed-plate filter presses. The presses are dressed with cloths of cotton, Dynel, polypropylene, etc. Some provide separate channels for efficient washing, others have membranes for increasing the solids content of the presscake by pneumatic or hydraulic squeezing. The plates and frames are made of wood, cast iron, but more usually hard rubber, polyethylene, or polyester (Hunger, 2003).

Dyes are synthesized in the reactor, filtered, dried, and blended with other additives to produce the final product. The synthesis step involves reactions such as sulfonation, halogenation, amination, diazotization, and coupling followed by separation processes which may include distillation, precipitation, and crystallization. In general, organic compounds such as naphthalene are reacted with an acid or an alkali along with an intermediate (such as a nitrating or a sulfonating compound) and a solvent to form a dye mixture. The dye is then separated from the mixture and purified. On completion of the manufacture of actual colour, finishing operations including drying, grinding, and standardization are performed and these are important for maintaining consistent product quality (Kirk-Othmer., 1980 and Hunger, 2003).

2.6 MULTI-COMPONENT DYES

The study of biosorption of dyes from a single component dye solution has been well documented in literature using different types of adsorbents. Only very little research have been done on the combined effects of two or more dyes and simultaneous removal of dyes from a mixture of dye solution. Gao *et al*., (2010) reported that there are many problems that need to be solved for multi-component biosorption namely: (i) to evaluate the interactions and competitions between biosorbates and biosorbent, (ii) the prediction and evaluation of multi-component biosorption equilibrium, (iii) to analyze a mixture of dyes simultaneously. Nevertheless, the work conducted by Vijiayaraghavan and Yun (2008), revealed that the nature of the mechanism and extent of competition have not been fully understood. O'Mahony *et al*., (2002) studied the adsorption of multicomponent dye solutions containing equal concentrations of the Reactive Red, Reactive Blue 19, and Reactive Orange 16 dyes with a maximum total dye concentration of 450 mg dm^{-3} by *Rhizopus* biomass. They observed that uptake of each of the dyes from multicomponent solution at pH 2.0 by *Rhizopus* biomass increased with increasing solution concentration suggesting a direct competition mechanism and no preferential dye binding.

Generally, spectrophotometric methods are used for the analysis of components in multi-component systems, because these methods are more economic and simple, compared to methods such as chromatography and electrophoresis (Rojas and Ojeda, 2009). But the simultaneous analysis of components in a multi-component solution by spectrophotometric methods can also be very complex due to the overlapping adsorption bands of the components and spectral interferences (Sőzgen and Tutem, 2004; Lbabpour and Lee, 2006). Rojas and Ojeda, (2009), further suggested that derivative spectrophotometry which is based on the analysis of derivative spectra, is a very useful analytical technique to solve binary and ternary solutions with over lapping. Recent researchers have focused on the development of reliable, fast and sensitive methods for the determination of dyes in multi-component systems.

2.7 TECHNIQUES USED FOR DYE REMOVAL

Several physical, chemical and biological decolourization methods have been reported, however, few have been accepted by the paper and textile industries (Ghoreishi and Haghighi, 2003). Some of the main treatment techniques used to remove dyes from aqueous streams reviewed by Vaghetti *et al*. (2009) include coagulation and flocculation, reverse

osmosis, electroflotation, membrane filtration, irradiation and ozonation, and adsorption. A summary of the advantages and disadvantages of these methods reviewed is shown in Table 2.2.

Table 2.2 Advantages and disadvantages of the current methods of dye removal from industrial effluent (Robinson, et al, 2001).

Physical/ Chemical Methods	Advantages	Disadvantages
Fentons Reagent	Effective decolourisation of both soluble and insoluble dyes	Sludge generation
Ozonation	Applied in gaseous state: no alteration of volume	Short half-life (20 min)
Photochemical	No sludge production	Formation of by-products
NaOCl	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
Cucurbituril	Good sorption capacity for various dyes	High cost
Electrochemical destruction	Breakdown compounds are non-hazardous	High cost of electricity
Activated carbon	Good removal of wide variety of dyes	Very expensive
Peat	Good adsorbent due to cellular structure	Specific surface areas for adsorption are lower than Activated carbon
Wood chips	Good sorption capacity for acid dyes	Requires long retention times

Silica gel	Effective for basic dye removal	Side reactions prevent commercial application
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O_2
Electrokinetic coagulation	Economically feasible	High sludge production

2.7.1 Classification of dye removal methods

Over the last few decades, society has become increasingly sensitive towards the protection of the environment (Hasan, 2008). Due to this problem mankind is concerned about the potential adverse effects of the chemical industry on the environment. Dyes are highly visible material, thus the minor release of dyes into the environment may cause the appearance of colour. In the last few years, information on the environmental consequences of dyestuff usage have been available and the dye manufacturers, users and government themselves have been taking substantial measures to treat the dye containing wastewaters (Gupta and Sushas, 2009). Gupta and Sushas, (2009) further reported that initially there was no discharge limit therefore the treatment of dye wastewater started with some physical treatments such as sedimentation and equalisation to maintain the pH, total dissolved solids (TDS) and total suspended solids (TSS) of the discharged water. Therefore, the requirement to develop new and improved methods to remove colour from wastewater before it is discharge to the receiving waters has increased.

2.7.1.1 Sedimentation Methods

Sedimentation is the basic form of primary treatment used at most municipal and industrial wastewater treatment facilities (Cheremisinoff, 2002). Chemical flocculants, sedimentation basins, and clarifiers, are a number of process options available to enhance gravity settling of suspended particles (Gupta and Sushas, 2009).

2.7.1.2 Filtration Technology

Filtration technology is an integral component of drinking water and wastewater treatment applications which includes microfiltration, ultrafiltration, nanofiltration, and reverses osmosis. This technology has been used for colour removal (Cheremisinoff, 2002; Avlonitis et al., 2008). Among the treatment applications is microfiltration which is not often used for wastewater treatment since it has large pore size. Though ultrafiltration and nanofiltration techniques are effective for the removal of all classes of dyestuffs, dye molecules cause frequent clogging of the membrane pores making the separation systems of limited use for textile effluent treatment (Marmagne and Coste, 1996; Cheremisinoff, 2002). The main drawbacks for the ultrafiltration and nanofiltration are high working pressures, significant energy consumption, high cost of membrane and a relatively short membrane life which makes their use limited for treating dye wastewater. Reverse osmosis forces water, under pressure, through a membrane that is impermeable to most contaminants. The membrane is somehow better at rejecting salts than it is at rejecting non-ionized weak acids and bases and smaller organic molecules generally molecular weight below 200 mol^{-g}. Reverse osmosis (Marcucci et al., 2001; Al-Bastaki, 2004; Sostar-Turk et al., 2005) is an effective decolouring and desalting process against the most diverse range of dye wastes, and has been successfully employed for recycling. The water produced by reverse osmosis, is close to pure H_2O (Gupta and Sushas, 2009)

2.7.1.3 Biological Methods

Biological treatment is often the most economical alternatives when compared with other physical and chemical processes. Biodegradation methods such as fungal decolourization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents (Hasan, 2008). Treatment is required because many microorganisms such as bacteria, yeasts, alges and fungi are able to accumulate and degrade different pollutants (McMullan *et al*., 2001 and Fu and Viraraghavan, 2001). However, their application is often restricted because of technical constraint. According to Bhattacharyya and Sharma, (2003), biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Further, biological treatment is incapable of obtaining satisfactory colour elimination with current conventional biodegradation processes (Robinson *et al*., 2001). Moreover, although many organic

molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin (Ravi Kumar et al., 1998).

2.7.1.4 Chemical Methods

These chemical methods include coagulation or flocculation combined with precipitation-flocculation with Fe(II)/$Ca(OH)_2$, electroflotation, flotation and filtration, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes (Crini, 2006). These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem (Gupta and Sushas, 2009; Kace and Linford, 1975; Lee *et al*., 2006). There is also the possibility that a secondary pollution problem will arise because of excessive chemical use.

Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for the pollutant degradation (Gupta and Sushas, 2009). Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive(Robinsin, T. *et al*., 2001). The high electrical energy demand and the consumption of chemical reagents are common problems (Robinsin, T. *et al*., 2001).

2.7.1.5 Physical Methods

Different physical methods are also widely used, such as membrane – filtration processes and adsorption techniques. The major disadvantages of the membrane processes is that they a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability (Hasan, 2008).

In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent. This process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application (Hasan, 2008).

2.8 Adsorption

2.8.1 What is Adsorption?

Adsorption is a well known equilibrium separation process used to remove colours, odour, organic, metals and inorganic pollutants from the industrial wastewater (Wang, *et al*., 2003; Rafatullah, *et al*., 2010). However, Derbyshine *et al*. (2001); Jain *et al*. (2003), Ho and McKay, (2003) reported that adsorption is more economical compared to most other processes. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants (Rafatullah, *et al*., 2010). Decolourisation is a result of two mechanisms: adsorption and ion exchange (Slokar and Le Marechal, 1998), and is influenced by many physio-chemical factors, such as, dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time (Kumar et al., 1998). Adsorption also does not result in the formation of harmful substance.

2.8.2 Factors that affect adsorption

The most important factors affecting adsorption are:

- *Surface area of adsorbent*. Larger sizes imply a greater adsorption capacity.

- *Particle size of adsorbent*. Smaller particle sizes reduce internal diffusional and mass transfer limitation to the penetration of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly full adsorption capability can be attained).

- *Contact time or residence time*. The longer the time, the more complete the adsorption will be, therefore larger equipment will be required.

- *Solubility of solute (adsorbate) in liquid (wastewater)*. Substances slightly soluble in water will be more easily removed from water (i.e., adsorbed) than substances with high solubility. Also, non-polar substances will be more easily removed than polar substances since the latter have a greater affinity for water.

- *Affinity of the solute for the adsorbent (carbon)*. The surface of activated carbon is only slightly polar. Hence non-polar substances will be more easily picked up by the

carbon than polar ones.

- *Number of carbon atoms*. For substances in the same homologous series a larger number of carbon atoms is generally associated with a lower polarity and hence a greater potential for being adsorbed (e.g., the degree of adsorption increases in the sequence).

- *Size of the molecule with respect to size of the pores*. Large molecules may be too large to enter small pores. This may reduce adsorption independently of other causes.

- *Degree of ionization of the adsorbate molecule*. More highly ionized molecules are adsorbed to a smaller degree than neutral molecules.

- The degree of ionization of a species is affected by the pH (e.g., a weak acid or a weak basis). This, in turn, affects adsorption.

2.8.3 Adsorbent for dye removal

Tables 2.3 and 2.4 below shows various adsorbents and their capacities used for the removal of Methyl violet and Methylene blue.

2.8.3.1 Commercial Adsorbents

2.8.3.1.1 Activated carbon

Activated carbon has been the most widely used and popular adsorbent in effluent treatment throughout the world (Bhatnagar and Sillanpää, 2010). Bhatnagar and Sillanpää (2010) reported that charcoal is the most commonly used precursor for activated carbon, has been recorgnized as the oldest adsorbent known in wastewater treatment. However, the authors further reported that activated carbon is produced by a process consisting of raw material dehydration and carbonization followed by activation. Activated carbon has a large surface area and a very porous structure. Activated carbon has been found to be a versatile adsorbent, which can remove diverse types of pollutants such as metals ions (Perez-Canadela *et al*., 1995; Gabaldon *et al*., 1996; Gabaldon, *et al*., 2000; Sanchez-Polo *et al*., 2002), dyes (Walker *et al.,* 1999; Pelekani, *et al.,* 2000; Al-Degs *et al.,* 2001; Pereira *et al*., 2003; Gomez *et al.,* 2007) detergents (Bele *et al .,* 1998; Maihas *et al.,* 2002).

2.8.3.1.2 Silica gel

Silica gels are classified into three types namely: regular, intermediate and low density gels. Bhatnagar and Sillanpää (2010), has reported that the regular density silica gel is prepared in an acid medium and shows high surface area approximately 750 $m^2 g^{-1}$. The authors reported that intermediate and low density silica gels have lower surface areas approximately 300–350 and 100–200 $m^2 g^{-1}$ respectively. The gel is considered a good adsorbent and is used in many industries (Ahmed and Ram, 1992; Backhaus *et. al.*, 2001). The modified forms of silica have also been widely explored for the removal of different pollutants (Moriguchi *et al*., 2005; Saad *et al.,* 2008; Wang *et al*., 2009).

2.8.3.1.3 Zeolite

Zeolites are aluminosilicates with Si/Al ratios between one and infinity (Bhatnagar and Sillanpää, 2010). The authors reported that there are 40 natural and over 100 synthetic zeolites which are also considered as selective adsorbents. Zeolite-based materials are extremely versatile and their main use include detergent manufacture, ion-exchange resins (i.e. water softeners), catalytic applications in the petroleum industry, separation process (i.e. molecular sieves) and as an adsorbent for water, carbon dioxide and hydrogen sulfide (Bhatnagar and Sillanpää, 2010). Recently, Wang and Peng,(2009) discussed the role of natural zeolites as effective adsorbents in water and wastewater treatment.

2.8.3.2 Low-cost alternative adsorbents

2.8.3.2.1 Agricultural waste as low-cost adsorbent

Agricultural materials particularly those containing cellulose shows potential sorption capacity for various pollutants (Bhatnagar and Sillanpää, 2010). The basic components of the agricultural waste materials include hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch, containing variety of functional groups. Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable nature and low cost are viable alternative for water and wastewater remediation. However, Ahmedna *et al*., (2000), reported that agricultural wastes are a rich source for activated carbon production due to its low ash content and reasonable hardness. Therefore, conversion of agricultural wastes into low-cost adsorbents is a promising alternative to solve environmental problems and also to reduce the preparation costs. In the last several decades, various agricultural wastes have been explored as low-cost adsorbent. Some of them include the shells and/or stones of fruits like nuts (Nguyen *et al*.,

1995; Ahmadpour *et al*., 1997; Toles *et al*., 1998), peanuts (Wafwoyo et al., 1998), olive wastes (Nyazi *et al*., 2005), almonds (Christopher and Wayne, 2002*), apricots* stones (Soleimani and Kaghazchi, 2008) and cherries (Lessier *et al*., 1994) and wastes resulting from the production of cereals such as rice (Khalil, 1996), maize (Elizalde-Gonzalez *et al*., 2008) and corn (Tsai *et al*., 2001) as well as sugar cane bagasse (Girgis *et al*., 1994) and coir pith (Namasivayam and Sangeetha, 2006). These agricultural waste materials have been used in their natural form or after some physical or chemical modification.

2.8.3.2.2 Industrial by-products

Widespread industrial activities generate huge amount of solid waste materials as by-products. Some of these materials are being put to use while others find no proper utilization and are dumped elsewhere. Industrial waste materials are available almost free of cost and causes major disposal problem. If solid wastes could be used as low-cost adsorbents, it will provide a two-fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly the low-cost adsorbent if developed can reduce the pollution of wastewaters at a reasonable cost. In view of the low cost of such adsorbents, it would not be necessary to regenerate the spent materials (Bhatnagar and Sillanpää, 2010).

Because of their low cost and local availability, industrial solid wastes such as metal hydroxide sludge, fly ash and red mud are classified as low cost materials and can be used as adsorbents for dye removal (Namasivayam and Sumithra, 2005).

Table 2.3 Sorption capacities for the removal of Methyl violet by various adsorbents

Material	**Methyl violet Adsorption Capacity ($mg.g^{-1}$)**	**Reference**
Cellulose-based wastes	11.50	Annadurai, *et al*., 2002
Bagasse fly ash	26.25	Mall, *et al*., 2006
Crosslinked amphoteric starch	333.33	Xua, *et al*., 2006
Sepiolite	2.60	Ozdemir **,** *et al*., 2006
Sepiolite	2.33	Dogan, *et al*., 2007
Mansonia Sawdust	16.11	Ofomaja, 2008

Table 2.4 Sorption capacities for the removal of Methylene blue by various adsorbents

Material	**Methylene blue Adsorption Capacity ($mg.g^{-1}$)**	**Reference**
Cereal chaff	20.3	Han, *et al*., 2006
Rice husk	40.60	Vadivelan and Vasanth Kumar, 2005
Raw beech sawdust	9.78	Batzias and Sidiras, 2004
Raw *P. oceanica* fibres	5.56	Ncibi, *et al*., 2007
Palm Kernel fibre	223.43	Ofomaja, 2007
Mansonia Sawdust	28.89	Ofomaja, 2008

2.9 What is biosorption?

Biosorption is the passive uptake of pollutants from aqueous solutions by the use of biological materials. Biosorption is one of the popular and attractive separation process used for the removal of colour from aqueous wastewater (Akar *et al*., 2009). The term "biosorption" is also used to indicate a number of metabolism-independent processes (physical and chemical adsorption, electrostatic interaction, ion exchange, complexation, chelation, and microprecipitation) taking place essentially in the cell wall (Aksu, 2005). However, Vijiayaraghavan and Yun,(2008), reported that one of the problem with biosorption is the separation of biosorbent and the treated effluent after batch or counter current contacting, because most biosorbents are in the form of dispersed microorganisms, which are small particle size, low density, poor mechanical strength and little rigidity. The process is simple in operation and very similar to conventional adsorption or ion-exchange, except that sorbent of biological origin is employed. The process depends on environmental factors including type of biomass, solution pH and the type of pollutant (Akar *et al.*, 2009; Colak *et al.*, 2009).

2.9.1 Biosorption Mechanism

The biosorption process involves a solid phase (biological material; sorbent or biosorbent) and a liquid phase (liquid water; solvent) containing different species to be sorbed (sorbate; metal ions or dyes). The sorbate is attracted to the sorbent and removed from water by

different mechanism due to the high affinity of the sorbent for the sorbate. This process continues until equilibrium is reached between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and the liquid phases. Biosorption of dyes occurs mainly through interactions such as complexation, adsorption by physical forces, precipitation, entrapment in inner spaces, ion-exchange due to a surface ionization, and hydrogen bonds (Sud *et al*., 2008).

2.9.2 Advantages and limitation of biosorption

The advantages of biosorption over conventional treatment methods includes high selectivity and efficiency, low cost, good removal performance, minimization of chemical and biological sludge, possibility of metal recovery and regeneration of biosorbent. The limitations of biosorption include first of all a shorter life time of biosorbent when compared with conventional sorbents (Gadd, 2009).

2.9.3 Factors that affect biosorption

The major factors that affect biosorption properties are (i) pH, (ii) temperature, (iii) initial concentration of dyes, (iv) biomass concentration in solution.

2.9.3.1 Effect of pH on dye biosorption

The effect of pH on biosorption of cationic dyes is similar as inorganic cations, since the mechanism is similar organic cations are also bound to negatively charged functional groups exposed by cellular surfaces (Chojnacka, 2010). The solution pH is the most important parameter in biosorption process since it affects the biosorption capacity, the colour of the dye solution and the solubility of some dyes. The pH determines protonation or deprotonation of dyes binding sites and thus influences the availability of the site to the sorbate. By lowering pH it is also possible to release dyes from the binding site. This property is used for the recovery of dye cations and regeneration of the biosorbent.

Various researchers have investigated the effect of pH on colour removal. For example, Mittal and Gupta (1996) studied the effect of pH on the biosorption of three cationic dyes, Orlamar Red BG, Orlamar Blue G and Orlamar Red GTL by dead fungus of *F*. carnea and their results showed that colour removal decreased with decreasing pH due to repulsive forces between coloured dye cations in solution and biosorbent surface charged positively at pH values lower than 3.0.

Aksu and Tezer (2000) also examined the effect of initial pH on fungal (dried R. arrhizus) binding of reactive dye Remazol Black B and they found maximum uptake at pH 2.0. They explained that the higher uptakes at lower pH value was due to electrostatic attractions between negatively charged dye anions and positively charged cell surface.

2.9.3.2 Effect of temperature on dye biosorption

Different dye industrial wastewaters are discharged at relatively high temperatures (50 – 60 °C), so temperature is an important design parameter affecting the biosorption capacity in the real application of biosorption by biomass (Fu and Viraraghavan, 2001). Gallagher *et al.*, (1997) reported that biosorption of Reactive Brilliant Red by R. oryzae was a physical adsorption due to increase of biosorption capacity with decreasing temperature.

Aksu and Tezer, (2000) also reported the effect of temperature on the biosorption of Remazol Black B reactive dye by R. arrhizus and their results indicated that optimum adsorption temperature was 35°C and adsorption decreased with further increasing temperature due to the decreased surface activity. Aksu *et al.*, (1992) reported on the adsorption of copper (II) by C. *vulgaris* and *Zramigera* that temperature does not influence the biosorption process with the temperature range 20-30°C.

2.9.3.3 Effect of initial dye concentration on dye biosorption

The concentration of the dye also affects the efficiency of colour removal. Initial dye concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. Hence, a higher initial concentration of dye may enhance the adsorption process (Aksu, 2005).

Recently, Chu and Chen, (2001) reported the effect of dye concentration on adsorption of Basic Yellow 24 using dried activated sludge biomass. Uptake of the dye increased from 18 to 90 mg g^{-1} with increasing dye concentration from 50 to 300 mgL^{-1}. O'Mahony *et al.*, (2002) reported that the uptake of Reactive Red, Rective Blue 19 and Reactive Orange 16 dyes by oven-dried *R. arrhizus* increased with increasing dye concentration.

2.9.3.4 Effect of biomass concentration on dye biosorption

Biological materials applied as adsorbents, also known as biosorbent, contain special surface properties which enable them to absorb different kinds of pollutants from solutions. Both

living and dead biomass can be used to remove pollutants from industrial wastewater. The use of dead biomass for water treatment is advantageous because (i) they do not require a constant supply of nutrients hence a decrease in the level of chemical oxygen demand and biological oxygen demand, (ii) it is not affected by toxic wastes and (iii) can be regenerated and reused for many cycles. The mechanism of pollutants binding by inactive biomass may depend on the chemical nature of pollutant (species, size, ionic charge), type of biomass, its preparation and its specific surface properties and environmental conditions (pH, temperature, ionic strength, existence of competing organic or inorganic ligands in solution) (Aksu, Z. 2005). The economy of environmental remediation dictates that the biomass must come from nature or even has to be a waste material. (Vieira and Volesky, 2000). Bacterial, fungal, plant or animal origin, as biosorbent, are selective and renewable sorbents.

The concentration of biomass in solution influences the specific uptake of dyes. An increase in biomass results in the increase in dye uptake or dye removal efficiency. This is due to the increase in binding sites as the biomass species surface area increases. A decrease in biomass results in the decrease in dye uptake. This is due to the decrease in binding sites as the biomass species surface area is decreased.

2.10 Types of biosorbent

Recent investigation has shown that the use of algae, fungi, and bacteria as biosobents are eco-friendly, low-cost and effective (Das, *et al*., 2008).

2.10.1 Algae as biosorbent

Algal biomass is emerging as an attractive, economical and effective biosorbent because of its advantages. Algae are autotropic and produces large biomass due to their low requirement of nutrients unlike other biomass, such as bacteria and fungi. The binding of metals ions on the surface of the algae depends on conditions like ionic charge of metal ion, chemical composition of metal ion solution and algal species (Freire-nordi *et.al.,* 2005; Gupta *et. al.,* 2001; Sheng *et. al.,* 2004).

2.10.2 Fungi as biosorbent

Fungi as biosorbent are efficient and economical for the removal of pollutants from aqueous solution. It has an advantage of high percentage of cell wall material which shows excellent metal binding properties (Horikoshi *et.al.,* 1981). Large quality of fungal- biomass is available from antibiotic – and food- industries.

2.10.3 Bacteria as biosorbent

Bacteria are one of the microorganism group most widely studied for the ability to treat dye wastewater (Gupta and Suhas., 2009). Bacteria, present in wastewater, secrets enzymes that breaks down organic compound. According to Beveridge, (1989) bacteria make excellent biosorbents because of their high surface-to-volume ratios and a high content of potentially active chemosorption sites such as on teichoic acid in their cell walls.

2.10.4 Pine Cone as a biosorbent

Pine cone as a biosorbent is widely studied for its ability to treat industrial wastewater. Recent investigations have shown that pine cone possess impressive biosorption capacities for the biosorption of heavy metal ions and dye (Özer and Turabik, 2009). According to Ofomaja and Naidoo, (2011) one major advantage for the use of pine cone powder as biosorbent is the large removed of dyes and metal ions from aqueous solution at a shorter contact period.

2.10.4.1. Advantages of pine cone as a biosorbent

The advantages of pine cone as a biosorbent includes: (i) natural availability, (ii) cheap and cost effective, (iii) removes pollutants at low concentration, and (iv) is modified easily.

2.10.4.2 Limitation of pine cone as a biosorbent

Pine cone applied as a biosorbent has certain limitations since it contains lignin, resin acid and coloured plant pigments. It has low binding capabilities, low filtration properties and the leaching of coloured plant pigments into treated water. These limitations can be overcome by biosorbent modification. Biosorbent modification is a process of chemically or physically manipulating the surface properties of pine cone materials such as type and amount of functional groups, surface area and porosity by extraction of plant chemical components so as to improve its adsorptive ability. The cellulose material present in pine cone is responsible for dye removal from wastewater (Wojnárovits *et al,* 2010). Some of the types of biosorbent modifications of pine cone powder includes: (i) acid washing (HCl and H_2SO_4 solutions) , (ii) base washing (NaOH and KOH solutions), (iii) Fenton's reagent (Fe^{2+} and H_2O_2), (iv) thermochemical reactions with polycarboxylic acids, (v) Inorganic acid oxidation and (vi) grafting of functional monomers onto adsorbents surface.

2.10.4.3 Fenton Reagent Theory

Fenton's reagent modification also known as Fenton's oxidation involves the addition of hydrogen peroxide to a solution containing organic substrate in presence of ferrous salts, generating species that are strongly oxidative ($^{\cdot}OH$ radicals) with respect to organic compounds. The $HO^{\bullet}$ radical is traditionally regarded as the key oxidizing species in the Fenton processes. The main kinetic step for $HO^{\cdot}$ production and hydro peroxide in the process is:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + HO^{\cdot} \quad (2.1.1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+} \quad (2.1.2)$$

$$HO^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad (2.1.3)$$

In the above reactions, iron goes between Fe^{2+} and Fe^{3+}, and plays the role of catalyst. Hydroxyl radicals ($HO^{\cdot}$) can oxidize organics (RH) by abstraction of protons producing organic radicals (R•), which are highly reactive and can be further oxidized (Walling and Kato, 1971; Venkatadri and Peters 1993; Lin and Lo 1997).

$$RH + HO^{\cdot} \rightarrow H_2O + R^{\cdot} \quad (2.1.4)$$

Argun et al. (2008) showed that the change in oxidation/reduction potential (ORP) of the solution during Fenton's oxidation using different H_2O_2/Fe^{2+} ratios can be used in monitoring the progress of the oxidation process. The authors were able to determine the optimum H_2O_2/Fe^{2+} ratio using this method.

Walling (1975) simplified the overall Fenton chemistry (Eq. (2.1.1)) by accounting for the dissociation water as

$$2Fe^{2+} + H_2O_2 + 2H^{+} \rightarrow 2Fe^{3+} + 2H_2O \quad (2.1.5)$$

This equation suggests that the presence of H^{+} is required in the decomposition of H_2O_2, indicating the need for an acid environment to produce the maximum amount of hydroxyl radicals. The Eq. (4.1.5) indicates that the process is pH sensitive. The pH value affects the activity of both the oxidant and the substrate, the speciation of iron, and hydrogen peroxide decomposition (Zhang et al., 2005). Therefore, change in solution pH during the Fenton's oxidation process may also be applied to monitor the progress of the oxidation.

2.10.4.4 Grafting as a method used for biosorbent modification

Grafting or graft copolymerization is the modification process whereby a polymer containing a known functional group is added onto the surface of the biosorbent particles to increase its binding capacity. The product of grafting has the advantage of removing colour present in wastewater since (i) new functional groups are introduced onto the biosorbent (Wojnárovits *et al*, 2010) and (ii) forms stronger bonds between modified agent and the biosorbent. During chemical grafting, the polymers are covalently bonded (modified) onto the polymer chain (biosorbent particles) as follows:

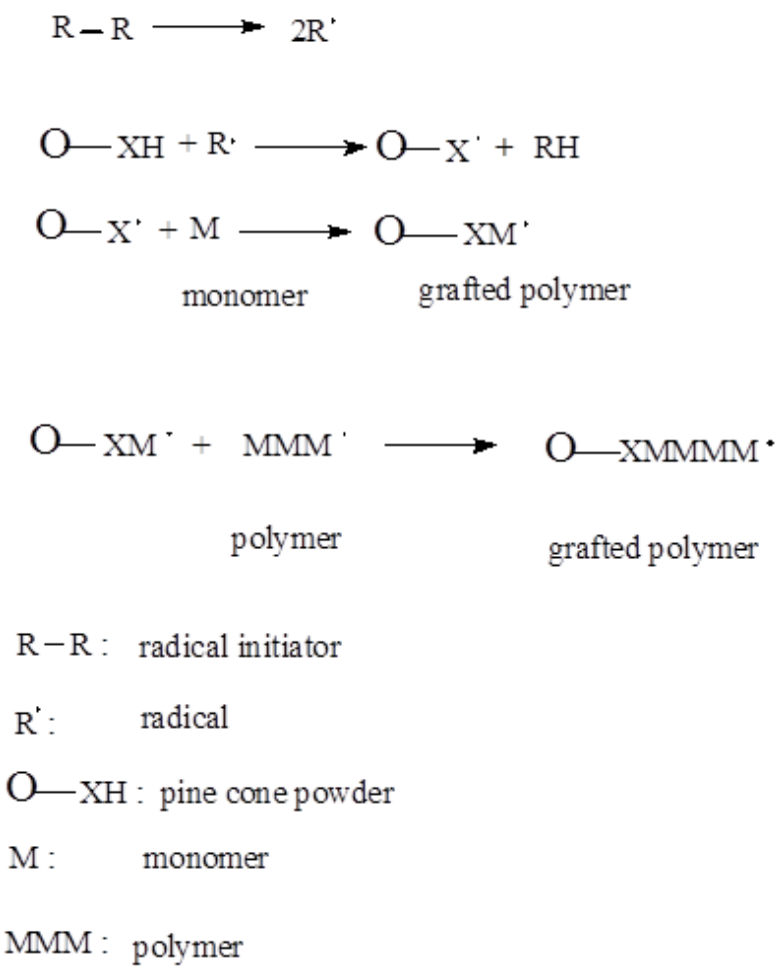

Fig 2.1: Schematic representation of chemical grafting.

Monomers are grafted onto the base material surface with the purpose of adding new functional groups. For example when acrylic acid or methacrylic acid is used, COOH and COO^- functional groups are grafted on the biosorbent. These carboxylic groups have two lone pairs of electrons on the oxygen atoms. The two carbonyl groups are required to form a

chelate with a divalent metal, e.g. with Cu(II) and Pb(II) (O'Connell et al., 2008). Using acrylamide or methacrylamide NH_2 functional groups are grafted on the biosorbent. The amino groups have a lone pair of electrons on the nitrogen atom and may form a covalent bond with the metal e.g.Hg(II) (Biçak *et al*.,1999).

Literature survey shows that grafting with a mixture of two monomers have been performed e.g. grafting of binary mixtures of methyl methacrylate and some vinyl monomers onto mulberry silk fibre (Banyal *et al*., 2011) and grafting of Acrylamide (AAm) and acrylic acid (AAc) onto cellulose-based hydrogels for water technologies (Ghanshyam *et al.*,2003).

2.10.4.5 Techniques of grafting

Chemical, radiation, photochemical and plasma-induced grafting are some of the techniques that are used to graft different monomer onto polymeric backbones. In each technique, numerous parameters are variable such as method of initiation, type and concentration of monomer, cellulose source, grafting time, temperature, presence of cross-linking agents, etc. The properties of the grafted co-polymer depend on the monomer used for grafting, the grafting level, the length and distribution of the grafted chains (Wang and Xu, 2006). Intensive research work is done in order to optimize the variable parameters of the investigated polymerization processes. The optimized values are dependent on the source of cellulose, on the chemicals and on the grafting technique.

2.10.4.5.1 Grafting initiated by chemical means

Grafting initiated by chemical means can take place by free radical and ionic polymerization. In chemical grafting process the role of the initiator is very important as it determines the path of the grafting process. Potassium permanganate, ceric ammonium nitrate, iron (II)-hydrogen peroxide redox systems (Fenton reaction), peroxides, hydroperoxides, diazo compounds, and potassium persulfate (Shibi and Anirudhan, 2006; Liu and Sun, 2008; O'Connell et al., 2008) are examples of initiators that can be used. In free radical polymerization, free radicals are produced from the initiators and transferred to the substrate to react with monomer to form the graft co-polymers. In ionic polymerization often a Lewis base liquid is the reactant, e.g. alkyl aluminium (R_3Al), or BF_3 (Bhattacharya and Misra, 2004; Glaied et *al*., 2009).

2.10.4.5.2 Grafting initiated by radiation technique

In the radiation technique, the medium is important than the presence of an initiator e.g. if irradiation is carried out in air, peroxides may be formed on the polymer. The lifetime of the free radical depends upon the nature of the backbone polymer. Chemical grafting can occur viz pre-irradiation, mutual irradiation technique and peroxidation.

2.10.4.5.3 Photochemical grafting

In this process grafting is initiated when a macromolecule containing a chromophore absorbs light and gets dissociate into reactive free-radicals. If the absorption of light does not lead to the formation of free-radical sites through bond rupture, this process can be promoted by the addition of photosensitizers, e.g. benzoin ethyl ether, dyes, such as Soduim-2,7 anthraquinone sulphonate or acrylated azo dye, aromatic ketones (such as benzophenone, xanthone) or metal ions UO_2^{2+}. Chemical grafting using photochemical technique can be achieved in two ways: with or without a sensitizer (Peng *et al*., 2001; Bellobono *et al*., 1981., Kubota *et al*., 2001). The mechanism without sensitizer involves the generation of free radicals on the backbone, which react with the monomer free radical to form the grafted co-polymer. On the other hand, in the mechanism 'with sensitizer', the sensitizer forms free radicals, which can undergo diffusion so that they abstract hydrogen atoms from the base polymer, producing the radical sites required for grafting.

2.10.4.5.4 Plasma radiation induced grafting

In this method the plasma, which contains electrons is used to initiate grafting. The electron induced is excitated, ionizated and dissociated. Thus, the accelerated electrons from the plasma have sufficient energy to induce cleavage of the chemical bonds in the polymeric structure, to form macromolecule radicals, which subsequently initiate graft co-polymerization (Bhattacharya and Misra, 2004).

2.11 Cationic dyes of interest

In this research, methylene blue and methyl violet are the two cationic dyes that will be targeted for analysis due to their widespread use in textile industry and high stability in water (Özer and Turabik, 2009). Dyes have been shown to have harmful effects on living organisms on short periods of exposure (Ofomaja, 2008). Methylene blue has a chemical formula, ($C_{16}H_{18}N_3$ SCI) and is a heterocyclic aromatic compound. This means Methylene blue is an organic compound that has one or more of the carbon atoms in the backbone of the molecule

being replaced with an atom other than carbon. These heteroatom includes nitrogen, oxygen and sulphur. Methylene blue at room temperature appears as a solid, odourless, dark green powder that turns blue when dissolved in water. It is most commonly used for dyeing cotton. Ingestion of methylene blue through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea, and gastritis. Once inhaled it can give rise to short periods of rapid difficult breathing. Accidental large dose creates abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful urination, and methemoglobinemia (Ofomaja, 2008).

Methyl violet also known as Triphenylmethane has a chemical formula, $(C_6H_5)_3CH$. It structure has three aromatic rings attached to a central carbon atom. The colour of the dye can be altered depending on the amount of attached methyl groups. Due to the presence of extended conjugated double bonds the electron pairs can be delocalized enough to cause light absorption. Methyl violets are mixtures of tetramethyl, pentamethyl and hexamethyl pararosanilins and are referred to as Methyl violet 10B (Mittal, *et. al.,* 2008). Methyl violet is used to dye cotton, silk, paper, bamboo, weed, straw and leather. This dye also finds application in other areas such as in biomedical fields where it is the active ingredient in Gram's biological stain for bacteria classification and in the laboratory as a pH indicator to test pH ranges from 0 to 1.6. (Lillie, *et al.,1977*). The authors reported that at low pH, Methyl Violet becomes yellow in colour and becomes bluish violet at an alkaline end. Long-term exposure of methyl violet may cause damage to the mucous membranes and gastrointestinal tract (Ghosh, and Bhattacharyya, 2002). When decomposed, this dye can release toxic substances such as CO, CO_2, NO, etc. Methyl violet can cause irritation to the respiratory and gastrointestine systems when it is inhaled, whilst direct contact can cause pain and congestion for animals (Li, *et. al.*, 2010).

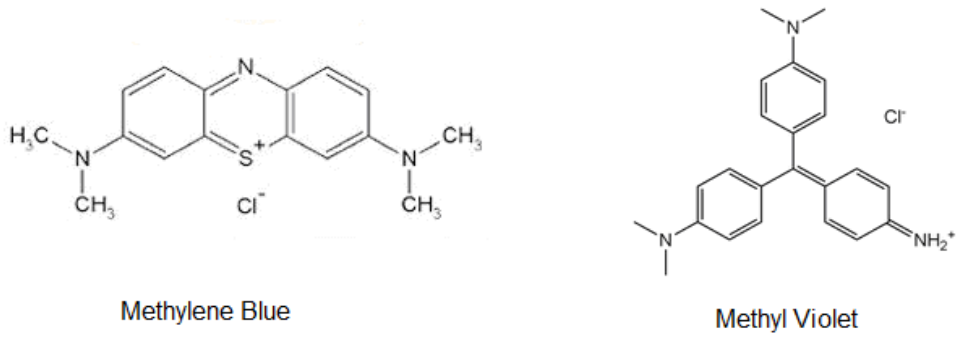

Fig.2.2 Structures of the cationic dyes.

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CHAPTER THREE

EXPERIEMENTAL PROCEDURE

3.1 INTRODUCTION

This chapter describes the models and techniques used to interpret results, experimental procedures used for sample collection and preparation, the optimisation processes in the grafting of pine cone powder and competitive removal of the two cationic dyes by the raw and grafted pine cone powder. It is therefore, divided into three sections; the first section involves collection and preparation. Sample preparation was necessary to remove organic compounds present in the pine cone powder which leaches into the treated water. The second section includes grafting procedure and parameters. The grafting process involves the optimization of the initiator concentration, to determine the grafting efficiency by monitoring total monomer conversion, the percentage grafting, and the rate of homopolymer formation and to determine the effect of grafting on the surface charge of pine cone powder. The third section involves the application of the raw and the grafted pine cone powder for the dye removal from aqueous water using single and binary component systems. Derivative spectrophotometry was applied to resolve the problems of overlapping spectra in the binary-component system. The kinetics and thermodynamics of dye biosorption in single and binary component system was determined.

3.2 MODELS AND TECHNIQUES

These are the different kinetic models used:

3.2.1 Adsorption diffusion models

3.2.2 Adsorption reaction models

3.2.2.1 Pseudo-first order equation

In (1898), Lagergren presented a first-order equation to describe the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal, which is believed to be the earliest model pertaining to the adsorption rate based on the adsorption capacity (Ho, Y.S, 2004). It can be presented as follows:

$$\int \frac{dx}{dt} = k \int (X - x) \qquad (3.2.0)$$

X and x (mg g^{-1}) are the adsorption capacities at equilibrium and at time t, respectively. k (min^{-1}) is the rate constant of pseudo-first order adsorption. Equation (3.2.0) can be integrated with boundary conditions t = 0 to t = t and x = 0 to X = x:

$$\ln(\frac{X}{X-x}) = kt \qquad (3.2.1)$$

and

$$x = X(1-e^{-kt}) \qquad (3.2.2)$$

Equation (3.2.2) may be rearranged to the linear form:

$$\log(X-x) = \log X - \frac{kt}{2.303} \qquad (3.2.3)$$

The most popular form used is:

$$\log(q_e - q_t) = \log(q_e) - \frac{kt}{2.303} \qquad (3.2.4)$$

q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium and at time t respectively.

k (min^{-1}) is the rate constant of pseudo-first order adsorption.

The equation applicable to experimental results generally differs from a true first order equation in two ways (Aharoni and Sparks, 1991).

(i) The parameter $k_1(q_e - q_t)$ does not represent the number of available sites.

(i) The parameter $\log(q_e)$ is an adjustable parameter and often it is found not equal to the intercept of a plot of $\log(q_e - q_t)$ against t, whereas in a true first order $\log(q_e)$ should be equal to the intercept of a plot of $\log(q_e - q_t)$ against t.

Several authors have used pseudo-first order kinetic models to analyse data from the adsorption of pollutants from wastewater onto biological materials. Ofomaja, 2007 has successfully used the pseudo-first-order equation in determining the sorption of methylene blue uptake on to palm kernel fibre.

3.2.2.2 Pseudo –second-order equation

In 1995, Ho was the first to describe a kinetic process of the adsorption of divalent metal ions onto peat (Ho and McKay, 1998), in which the chemical bonding among divalent metal ions and polar functional groups on peat. Peat contains groups such as aldehydes, ketones, acids, and phenolics which are responsible for the cation-exchange capacity of the peat. Therefore, the peat-metal reaction has been presented as shown in Eqs. (3.2.5) and (3.2.6), which can be dominant in the adsorption of Cu^{2+} ions onto peat (Coleman *et al.*, 1956):

$2P^- + Cu^+ \leftrightarrow CuP$, (3.2.5)

and

$2HP + Cu^+ \leftrightarrow CuP + 2H^+$, (3.2.6)

where P− and HP are active sites on the peat surface.

The assumption of the above two equation is that the adsorption may be second order and the rate limiting step may be chemical adsorption involving valent forces through sharing or the exchange of electrons between the peat and divalent metal ions. The rate of pseudo-second-order reaction may be dependent on the amount of solute adsorbed on the surface of peat and the amount adsorbed at equilibrium. The rate expression for the adsorption described is:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (3.2.7)$$

Separating the variables in Eq. (3.27) gives:

$$\frac{dq_t}{(q_e - q_t)^2} = kdt \,, \quad (3.2.8)$$

integrating this for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \,, \quad (3.2.9)$$

which is the integrated rate law for a pseudo-second order reaction.

Eq. (3.2.9) can be rearranged to obtain:

$$q_t = \frac{t}{\frac{1}{kq_e^2} + \frac{t}{q_e}} \,, \quad (3.2.10)$$

which has a linear form of

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \,. \quad (3.2.11)$$

h is defined to be the initial sorption rate (mg/g min) as q_t/t approach to 0.

$$h = kq_e^2 \,, \quad (3.2.12)$$

then Eqs. (3.2.10) and (3.2.11) become:

$$q_t = \frac{t}{\frac{1}{h} + \frac{t}{q_e}}, \qquad (3.2.13)$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t. \qquad (3.2.14)$$

By plotting t/q_t against t, the constants can be determined experimentally and should give a linear relationship with the slope of $1/ q_e$ and intercept of $1/ kq^2_e$. When the plot of the experiment forms a straight line, it is believed that biosorption follow the pseudo-second order mechanism. And when chemical adsorption is the rate controlling step, the pseudo-second-order model is more likely to predict the behavior over the entire concentration range of the adsorption process.

The predicted value was then calculated by rearranging the above equation to form:

$$q_t = \frac{q_e^2 k_2 t}{1} + q_e k_2 t \qquad (3.2.15)$$

Wu *et al.,* 2009 applied pseudo-second order on the adsorption of phenol,4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), and methylene blue (MB) from water onto activated carbons from firewood with potassium hydroxide (KOH) activation.

3.2.3 Adsorption isotherm used

3.2.3.1 Langmuir

In 1916, Irving Langmuir published an isotherm for gases adsorbed on solids, which retained his name. Langmuir adsorption isotherm is an empirical isotherm derived from a proposed kinetic mechanism. It is based on four hypotheses listed below:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
2. Adsorbed molecules do not interact.
3. All adsorption occurs through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

The Langmuir adsorption model assumes that maximum adsorption corresponds to a saturated monolayer of solutes on the adsorbent surface and is only valid for single-layer adsorption. According to the Langmuir model, there are a fixed number of sites available on the adsorbent surface, and all sites have the same adsorption energy. Furthermore, each molecule adsorbed is affixed to a specific site, and there is no transmigration of adsorbate in the plane of surface (Keinath, 1971; Weber, 1972). The Langmuir equation is used for homogeneous surfaces.

The rate of sorption to the surface should be proportional to a driving force times an area. The driving force is the concentration of the solution and the area is the amount of bare surface. If the fraction of covered surface is ϕ, the rate per unit of surface is:

$$r_a = k_a C(1-\phi) \qquad (3.3.1)$$

The desorption from the surface is proportional to the amounts of surface covered:

$$r_d = k_d \phi \qquad (3.3.2)$$

where k_a and k_d are the rate constants, r_a the sorption rate, r_d the desorption rate, C the concentration in the solution and ϕ the fraction of the surface covered.

The two rates are equal at equilibrium and we find that:

$$\phi = \frac{k_a C_e}{k_a + K_d C_e} \qquad (3.3.3)$$

and

$$k_a = \frac{k_a}{k_d} \qquad (3.3.4)$$

Since q_e is proportional to ϕ:

$$\phi = \frac{q_e}{q_m} \qquad (3.3.5)$$

The saturated monolayer sorption capacity, q_m, can be obtained. When ϕ approaches 1, then $q_e = q_m$.

The saturated monolayer isotherm can be represented as a linear form:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \qquad (3.3.6)$$

The above equation can be rearranged to the following form:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{C_e}{q_m} \qquad (3.3.7)$$

where C_e is the equilibrium concentration (mg dm^{-3}), q_e the amount of dye adsorbed (mg g^{-1}), q_m is q_e for a complete monolayer (mg g^{-1}), K_a the sorption equilibrium constant (mmol/dm^{-3}). A plot of C_e/q_e versus C_e should give a straight line of slope $1/q_m$ and an intercept of $1/K_a q_m$.

3.2.3.2 Freundlich isotherm

Freundlich adsorption isotherm is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. The surface coverage for each energy level can be represented by the Langmuir equation (Weber, 1972; Sheindorf et aI., 1981).

The Freundlich isotherm is

$$q_e = K_F C_e^{1/n} \qquad (3.3.8)$$

where K_F and $1/n$ are the Freundlich constants characteristics of the system, indicating the sorption capacity and sorption intensity, respectively. Equation (3.3.7) can be linearized in logarithmic form Eq. (3.3.8) and the Freundlich constants can be determined.

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (3.3.9)$$

3.2.3.3 BET Isotherm

The BET model was developed by Brunauer and coworkers in 1938 and assumes multilayer adsorption, and multiple, incomplete layers are possible. Both the Langmuir and the BET isotherm share the assumption that the adsorption system is homogeneous; therefore, there is uniform energy of adsorption on the surface. Furthermore, the Langmuir isotherm applies to each layer defined by the BET mode1. (Keinath, 1971; Weber, 1972). Secondly, the adsorption on surface is localized, that is an adsorbed atom or molecules are adsorbed at definite, localized sites. Thirdly each site can accommodate only one molecule or atom and lastly there is no interaction among adsorbed molecules.

From the above assumptions, the BET isotherm for adsorption from solution becomes (Brunauer *et al*., 1938):

$$q = \frac{K_B C_e q_m}{(C_s - C_e)\left[1 + \left(K_B - 1\left(\frac{C_e}{C_s}\right)\right)\right]} \quad (3.3.4)$$

Where C_e is the concentration of solute remaning in solution equilibrium (mg dm^{-3}), C_s the saturation concentration of solute (mg dm^{-3}), q the amount of solute adsorbed per unit weigh of adsorbent (mg g^{-1}), q_m the amount of solute adsorbed per unit weigh of adsorbent in forming a complete monolayer on the surface (mg g^{-1}) and K_B is the constant expressive of energy of interaction with the surface.

The equation can be written in the linearized form:

$$\frac{C_e}{(C_s - C_e)q} = \frac{1}{K_B q_m} + \left(\frac{K_B - 1}{K_B q_m}\right)\left(\frac{C_e}{C_s}\right) \quad (3.3.5)$$

A plot of $C_e/(C_s - C_e)q$ against (C_e/C_s) should give a striaght line and from the slope and intercept the values of K_B and q_m can be calculated.

3.3 ERROR METHODS

In this study both the linear coefficient of determination, r^2, and the non-linear Chi-square error analysis method was used to test the best fit of the isotherm model to the experimental data (Ofomaja *et al* 2010).

The coefficient of determination, r^2, is given by:

$$r^2 = \frac{\Sigma\left(q_m - \overline{q_t}\right)^2}{\Sigma\left(q_m - \overline{q_t}\right)^2 + \Sigma\left(q_m - q_t\right)^2} \quad (3.44)$$

where q_m is amount of metal ion on the surface of the pine cone powder at any time, t, (mg g^{-1}); q_t is the amount of metal ion on the surface of the sawdust at any time, t, (mg g^{-1}) obtained from experiment; and $\bar{q}_t$ is the average of qt, (mg g^{-1}).

The Chi-square test statistic is basically the sum of the squares of the difference between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models. The equivalent mathematical statement is:

$$\chi^2 = \Sigma\left(\frac{q_e - q_{e,m}}{q_{e,m}}\right) \quad (3.45)$$

$q_{e,m}$ equilibrium capacity obtained by calculating from model (mg g^{-1}). q_e experimental data of equilibrium capacity (mg g^{-1}) (Ofomaja *et al* 2010).

3.4 GRAFTING PARAMETERS

The following grafting parameters were determined for each grafted sample to determine the effectiveness on grafting:

The Percentage Grafting (PG) is the ratio of grafted polymer to original material

$$PG = \frac{(wt.\,of\,grafted\,material\,after\,extracting\,homopolymer - wt.\,of\,original\,material}{wt.\,of\,original\,material} \text{ x } 100$$

Homopolymer Converion (HC) is the monomer fraction that forms homopolymer

$$HC = \frac{wt.\,of\,homopolymer}{wt.\,of\,monomer} \text{ x } 100$$

Note: (i) wt. of homopolymer = wt. of crude product – wt of material after extraction of homoplymer.

(ii) wt. of monomer = wt of the volume of monomer measured.

Total Monomer Conversion (TMC) is the monomer fraction converted to polymer

$$TMC = \frac{(wt.\,of\,crude\,product - wt.\,of\,original\,material)}{wt.\,of\,monomer} \text{ x } 100$$

Grafting Efficiency (GF) is the fraction of the total synthetic polymer that is grafted onto the material.

$$GF = \frac{(wt.\,of\,grafted\,material\,after\,extracting\,homopolymer - wt.\,of\,original\,material)}{(wt.\,of\,grafted\,crude\,product - wt.\,of\,original\,material)} \text{ x } 100$$

Rate of polymerization (R_p) is the rate of total polymer formation (grafted product + homopolymer)

$$R_p = \frac{wt.\,of\,crude\,product}{(Molar\,mass\,of\,monomer\,x\,total\,reaction\,time\,x\,total\,volume\,of\,reaction\,mixture)} \text{ x } 100$$

Rate of graft polymerization (R_g) is the rate of monomer grafted onto the material

$$R_g = \frac{wt.\,of\,grafted\,material\,after\,extracting\,homopolymer}{(Molar\,mass\,of\,monomer\,x\,total\,reaction\,time\,x\,total\,volume\,of\,reaction\,mixture)} \text{ x } 100$$

3.5 COLLECTION AND PREPARATION

3.5.1 Sample Preparation

Pine cones was collected from a plantation in Sasolburg, Free State, South Africa and transported to the Vaal University of Technology chemistry laboratory. The pine cones were washed to remove impurities such as sand and leaves. The washed cones were dried at 90°C for 48hrs in the oven. The scales on the cones were removed and blended in a food processing blender. The pine cone powder was sieved and particles between 90 and 45µm collected and stored in a container.

3.5.2 Fenton's modification

Accurately weighed and oven dried (100 g) cone material was added into 500 cm^3conical flask containing 250 cm^3 of different ratios of Fenton's reagent solution (H_2O_2 fixed at 100,000 mg/dm^3 and Fe^{2+} varying from 50 to 5000 mg/dm^3). The mixtures were stirred at 200 rpm for all modification experiment at room temperature. The modified pine cone was separated from the solution by filtration, washed and dried at 90 ^{o}C. The optimum values for Fe^{2+} and H_2O_2 ratio were determined by monitoring the oxidation reduction potential (ORP), change in solution pH (Δ pH) before and after treatment and Acid number (AN). The ORP and pH of the solution was measured before and after the Fenton's reagent treatment using a pH meter Hanna HI2550 model pH meter.

3.5.3 Bulk Density

Bulk density determination was carried out in a density bottle of 25 cm^3. The raw and base treated pine cone powder were added to the density bottle with gentle tapping to ensure that the particles settle to the bottom and all air spaces are filled. The mass of the density bottle containing the pine cone powder was then determined. The mass of pine cone powder that occupied 25 cm^3 was then obtained from the mass of the bottle and pine cone powder minus the mass of empty bottle.

3.5.4 X-ray diffraction (XRD) analysis

The identification of chemical composition and crystallographic structure of modified pine cone powder was achieved by X-ray diffraction (XRD) analysis. XRD patterns were obtained with an X'Pert PRO X-ray diffractometer (PANalytical, PW3040/60 XRD; CuKα anode; λ = 0.154 nm). The samples were gently consolidated in an aluminium holder and scanned at 45 kV and 40 mA from 10° to 120° 2θ the exposure time for each sample was 20 minutes and

a step size of 0.02°. The diffraction patterns were analyzed using X'Pert High Score software (version 2.2.0) and plotted using OriginPro 7.0.

3.5.5 BET Surface Area

The Brunauer–Emmett–Teller (BET) surface area and pore size distribution were determined using computer-controlled nitrogen gas adsorption analyzer. Degassing was carried out for 1 hour at 90^o and increased to 120^o for 2 h. A mass of 0.2 g of pine cone was applied for analysis.

3.5.6 Fourier Transform Infra Red (FTIR) Analysis

A qualitative analysis of the main functional groups that were involved in metal uptake was determined with a FT-IR / FT-NIR Spectrometer Perkin Elmer Spectrum Model. A spectra of the monomer, pure and modified pine cone was measured within a range of 500–4000cm^{-1}. Approximately 5g of sample was used for characterization.

3.5.7 Acid Number

The acid number (AN) before and after the modification process will be determined using the method suggested by Matsuda (1987). Approximately 0.3 g of pine cone powder will be placed in a 200 cm^3 flat –bottom flask and 10 cm^3 of 0.1 mol/dm^3 aqueous solution of HCl and 100 cm^3 of distilled water will be added. The mixture will then be titrated using 0.1 mol/dm^3 aqueous solution of HCl and 100 cm^3 of distilled water will be added. The mixture will then be titrated using 0.1 mol/dm^3 aqueous solution of KOH in the presence of phenolphthalein as an indicator. The acid number will be determined from the following Eq.(1)

$$\text{AN} = \frac{(V-H).N.56.1}{m}[mgKOH/g] \qquad (1)$$

Where: V-volume of 0.1 mol/dm^3 KOH used for the titration of the solution [ml], H-volume of 0.1 M KOH used for the neutralization of 10 ml aqueous solution of 0.1 mol/dm^3 HCl [cm^3], N is the concentration of the KOH solution, m-sample weight (g).

3.6 GRAFTING PROCEDURE

3.6.1 Effect of initiator concentration on grafting procedure

Grafting was determined by mixing 20 g of the treated pine cone with 750 cm^3 of (0.0015, 0.0025, 0.005, 0.015, 0.020 mol/dm^3) at room temperature for 45 min. The pine cone powder

was filter and washed with distilled water and dried. 10 g (m_o) of pine cone powder was transferred into 500 cm^3 round bottom flask containing 10cm^3 acrylic acid in 125 cm^3 of hexane. Graft co-polymerization was carried out by mechanical stirring for 2 hr at 70 °C. The mixture was then filtered on a Buchner funnel, washed with 50 cm^3 acetone dried and weighed (m_1). To remove unreacted chemical and homopolymer, the resulting pine cone (m_1) was mixed with 250 cm^3 of hot water, stirred for 2 hr at room temperature. The washed solid was then stirred in 0.1 mol/dm Na_2CO_3 solution, filtered on a Buchner funnel and washed with 10 cm^3 acetone before drying to constant weight (m_2) at 70 °C. The solution pH and ORP were measured when pine cone powder was contacted with $KMnO_4$ solution and after stirring for 45 min using a pH meter Hanna HI2550 model pH meter.

3.6.2 Effect of plant material

Grafting was determined by mixing 20 g of the treated and untreated pine cone with 750 cm^3 of 0.020 mol/dm^3 $KMnO_4$ at room temperature for 45 min. The pine cone powder was filter and washed with distilled water and dried. 10 g (m_o) of pine cone powder was transferred into 500 cm^3 round bottom flask containing 10cm^3 acrylic acid in 125 cm^3 of hexane. Graft co-polymerization was carried out by mechanical stirring for 2 hr at 70 °C. The mixture was then filtered on a Buchner funnel, washed with 50 cm^3 acetone dried and weighed (m_1). To remove unreacted chemical and homopolymer, the resulting pine cone (m_1) was mixed with 250 cm^3 of hot water, stirred for 2 hr at room temperature. The washed solid was then stirred in 0.1 mol/dm^3 Na_2CO_3 solution, filtered on a Buchner funnel and washed with 10 cm^3 acetone before drying to constant weight (m_2) at 70 °C. The solution pH and ORP were measured when pine cone powder was contacted with $KMnO_4$ solution and after stirring for 45 min using a pH meter Hanna HI2550 model pH meter.

3.6.3 Effect of concentration at different temperature

Grafting was determined by mixing 20 g of the treated pine cone with 750 cm^3 of (0.0015, 0.0025, 0.005, 0.015, 0.020 mol/dm^3) $KMnO_4$ at room temperature for 45 min. The pine cone powder was filter and washed with distilled water and dried. 10 g (m_o) of pine cone powder was transferred into 500 cm^3 round bottom flask containing 10cm^3 acrylic acid in 125 cm^3 of hexane. Graft co-polymerization was carried out by mechanical stirring for 2 hr at 50, 70, 80, and 90 °C. The mixture was then filtered on a Buchner funnel, washed with 50 cm^3 acetone dried and weighed (m_1). To remove unreacted chemical and homopolymer, the resulting pine cone (m_1) was mixed with 250 cm^3 of hot water, stirred for 2 hr at room temperature. The

washed solid was then stirred in 0.1 mol/dm Na_2CO_3 solution, filtered on a Buchner funnel and washed with 10 cm^3 acetone before drying to constant weight (m_2) at 70 °C. The solution pH and ORP were measured when pine cone powder was contacted with $KMnO_4$ solution and after stirring for 45 min using a pH meter Hanna HI2550 model pH meter.

3.6.4 Determination of MnO_2 deposited

The amount of MnO_2 deposited onto pine cone powder was determined by adding 10 cm^3 of 0.2 mol/dm^3 oxalic acid and 10 cm^3 of 4 mol/dm^3 sulfuric acid to the pine cone powder treated with potassium permanganate in a conical flask. The mixture was gently heated to about 60 ºC and then titrated against a $KMnO_4$ solution of 0.05 mol/dm^3.

$$\text{The amount of } MnO_2 \text{ deposited} = \frac{Vx0.2.x100}{W} \text{ (meq/100g)} \qquad (2)$$

Where, V is the volume of $KMnO_4$ equivalent to the MnO_2 in the sample and W is the weight of the sample used.

3.6.5 Surface negative charge

One-half gram of pine cone powder, which had pH values < 3.0, was suspended in 25 cm^3 of 0.10 mol/dm^3 NaOH and stirred at 300 rpm for 16-20 hr in a glass stopped Erlenmeyer flasks. The flasks were kept stoppered during stirring to minimize the dissolution of carbon dioxide gas in the NaOH and the subsequent formation of Na_2CO_3. The flask contents were filtered by vacuum filtration through Whatman #4 filter paper and 10 cm^3 of the filtrate was added to 15.0 cm^3 of 0.10 mol/dm^3 HCl. The addition of excess HCl prevented any possible adsorption of carbon dioxide by the base and was particularly important if the solutions were required to stand for extended time periods before analysis. The solution was titrated with 0.10 mol/dm^3 NaOH until an end point. The results were expressed in mmoles H^+ neutralized OH^- per gram of pine cone powder.

3.6.6 TGA

An STA 6000 Instrument employed to measures the thermal analysis of pine cone powder. This instrument is capable of obtaining DSC and TGA measurements simultaneously. The raw and the treated pine cone powder were weighed into quartz crucibles. Thermal scans were performed from 30 to 700 °C at a heating rate of 10 ºC/min. An empty crucible was used as a reference. Thermal transitions were measured in terms of onset (T_o) and peak (T_m) gelatinization temperatures.

3.6.7 Ultraviolet Analysis

A Perkin-Elmer uv/vis spectrophotometer was used for scanning of the dyes to obtain the λ_{max} for each of the dyes. The methylene blue will be analyzed at wavelength 665 nm and the methyl violet will be analyzed at 520 nm. A 1cm reference cell and sample cell will be used for the analysis.

3.7 BATCH ADSORPTION KINETICS PROCEDURE

3.7.1 Optimization of methylene blue removal using raw, Fenton treated and acrylic acid grafted pine cone powder for single component.

3.7.1.1 Effect of solution pH

An accurately weighed amount (0.1 g) of pine cone was added to ten 250 cm^3 beakers containing 100 cm^3 of 500 mg/dm^3 of the dye solution adjusted to pH of 4, 6, 8, 10, 12 using either HCl or NaOH solutions. The solutions were stirred at 200 rpm at 298 K for 1 hr. The mixture was centrifuged and the clear supernatant was analyzed for the residual concentration of methylene blue (λmax = 664 nm at pH 12) left in aqueous solution spectrophotometerically.

3.7.1.2 Effect of biosorbent dose

The effect of sorbent dose on the equilibrium uptake of the dye was investigated with sorbent masses of 0.10, 0.50, 0.10, 0.20, and 0.30 g. The experiments were performed by adding the known weights of pine cone powder to five 250 cm^3 beakers containing 100 cm^3 of 900 mg/dm^3solution of Methylene blue at pH 12. The flasks were shaken at 200 rpm at 298 K for 1 hr. The mixture was centrifuged and the clear supernatant was analyzed for the equilibrium concentration of methylene blue (λmax= 664 nm) left in aqueous solution spectrophotometerically.

3.7.1.3 Kinetics studies

Kinetic experiments were carried out by agitating 100 ml of the methylene blue dye solution with 0.15 g of pine cone powder particle size ranging between 45–90 µm in a 250 ml beaker at 298 K at an optimum pH of 12, and at a constant agitation speed of 200 rpm. Samples (1 ml) were pipetted out at different time intervals, centrifuged and the concentration of methylene blue was analysed using UV spectrophotometer.

3.7.2 Optimization of methyl violet removal using raw, Fenton treated and acrylic acid grafted pine cone powder for single component.

3.7.2.1. Effect of solution pH

An accurately weighed amount (0.1 g) of pine cone was added to ten 250 cm^3 beakers containing 100 cm^3 of 500 mg/dm^3 of the dye solution adjusted to pH of 4, 6, 8, 10, and 12 using either HCl or NaOH solutions. The solutions were stirred at 200 rpm at 298 K for 1 hr. The mixture was centrifuged and the clear supernatant was analyzed for the residual concentration of methylene blue (λmax = 592.2 nm at pH 10) left in aqueous solution spectrophotometerically.

3.7.2.2. Effect of biosorbent dose

The effect of sorbent dose on the equilibrium uptake of the dye was investigated with sorbent masses of 0.10, 0.50, 0.10, 0.20, and 0.30 g. The experiments were performed by adding the known weights of pine cone powder to five 250 cm^3 beakers containing 100 cm^3 of 900 mg/dm^3solution of Methyl violet at pH 10. The flasks were shaken at 200 rpm at 298 K for 1 hr. The mixture was centrifuged and the clear supernatant was analyzed for the equilibrium concentration of methyl violer (λmax = 592.2 nm) left in aqueous solution using UV/VIS.

3.7.2.3 Kinetics studies

Kinetic experiments were carried out by agitating 100 cm^3 of the methyl violet dye solution with 0.15 g of pine cone powder particle size ranging between 45–90 µm in a 250 cm^3 beaker at 298 K at an optimum pH of 12, and at a constant agitation speed of 200 rpm. Samples (1 cm^3) were pipetted out at different time intervals, centrifuged and the concentration of methyl violet was analysed using UV spectrophotometer.

3.7.3 Optimization of a mixture of methylene blue and methyl violet removal using raw, Fenton treated and acrylic acid grafted pone cone powder for multi-component at different ratios.

3.7.3.1 Effect of biosorbent dose

The effect of sorbent dose on the equilibrium uptake of the dyes mixture was investigated with sorbent masses of 0.10, 0.50, 0.10, 0.20, and 0.30 g. The experiments were performed by adding the known weights of pine cone powder to five 250 cm^3 beakers containing 100 cm^3 dye mixture of 900 mg/dm^3solution of Methylene blue at pH 12 and 700 mg/dm^3 of Methyl violet at pH 10 separately. The flasks were shaken at 200 rpm at 298 K for 1 h. The

mixture was centrifuged and the clear supernatant was analyzed for the equilibrium concentration of methylene blue (λmax = 623.1 nm) and methyl violet (λmax = 561.8 nm) left in aqueous solution spectrophotometerically

3.7.3.3 Kinetics studies

Kinetic experiments were carried out by agitating 100 cm^3 of the dye mixture solution with 0.15 g of pine cone powder particle size ranging between 45–90 µm in a 250 cm^3 beaker at 298 K at an optimum pH of 12 for methylene blue and pH 10 for methyl violet, and at a constant agitation speed of 200 rpm. Samples (1 cm^3) were pipetted out at different time intervals, centrifuged and the concentration of methyl violet and methylene blue (λmax = 623.1 nm) and methyl violet (λmax = 561.8 nm) left in aqueous solution spectrophotometerically.

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CHAPTER FOUR

RESULTS AND DISCUSSION

4.1.1 INTRODUCTION

The results and discussion presented in this chapter is divided into four parts. The first part covers Fenton's reagent measurements.

The second part covers grafting measurements.

The third part covers the optimization process.

The fourth part covers the adsorption kinetics.

The fifth part covers the equilibrium adsorption studies which was performed on the pine/modified pine-methyl violet and pine-methylene blue systems. This enabled the examination of the relationship between the amount of methyl violet and methylene blue adsorbed on the adsorbent surface and that left in solution at given temperatures. From these studies the thermodynamic parameters such as entropy, enthalpy and free energy for each system were determined.

The sixth part covers the results and discussion of the simultaneous analysis of methyl violet and methylene blue dye components in multi-component solution. The analysis of multi-component adsorption system is a very complex problem due to overlapping absorption bands of dye components and spectral interferences. Second derivative spectroscopy was used to determine the wavelength maximum of each dye in a mixture of 1:1 ratio. Second derivative spectroscopy was employed since it provided better selectivity and resolved the overlapping spectra. The other problem in multi-component adsorption system is the simultaneous determination of each dye concentration remaining in solution.

4.1.2 RESULTS

4.1.2.1 Fenton Modification

Table 4.1.1 shows results obtained for the optimization process. When constant H_2O_2 concentration of 100,000 mg/dm^3 was applied and the initial concentrations Fe^{2+} varied from

50 to 5000 mg/dm^3 at a fixed initial solution pH, the final solution pH's were observed to increase slightly above the initial solution pH's. The changes in H^+ ions concentration (ΔH^+) were measured as follows:

$$\Delta[H^+] = \Delta[H^+_{Final}] - \Delta[H^+_{Initial}] \quad (4.1.6)$$

And $$pH = -\log [H^+] \quad (4.1.7)$$

The results showed the values of ΔH^+ increased from 1.714 to 1.776 mmol/dm^3 as Fe^{2+} reduced from 5000 to 1000 mg/dm^3 and as Fe^{2+} concentration decreased below 1000 mg/dm^3, the ΔH^+ of solution reduced to 0.880 mmol/dm^3 (Fe^{2+} = 50 mg/dm^3). The ratio of concentrations of H_2O_2 to Fe^{2+} was 100 at the highest values of ORP and change in solution pH. Argun et al.(2008) obtained a maximum ORP ratio for H_2O_2 to Fe^{2+} to be 100 using 10,000 mg/dm^3 of H_2O_2 to 100 mg/dm^3 Fe^{2+}. The authors found that this treatment ratio gave maximum activation of their biosorbent. The surface properties of the Fenton's treated sample were at optimum conditions were then compared with that of the raw pine.

4.1.2.2 Changes in properties of pine cone due to Fenton's reagent treatment

The results shown in Table 4.1.2 reveal that on treatment with Fenton's reagent, the bulk density of the pine cone was found to reduce by 50 %. This indicates that a sizable amount of substances have been extracted by Fenton's reagent treatment. The iodine capacity measurement was also carried out on pine cone before and after Fenton's reagent treatment. The results (displayed in Table 4.1.2) shows that the raw pine had an iodine capacity of 23.7 mg/g while after treatment, the iodine capacity increased to 33.6 mg/g. The iodine capacity gives an indication of the amount of macropore spaces in a powder material; therefore the increase in iodine capacity confirms the introduction or opening of void spaces due to Fenton's reagent treatment. Fenton's reagent, is an advance oxidative reagent, therefore it is likely to cause oxidation of the pine cone surface. A look at the results for surface negative charge in Table 4.1.2, reveals that the treated pine cone has a higher surface negative charge as compared to the untreated pine. Oxidation of pine cone surface will therefore introduce acidic functional groups of the pine surface which will contribute to the negative charges on the surface.

Changes in the structure of the pine cone were determined using X-ray diffraction analysis of the pine cone before and after Fenton's oxidation. The XRD spectra's for pine cone before

and after Fenton's reagent treatment are shown in Fig.4.1.1. The results in Fig.4.1.1 shows the XRD pattern of raw pine and Fenton's reagent treated pine cone. For the raw pine the characteristic main peaks of cellulose (I) at the 2θ of 15.3◦, 21.4◦, 27.5◦ and 34.0◦ can be observed. These peaks are indicative of highly organized crystalline cellulose (Zhu *et al*., 2008). Secondary peaks corresponding to cellulose (II) which are indicative of less organized and amorphous polysaccharide materials were also observed at the 2θ of 26.1◦, 32.2◦ and 44.1◦ on the XRD spectra. The spectra indicate that the pine cone is composed basically of crystalline cellulose. When pine cone was treated with Fenton's reagent, several changes where observed in the intensities of peaks.

All peaks associated with cellulose (I) at 2θ of 15.3◦, 21.4◦,27.5◦ and 34.0◦ were found to reduce in intensity. This result indicates that crystalline cellulose was affected by Fenton's reagent treatment. According to Zhang et al. (2007), hemicelluloses play bridging role between lignin and cellulose forming a rigid network. This rigid structure and particularly the crystalinity of cellulose (I) may cause resistance of penetration of modifying reagents into the plant structure. The XRD pattern of the Fenton's reagent treated sample therefore indicates that breakdown of lignin seal and disruption of crystalline cellulose had taking place. It will also be observed that the cellulose (II) peaks representing amorphous cellulose at 2θ of 26.1◦ and 44.1◦where enhanced.

4.1.2.3 Bulk density measurements

On treatment of pine cone powder with Fenton's reagent, oxidation and extraction of plant organic components occurs which was seem from the discoloration of the Fenton's reagent solution after treatment. The value for bulk density obtained for the raw pine cone material was 0.6457 g/cm^3. When treated with Fenton's reagent of increasing Fe^{2+} concentration at a fixed H_2O_2 concentration (100,000 mg/dm^3), the values of bulk density was observed to decrease sharply from its initial value in the raw sample down to 0.2480 g/cm^3 for Fe^{2+} concentration of 2000 mg/dm^3.When concentration of Fe^{2+} was further increased to 5000 g/cm^3 the value for bulk density

Table 4.1.1 Variation of Fe^{2+} concentration between 5,000 to 50 mg/dm^3 at fixed concentration of H_2O_2 of 100,000 mg/dm^3.

Fe^{2+} Conc. (mg/dm^3)	Initial pH	Final pH	ΔH^+ ion (mmol/dm^3)	ORP (mV)
5,000	2.38	2.61	1.714	251.9
2,000	2.42	2.72	1.896	253.5
1,000	2.53	2.93	1.776	239.6
833	2.63	3.20	1.713	231.1
500	2.55	2.92	1.616	218.5
400	2.81	4.31	0.150	168.7
100	3.00	4.89	0.987	108.3
83	3.01	4.84	0.963	108.4
50	3.05	4.94	0.880	103.4

Table 4.1.2: Some properties of raw and Fenton's reagent treated pine cone

Sample	Property
	Bulk Density (g/cm^3)
Raw	0.499
Fenton's reagent treated	0.248
	Iodine Number (mg I_2/g pine cone)
Raw	23.7 ± 0.09 mg/g
Fenton's reagent treated	33.6 ± 0.09 mg/g
	Surface Negative Charge (mol H^+/g pine cone)
Raw	0.00122
Fenton's reagent treated	0.00167

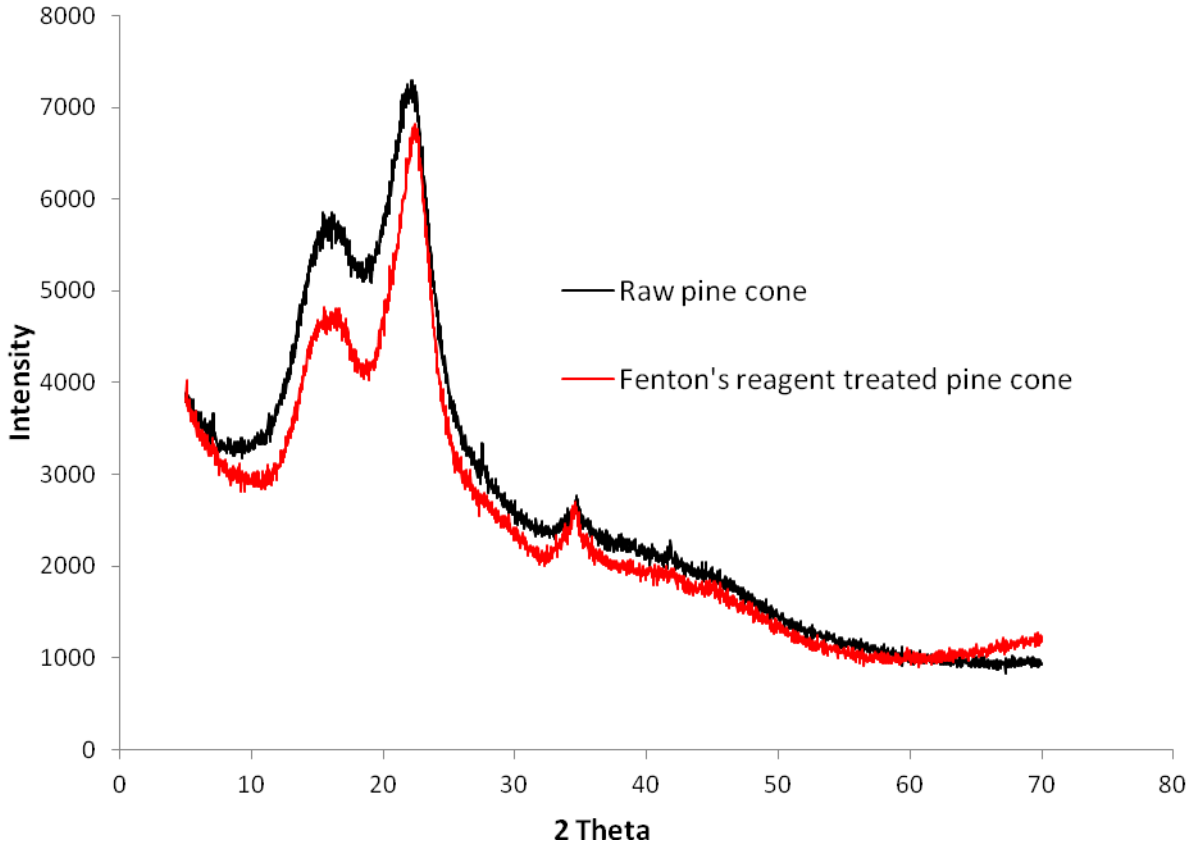

Fig. 4.1.1 X-ray diffraction patterns of raw pine cone and Fenton's reagent treated pine cone.

increased slightly rather than decreasing. The decreasing values of bulk density may therefore be explained by the oxidation and extraction of plant components for the pine cone matrix. This oxidation process increases extraction with increasing concentration of Fe^{2+} in the Fenton's reagent solution up to a concentration of 2000 mg/dm^3 Fe^{2+} which was observed to the optimum.

4.1.2 4 BET surface area determination

The BET surface area of the samples were also compared to confirm the fact that pores spaces were opened in the Fenton's reagent treated samples as compared with the raw samples. The value for BET surface area of the raw pine cone was found to be 4.39 m^2/g and the total pore volume and the micropore volumes were obtained to be 0.040 cm^3/g and 0.011 cm^3/g respectively. When Fenton's reagent treatment was applied to the pine cone sample and the concentration of Fe^{2+} increased the values for BET surface area, total pore volume and micropore volume increased. When 2000 mg/dm^3 of Fe^{2+} was applied the values of BET surface area, total pore and micropore volumes were as high as 27.45 m^2/g, 0.173 and 0.243 cm^3/g respectively. Further increase in Fe^{2+} concentration in the Fenton's reagent solution did not produce any increase in the surface area or pore volumes instead a slight decrease was observed. These results confirm the fact that oxidation and extraction of plant organic component occurred.

4.1.2.5 FTIR for Fenton modified pine cone

Since the pine cone surface consist of several functional groups, analysis of these groups before and after treatment was performed in other to determine the effect of Fenton's oxidation on the pine cone surface. Fig 4.1.2 shows the FTIR analysis of raw pine cone and Fenton modified pine cone using H_2O_2/Fe^{2+} = 100. Several peaks were observed from the spectra of the raw pine cone indicating that raw pine cone is composed of various functional groups. The broad intense spectra bands observed at 3342.65 cm^{-1} are indicative of unbounded–OH (Perez-Marıın et al., 2007) and the peak observed at 2927.95 cm^{-1} represents the aliphatic C–H group while the peak at

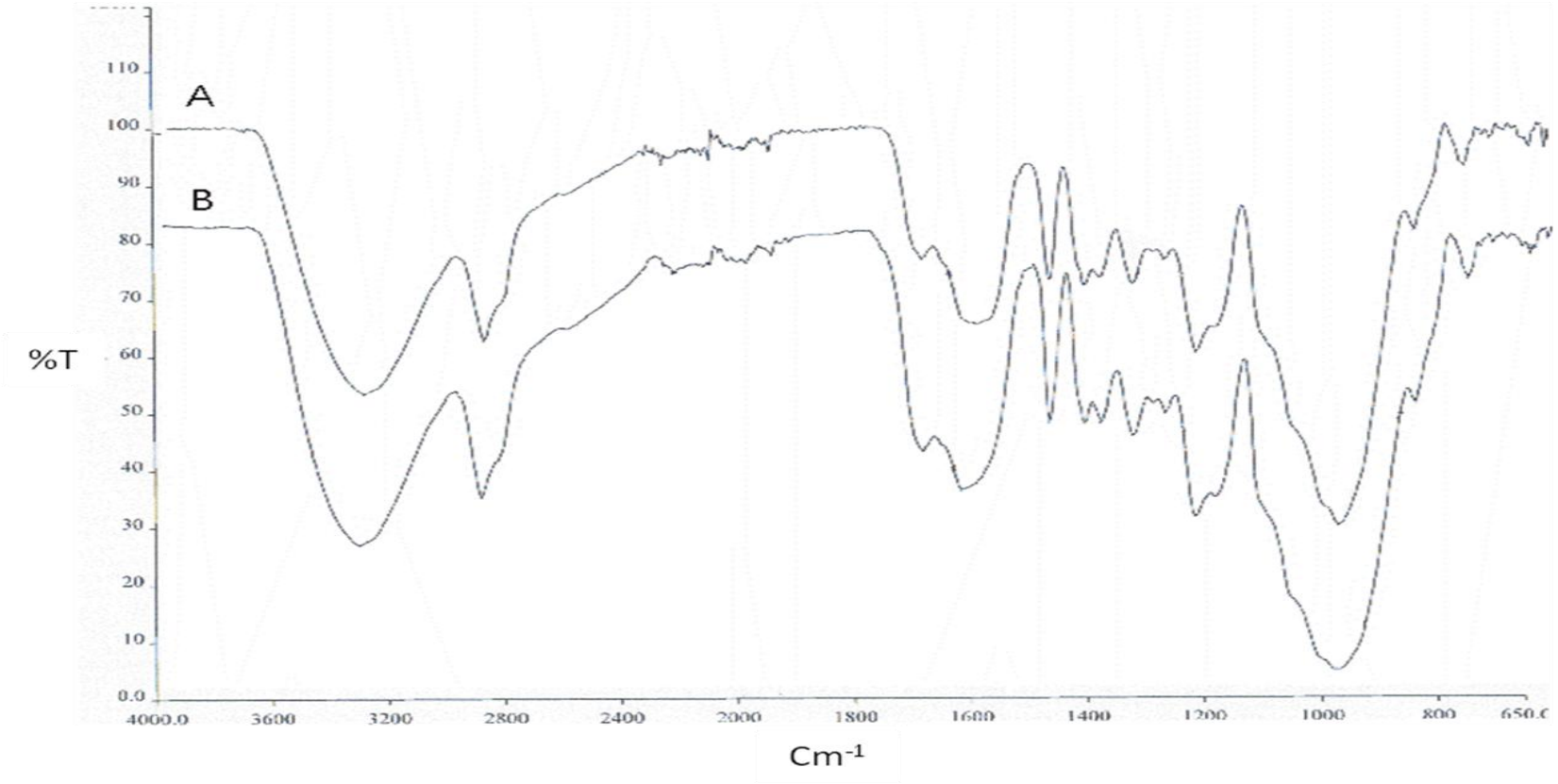

Fig 4.1.2: FTIR analysis of (A) Raw pine cone and (B) Fenton modified pine cone using H_2O_2/Fe^{2+} =100

1607.67cm^{-1} corresponds to the C=O stretch. The peaks between 1023.26 and 559.32cm^{-1} may be assigned to the –C–C– and –CN stretching, respectively (Malkoc, 2006). A comparison between the FTIR spectra's of the raw pine cone and the pine cone modified with H_2O_2/Fe^{2+} = 100 showed some differences in band intensities, indicating the functional groups on the surface has been modified. The band at 3342.65 cm^{-1} and peak at 1697.57 cm^{-1} increased in intensity while the wavelength slightly shifted for the modified sample. This may suggest that the C=O and –OH groups increased on the surface after oxidation. An increase in carboxylic functional group is only likely to occur if Fenton's treatment had lead to oxidation of primary or secondary alcohols of the pine cone surface.

4.1.2.6 Acid Number Analysis

The conversion of free -OH groups on wood products has been measured by acid number (AN mg KOH/g) determination (Doczekalska et al., 2007; Papadopoulos et al., 2010). As the number of free -OH groups on wood products decreases the acid number increases. When the H_2O_2 concentration was kept constant at 100,000 mg/dm^3 and Fe^{2+} concentration varied between 50 and 5000 mg/dm^3 for the pine cone oxidation, the acid number of all the oxidized samples were observed to be higher than for the raw pine cone (Fig. 4.1.3). The plot of acid number versus concentration of Fe^{2+} revealed that the raw pine cone had the least acid number (1.87 mg KOH/g), indicating that it had the highest amount of –OH groups on its surface. Doczekalska et al. (2007) obtained acid number for pine wood to be 1.1 mg KOH/g which is close to the values obtained in this study. The acid number was found to increase from 3.74 to 26.18 mg KOH/g) as the concentration of Fe^{2+} increased from 50 to 1000 mg/dm^3. When Fe^{2+} concentration was increased above 2000 mg/dm^3 (i.e., 5000 mg/dm^3), the acid number dropped to 22.44 mg KOH/g. This concentration of Fe^{2+} (2000 mg/dm^3) also corresponds to the concentration of Fe^{2+} that gave the optimum oxidation. The results indicate that Fenton's oxidation destroyed lignin and tannins which contain hydroxyl groups and may also convert carbohydrates –OH thereby reducing acid number.

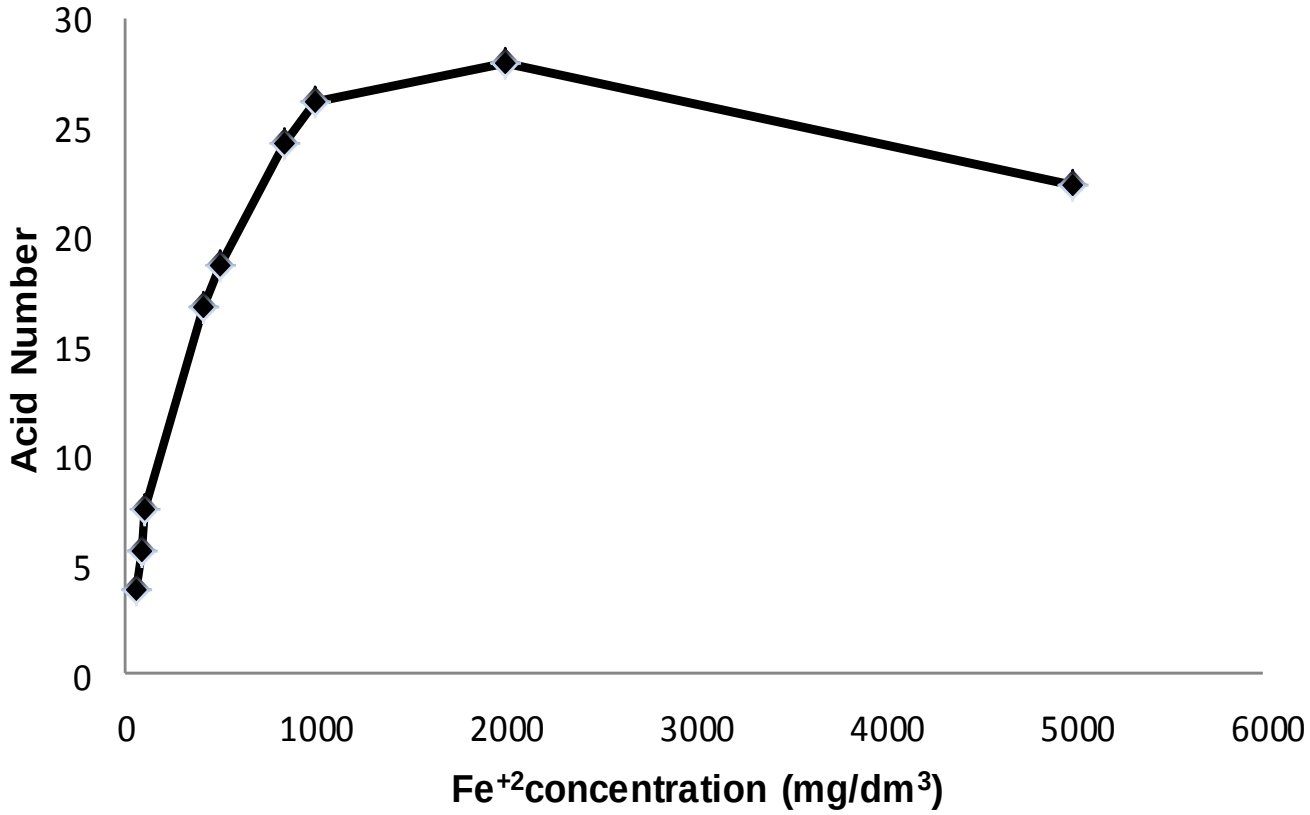

Fig 4.1.3: The plot of acid number versus concentration of Fe^{2+}

4.2 GRAFTING

4.2.1 Effect of initiator concentration on grafting reaction

In this study, $KMnO_4/HNO_3$ mixture was applied as the radical initiator and various concentrations of $KMnO_4$ (0.0005-0.020 mol/dm^3) in a fixed concentration of the HNO_3 was investigated as the free radical initiator system.

$KMnO_4$ is a strong oxidizing agent which when kept under acidic conditions, the MnO_4^- (Mn^{7+}) is reduced to MnO_2 (Mn^{4+}) as shown below:

$$MnO_4^- + 3e^- + 4H^+ \rightarrow MnO_2 + 2H_2O \qquad E^o = 1.68\ V \qquad (4.2.1)$$

Manganese (IV) (Mn^{4+}) can then react with acid (HNO_3) in solution and become reduced to manganese (III) (Mn^{3+}), hydrogen ion and nitrate radical as shown below:

$$Mn^{4+} + HNO_3 \rightarrow Mn^{3+} + H^+ + NO_3^{\cdot} \qquad (4.2.2)$$

The nitrate radical produced abstracts hydrogen ion from the substrate to transfer the radical site to the substrate molecules as shown in Eq.(4.2.3) below:

$$PineCone - OH + NO_3^{\cdot} \rightarrow PineCone - O^{\cdot} + HNO_3 \qquad (4.2.3)$$

Therefore, varying the initial concentration of $KMnO_4$ in Eq. (4.2.1) will led to variation in the ORP of the solution in first stage, and this can be applied in determining the efficiency at that stage. Preparation of $KMnO_4$ in acidic medium causes an increase in solution ORP due to generation of Mn^{4+} ions in solution. This ORP values then decrease as Mn^{4+} is reduced to Mn^{3+} in the presence of HNO_3 with the formation of the nitrate radical $\left(NO_3^{\cdot}\right)$ in solution and also due to NO_3 radical interacting with the pine cone powder surface. It will also be observed that Eq. (4.2.3) proceeds via release of hydrogen ion into bulk solution hence measuring the change in hydrogen ion concentration during the course of radical formation will determine the efficiency at this stage.

4.2.2 Effect of concentration at different temperature

The relationship between the ORP of the solution versus the various concentrations of $KMnO_4$ added before and after pine cone was added into the system is presented in Fig 4.2.1a. At this stage (Eq. (4.2.1)), the solution pH was kept constant and the initial concentration of $KMnO_4$ varied so that the variation in solution ORP is brought about by the change in concentration of the $KMnO_4$ added.

The values of the ORP when HNO_3 solution was added to solutions of low concentrations of $KMnO_4$ (without pine cone) was found to decrease sharply and then the decrease became gradual as $KMnO_4$ concentration increased above 0.005 mol/dm^3 (Fig. 4.2.1a). This observation suggests that more of the MnO_2 ions where produced at lower concentrations of $KMnO_4$ (at the fixed concentration and proportion of HNO_3) than for higher concentrations. After 45 min of contact of initiator system with pine cone, it was also observed that the final ORP values where lower for higher concentrations than for lower concentrations of $KMnO_4$ (Fig. 4.2.1a). A plot of the change in ORP (initial minus final values of ORP) (Figure not shown) indicates that the relationship between the change in ORP and initial $KMnO_4$ concentration is linear with a high correlation coefficient (r^2 = 0.9960) and that higher magnitudes of change occurred at higher initial concentration of $KMnO_4$ than at lower concentrations. The implication of these results is that, although a higher amount of MnO_2 is produced at lower initial $KMnO_4$ concentration, the conversion of Mn^{4+} to Mn^{3+} (Eq.(4.2.1)) which causes a reduction in the solution ORP is higher for the solution of higher initial $KMnO_4$ concentration than for the lower concentration. To confirm these results, the amount of MnO_2 deposited on the pine cone surface was determined using titrimetric method described by Mostafa (2005) in which the amount of MnO_2 deposited on a given weight of pine cone is given in meq/100 g of pine cone. The results as observed from Fig. 4.2.1b, reveals that the amount of MnO_2 deposited was higher for the solutions with higher production of MnO_2 (i.e., higher final ORP values or lower initial $KMnO_4$ concentrations) than for those with lower production of MnO_2 (i.e., lower final ORP values or higher initial $KMnO_4$ concentrations).

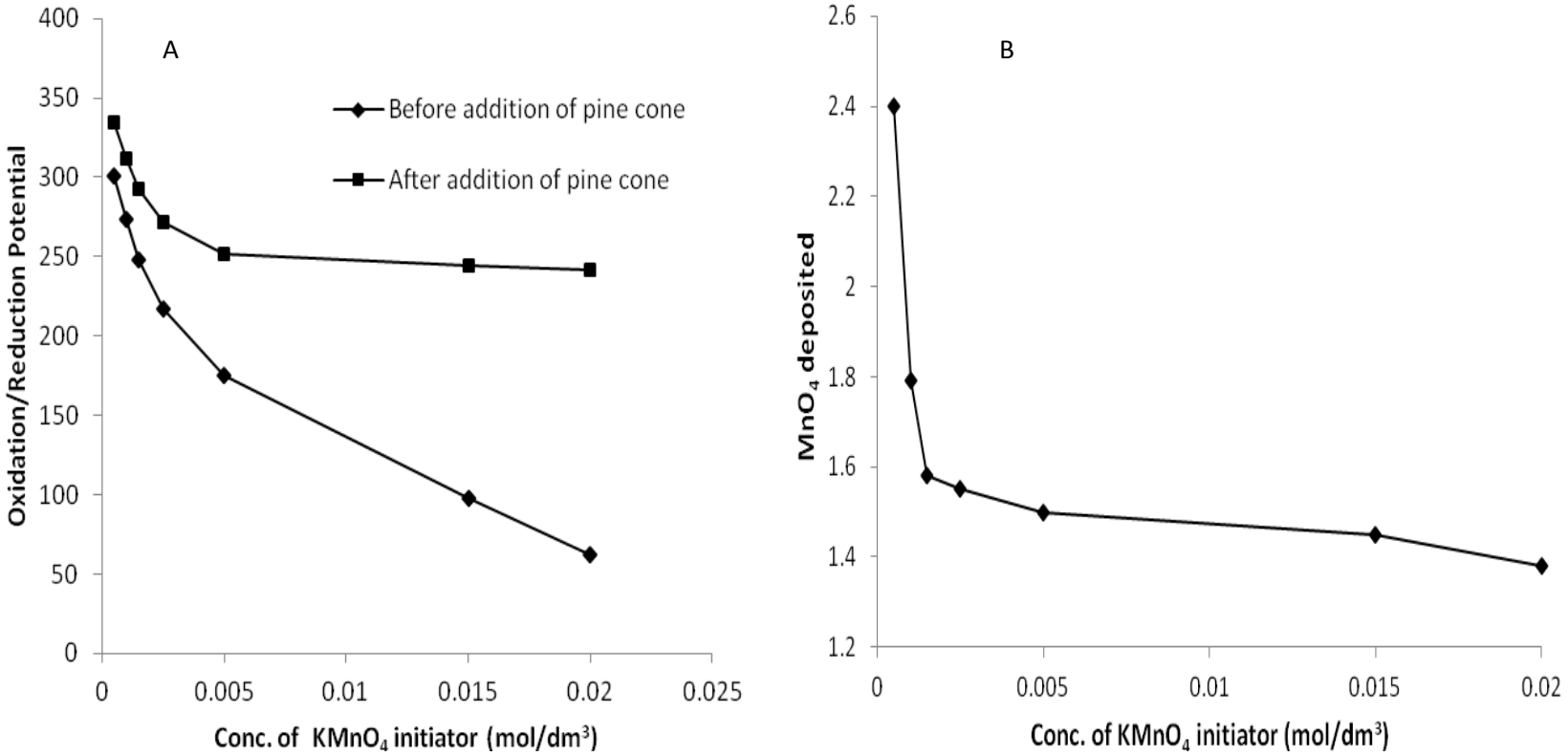

Fig 4.2.1: Relationship between initial $KMnO_4$ concentration and (A) oxidation/reduction potential, (B) MnO_4 deposited

Similar observation was made by Mostafa (2005) in the grafting of methacrylaminde onto cotton using $KMnO_4/HNO_3$ initiator system. Increased deposition of MnO_2 for solution with higher ORP values may be due to the large amount of this species present in solution, causing a reduction in the amounts of Mn^{4+} reduced to Mn^{3+} in the bulk solution. On the other hand, with solutions having lower production of MnO_2, lower amount of MnO_2 was deposited and the conversion of Mn^{4+} to Mn^{3+} was higher in the bulk solution.

Comparing the change in hydrogen ion concentration (ΔH^+), with the initial concentration of $KMnO_4$ in solution, it was observed that the change in hydrogen ion concentration was higher for solutions with higher initial $KMnO_4$ concentrations than for solutions with lower $KMnO_4$ concentrations. The values of the change in hydrogen ion concentration increased rapidly with increase in $KMnO_4$ concentration for lower $KMnO_4$ concentrations, but became almost constant after initial concentration of $KMnO_4$ 0.005 mol/dm^3 Fig 4.2.2. According to Eq.(4.2.2), the conversion of Mn^{4+} to Mn^{3+} occurs with a generation of hydrogen ions in solution (i.e., decreasing pH), therefore, it can be said that conversion of Mn^{4+} to Mn^{3+} is favoured by higher initial $KMnO_4$ concentrations than lower concentrations. This result therefore confirms the fact that lower amounts of MnO_2 was deposited for higher concentrations of $KMnO_4$ concentrations because Mn^{4+} conversion in solution is high, while at lower $KMnO_4$ concentrations, MnO_2 deposition is high due to lower Mn^{4+} conversion.

4.2.3 Effect of Fenton treatment on Grafting

Comparing certain parameters such as ORP, ΔH^+, acid number MnO_2 deposited on the raw pine treated with 0.020 mol/dm^3 $KMnO_4$ and that of the Fenton's treated pine with 0.020 mol/dm^3 $KMnO_4$ the effect of plant materials on the initiation process can be observed.

The values of final ORP and ΔH^+ obtained for the raw treated with 0.020 mol/dm^3 $KMnO_4$ were 2.6 mV and -0.00015 mmol/dm^3. The ORP and the ΔH^+ values were lower than for Fenton's treated sample (62.2 mV and -0.00016 mmol/dm^3), which indicates that the plant materials in the pine cone matrix can affect the initiation

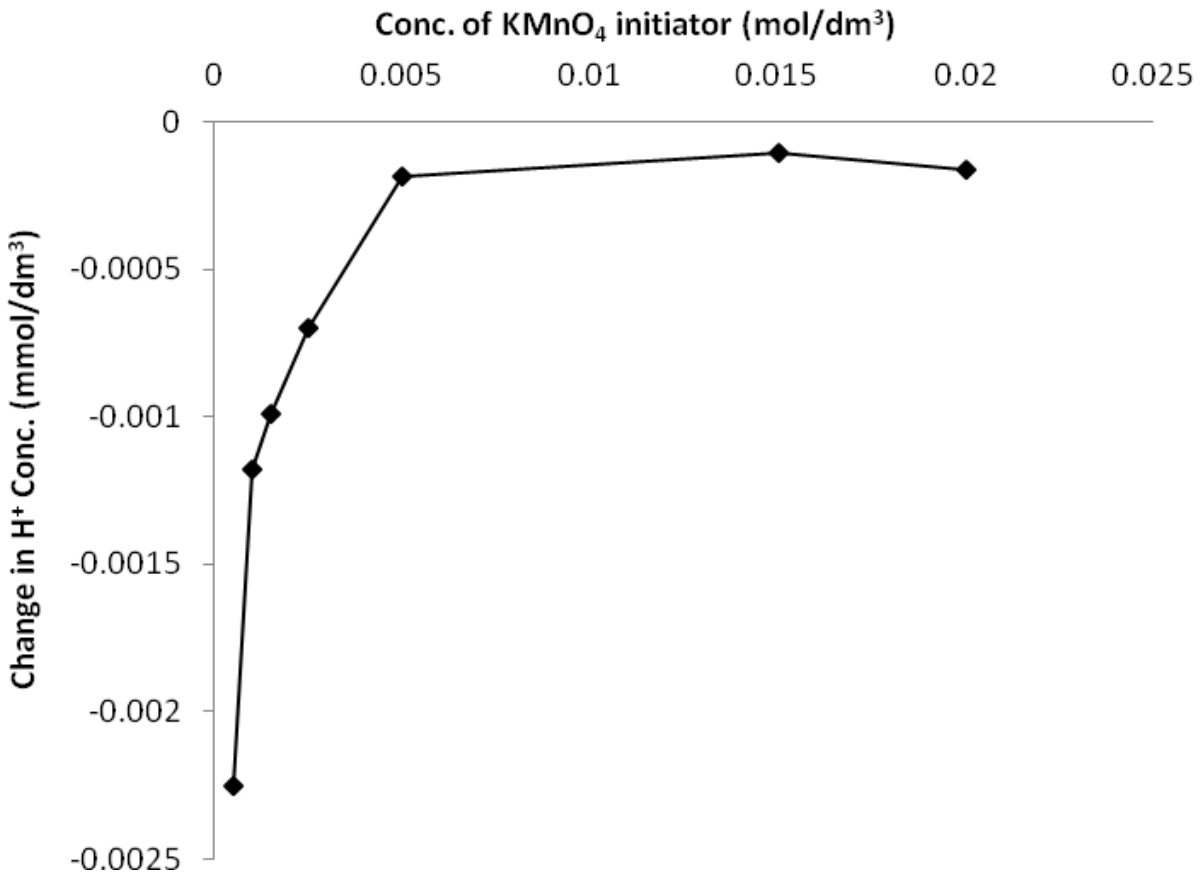

Fig. 4.2.2: Relationship between initial $KMnO_4$ concentration versus Change in H^+ concentration ($mmol/dm^3$).

reactions. Lower changes in ΔH^+ and ORP values mean that the conversion of Mn^{4+} to Mn^{3+} (i.e., the production of $NO_3^{\cdot}$ radicals) were lower compared with the Fenton's treated sample. The much lower values for the raw pine cone may therefore, be attributed to reduced possibility of radical formation on the pine cone surface. This suggests that plant components of a biosorbent can affect the radical initiation process for grafting monomers on the biosorbent.

4.2.4 Surface negative charge

The aim of grafting acrylic acid onto pine cone was to increase the amount of carboxylic acid functional groups on the pine material. Therefore, as the carboxylic acid functional groups increased, there will also be an increase in surface negative charge. The values of surface negative charge was determined by salt addition method for the Fenton's treated samples initiated with the varying concentrations of $KMnO_4$ and the raw pine cone initiated with 0.020 mol/dm^3 $KMnO_4$.

The surface charges of the Fenton's treated samples were found to decrease from 0.0027 to 0.0021 mol/g as the concentration of $KMnO_4$ increased from 0.0015 to 0.0200 mol/dm^3. This result indicates that the samples treated with lower concentrations of KMnO4 would likely have grafted more of the acrylic acid onto its surface than those treated with a higher concentration of $KMnO_4$.

4.2.5 FTIR analysis

Since a new functional group (carboxylic acid group) is grafted on the pine cone surface, FTIR analysis was carried out to determine the observed change in surface functional groups on the grafted pine cone. The FTIR spectra's in Fig. 4.2.3 a – c, shows the functional groups on the (a) acrylic acid monomer (b) raw pine (not grafted) and Fenton's treated pine (grafted) (c) raw (grafted) and Fenton's treated pine (grafted).

Fig. 4.2.3a shows the FTIR spectra for the acrylic acid monomer. The prominent peaks that can be identified in this spectra are those at 1635 and 1700 cm^{-1} which are attributed to asymmetric and symmetric stretching vibration of ionic carboxylic groups (–COO$^-$) and non-ionic carboxylic acid (-COOH) (Iqbal et al., 2009). Peaks

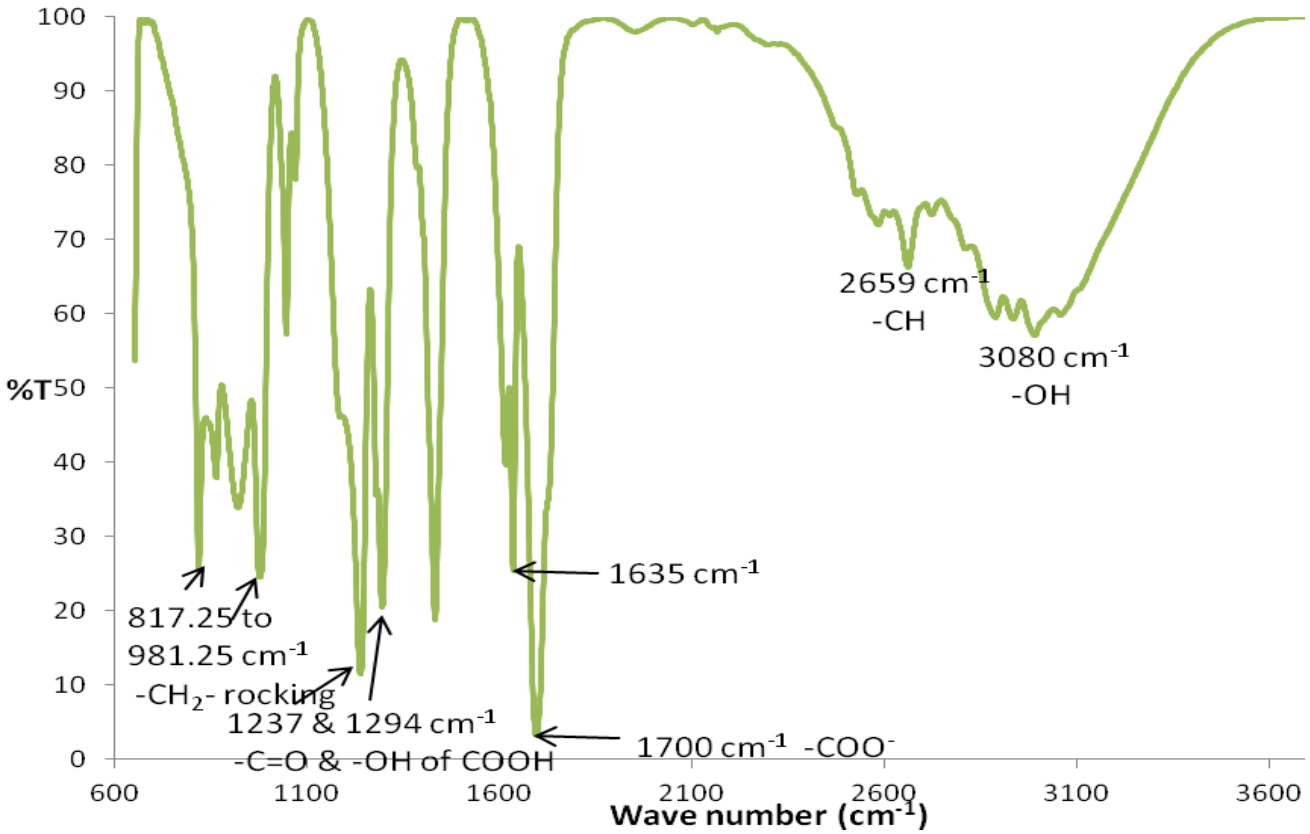

Fig 4.2.3: (A) Acrylic acid monomer

between 1237 and 1294 cm^{-1} indicating aliphatic acid group vibration due to deformation of C=O and stretching formation of –OH group of carboxylic acid (Iqbal et al., 2009), while the peaks between 972 and 812 cm^{-1} represents methylene rocking (Neira et al., 2007). The peak at 2659 cm^{-1} is indicative of C-H stretching (C sp^3), while -OH band is since at 3080 cm^{-1} (Neira et al., 2007).

Fig. 4.2.3 b shows the comparison between the spectra's of the raw pine cone (with no grafting) and the grafted Fenton's treated pine cone. It is observed that the major peaks in both samples were similar with differences only observed in the intensities of the peaks. The peaks at 811 and 2937 cm^{-1} in the raw pine representing the methylene rocking and C-H stretching (C sp^3) where found to shift slightly and extend sharply in intensity to 811 and 2933 cm^{-1} indicating an increase in C-C and C-H (C sp^3) concentration in the grafted pine cone. The peaks between 1259 cm^{-1} representing aliphatic acid group vibration due to deformation of C=O and stretching formation of –OH group of carboxylic acid in the raw pine and that at 1617 cm^{-1} were also found to shift and increase intensity to 1232 and 1700 cm^{-1} respectively. The increase in these groups indicates that carboxylic functions have been grafted into the pine cone. Finally the –OH band on the raw pine cone at 3334 cm^{-1} was found to increase and shifted slightly in the Fenton's treated grafted pine cone (3332 cm^{-1}), this confirms the fact that acrylic acid grafting was actual achieved.

Comparing the functional groups on the raw grafted pine cone and the Fenton's treated grafted pine cone, it was observed that very few differences in peak intensities were observed (Fig. 4.2.3c). For examples, higher peak intensities with slight shifts of –OH and $–COO^-$ were observed for the Fenton's treated and grafted pine cone (-OH = 3334 cm^{-1} and $–COO^-$ = 1700 cm^{-1}) as compared with the raw grafted pine cone (-OH = 3334 cm^{-1} and $–COO^-$ = 1700 cm^{-1}). Other minor differences were observed in the peaks representing –CH stretching (C sp^3) and C-O-C representing ester linkage which were at 2933 cm^{-1} and 1023 cm^{-1} in the Fenton's treated and grafted pine cone and at 2938 cm^{-1} and 1028 cm^{-1} in the raw and grafted pine cone.

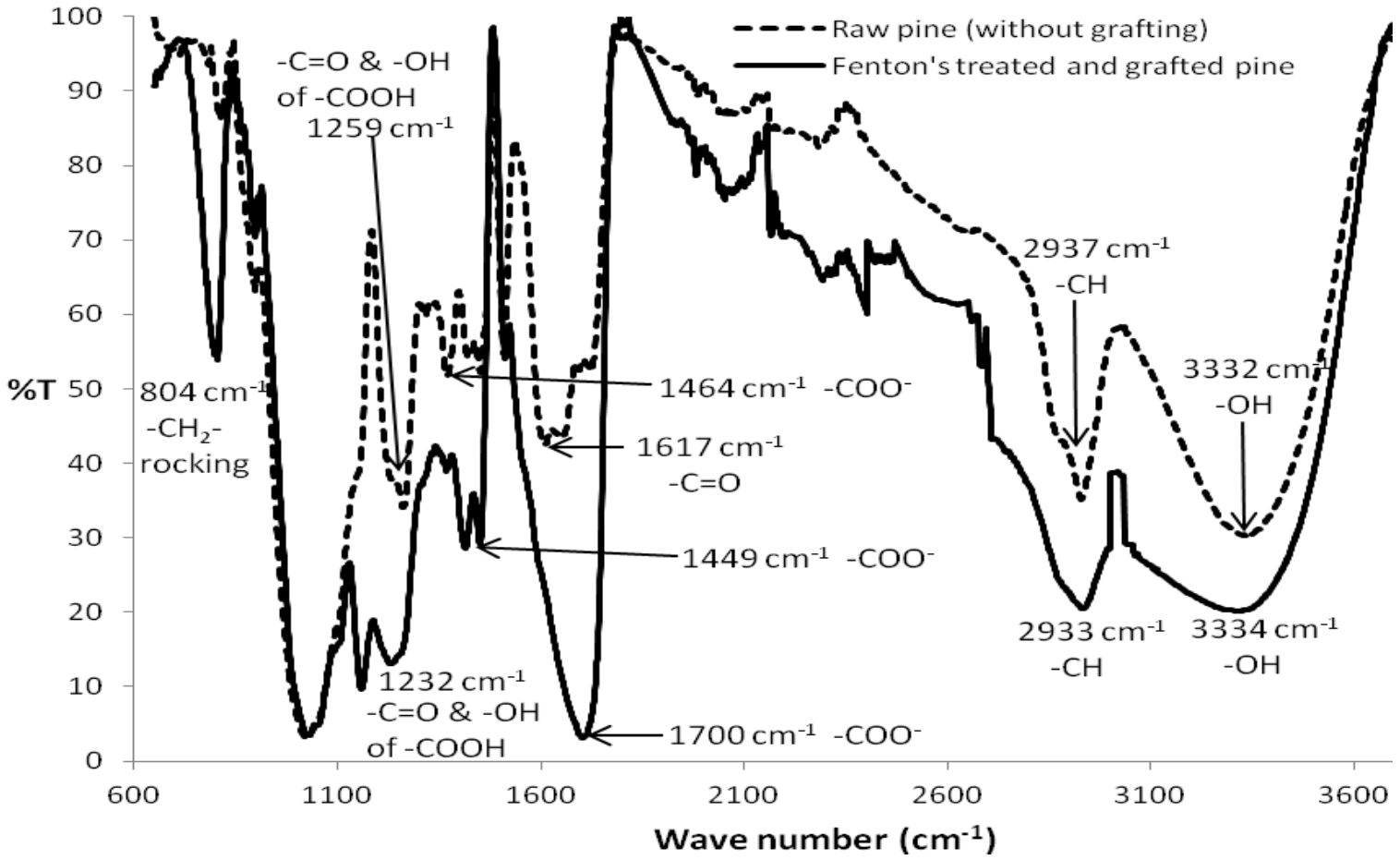

Fig 4.2.3: (B) Raw pine (without grafting) and Fenton's treated pine (grafted).

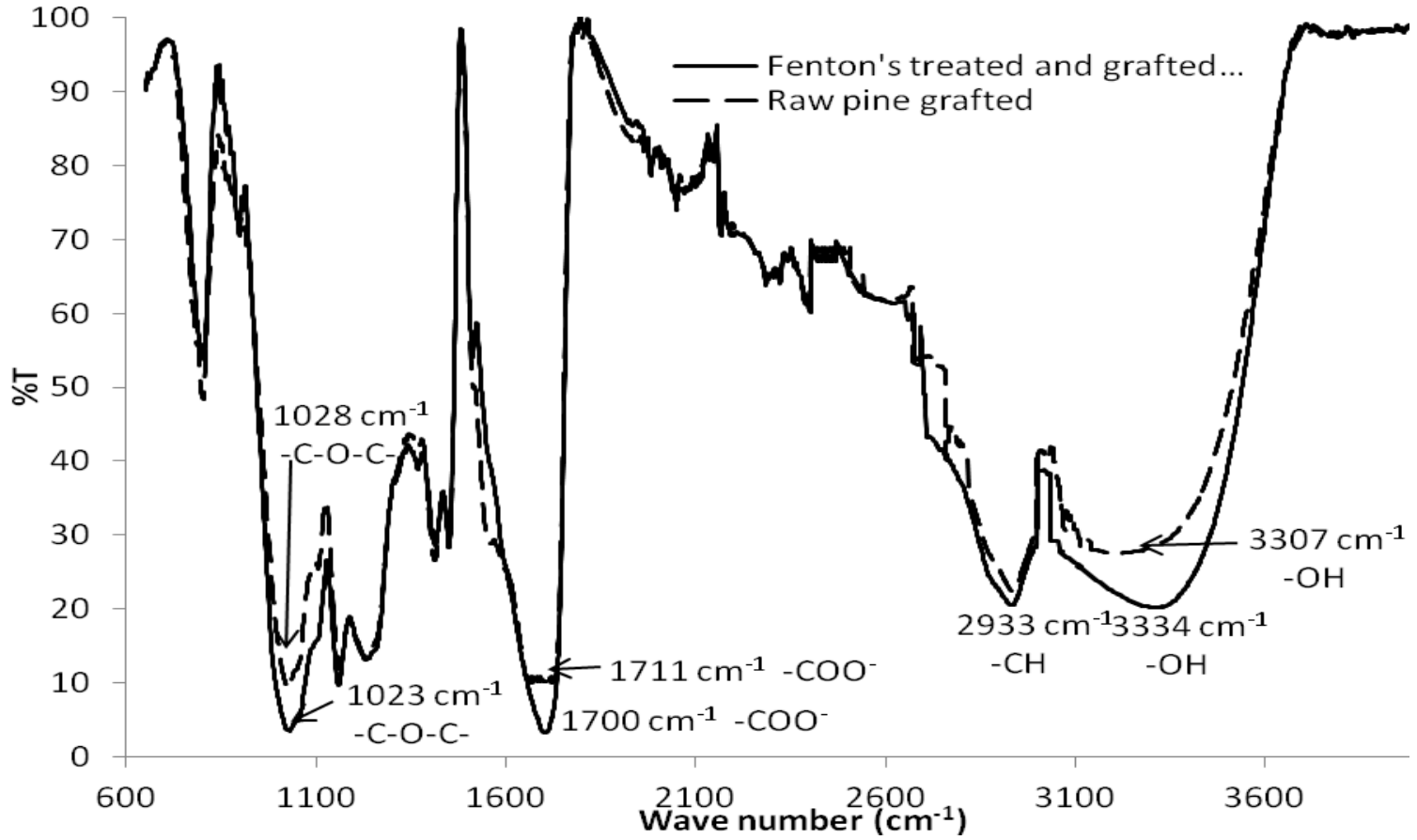

Fig. 4.2.3.(C): Raw pine (grafted) and Fenton's treated pine (grafted)

4.2.6 Thermogravimetric Analysis

Thermogravimetric analysis is usually performed in the determination of mass change in the composite polymer as a function of time and temperature. This analytical technique gives an indication of the reactions which occurs at the molecular level of the materials. Fig. 4.2.4a and b shows the thermogravimetric curve (Fig. 4.2.4a) and the derivative thermogravimetric (DTA) curves (Fig. 4.2.4b) for the raw pine cone, raw pine cone grafted with acrylic acid and Fenton's modified pine grafted with acrylic acid.

Fig. 4.2.4a shows an initial loss of weight loss at low temperature (below 140 ^{o}C) which can be attributed to desorption of water molecules from the materials. Several authors have shown this water loss below 140 ^{o}C for various cellulosic materials, while the stability of the cellulosic matrix reduces at higher temperatures causing instability and decomposition at higher temperatures (Dahou et al. 2010; Fares et al., 2011). The raw pine cone began to show signs of decomposition at 169 ^{o}C, whereas the grafted raw pine and Fenton's modified grafted pine cone started decomposing at 260 and 281 ^{o}C respectively. Final decomposition temperatures were observed at 495, 521 and 532 ^{o}C giving a total percentage decomposition of 60, 56 and 51 % for the raw pine, grafted raw pine and Fenton's modified grafted pine cone respectively. These results indicates that grafting of acrylic acid onto pine cone improved the thermal stability of the resulting material and that the thermal stability of the Fenton's treated and grafted pine cone may be higher due to higher amounts of acrylic acid grafting. Princi et al. (2005) also observed an increase in thermal stability for linen and cotton grafted with acrylic monomer over the raw linen and cotton materials.

Fig. 4.2.4b shows the DTA curves of the raw pine, grafted raw pine and Fenton's modified grafted pine cone respectively. The curves showed that endothermic peaks occurred at 336, 379 and 389 ^{o}C for the raw pine, grafted raw pine and Fenton's modified grafted pine cone respectively which are formed from single decomposition of the raw pine cone and its derivatives. The position of the endothermic peaks for the grafted raw pine and Fenton's modified grafted raw pine shifted from the raw pine by 34 and 44 ^{o}C respectively. Similar shifts in endothermic peaks after grafting of polymer onto bamboo cellulose has also been reported by Wan et al. (2011). This

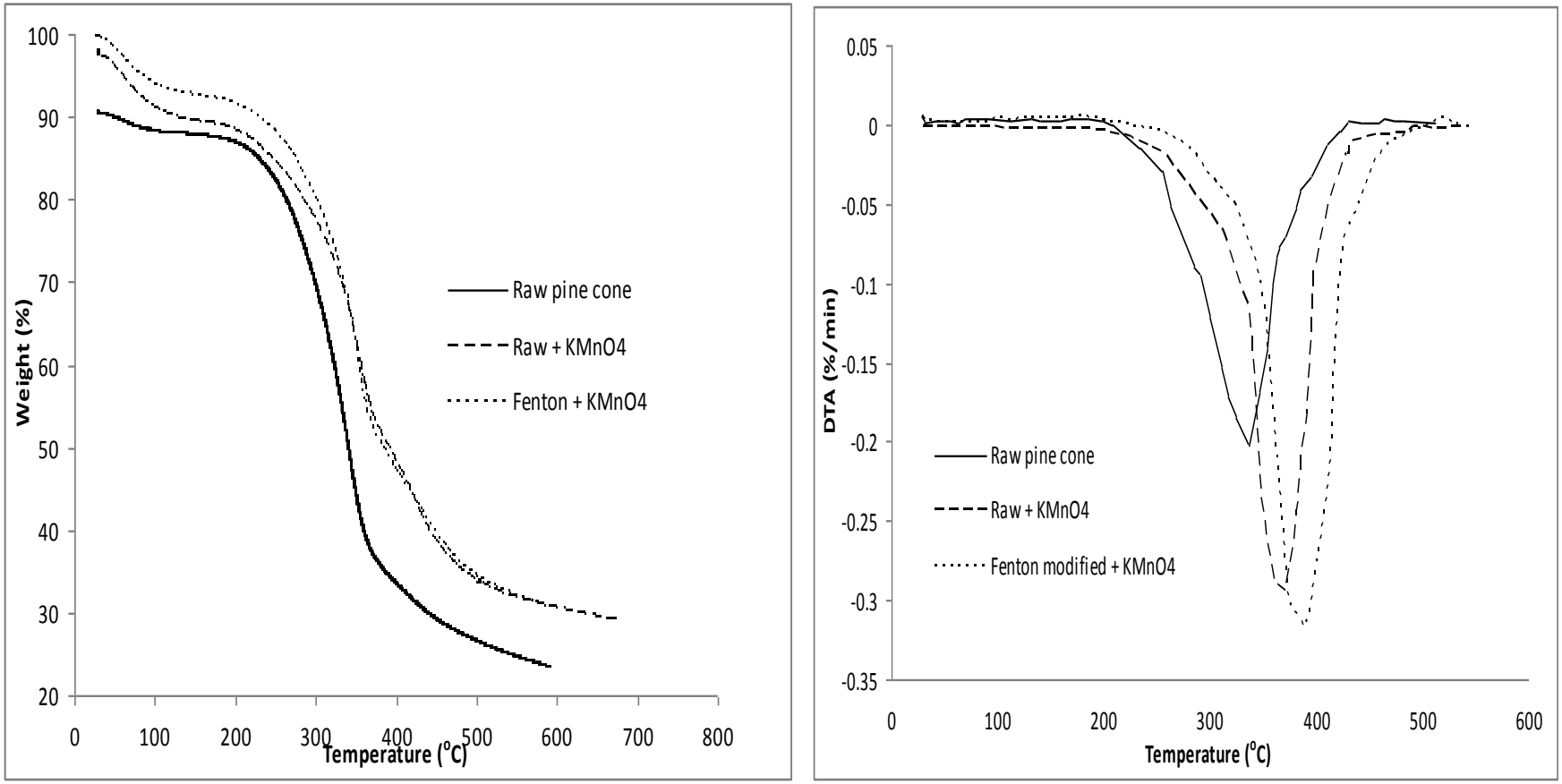

Fig. 4.2.4: Thermogravimetric Analysis, (A) Thermogravimetric curve (TGA) and (B) Derivative thermogravimetric (DTA)

results further supports the fact that the Fenton's treated samples may have higher amounts of pine cone-polymer bonds than the grafted raw sample.

4.2.7 Effect of $KMnO_4$ efficiency and plant components on grafting parameters

The grafting parameters examined in this study were the mass of crude and extracted products (crude product extracted with hot water and acetone), monomer conversion, homopolymer conversion, and grafting efficiency. These parameters were monitored against the increasing concentration of the radical initiator ($KMnO_4$). The results of this analysis are shown in Table 4.2.1. From the results, it was observed that as the concentration of the radical initiator increased, the mass of the crude product increased while the mass of the extracted product decreased. The reason for this is the fact that as initiator concentration increased from 0.0005 to 0.0200 mg/dm^3, the homopolymer formation (i.e., monomer units joined together and not grafted on the pine cone) increased and grafting efficiency decreased. Previous results showed that increase in $KMnO_4$ concentration caused the amount of MnO_2 deposited to decrease and the conversion of MnO_2 to Mn^{3+} to increase, thereby increasing NO_3 radical formation. Therefore, when initiator concentration is high in solution, higher conversion of MnO_2 in the bulk solution is observed and the possibility of Mn^{3+} initiating radical sites on monomer units rather than on the pine cone increases which also increases the possibility for homopolymer formation. The grafting efficiency therefore decreases since more of the monomers are linked to the homopolymer chain than to the pine cone biomaterial. The total monomer conversion also increases with increasing initiator concentration since both grafting and homopolymer formation takes place simultaneously.

Comparing the grafting parameters of the raw pine and the Fenton's treated pine cone initiated with 0.0200 mg/dm^3 $KMnO_4$, it will be observed that although the mass of the crude material was slightly lower for the raw grafted pine, its extracted product mass was much lower than for the Fenton's treated grafted pine cone. At the same initiator concentration of 0.0200 mol/dm^3, the Fenton's treated grafted pine had higher ORP value than the raw grafted sample, this should suggest that there was more conversion of Mn^{4+} to Mn^{3+}, but comparing the values of MnO_2 deposited, the raw grafted pine (1.62 meq/100 g) had higher MnO_2 deposited values than the Fenton's treated grafted pine (1.38 meq/100 g). The change in hydrogen ion concentration,

Table 4.2.1: Grafting parameters for the grafting of acrylic acid onto Fenton's modified and raw pine cone at different concentrations.

$KMnO_4$ Conc.	Mass of extracted prodt.	Mass of crude prodt.	Monomer conversion	Homopolyer conversion	Grafting Efficiency
0.0005	15.50	15.60	53.38	0.94	98.23
0.0010	14.91	15.80	55.26	8.49	84.64
0.0015	14.13	16.05	57.68	18.37	68.15
0.0025	13.76	16.26	59.63	23.81	60.07
0.0050	13.37	17.24	68.95	36.83	46.58
0.0150	12.60	18.21	78.27	53.46	31.70
0.0200	12.25	16.55	81.45	60.06	26.27
Raw + 0.0200	10.70	15.98	57.02	50.37	11.66

$KMnO_4$ Conc. (mol/dm^3)

ΔH^+, was found to be lower for the raw grafted pine than for the Fenton's treated sample, meaning that less Mn^{4+} to Mn^{3+} conversion took place. This result may be attributed to the fact that the conversion of Mn^{4+} to Mn^{3+} may have been resisted by the plant components on the biosorbent surface accounting for the lower amount of extracted product obtained for the raw grafted pine cone. This result is supported by the lower values of total monomer conversion and grafting efficiency of the raw grafted pine as compared with the Fenton's treated grafted pine material.

4.2.8 Percentage Methylene blue and Methyl violet removal

The values of percentage Methylene blue and Methyl violet removal by the raw, the grafted raw and the various Fenton's reagent samples along with the BET surface areas of the samples are shown in Table 4.2.2. The results revealed that the percentage methyl violet and methylene blue removal increased with increase in the concentration of $KMnO_4$ initial used for grafting of the pine cone or decrease in grafting efficiency. Examining the BET surface area values of the materials, it was observed that the surface areas of the samples decreased with grafting efficiency, suggesting that as grafting increased, the surface area of the biosorbent reduced due to higher density of the polymer chain on the surface.

When the BET values of the raw grafted sample was compared with the Fenton's treated grafted sample initiated using 0.0200 mol/dm^3 $KMnO_4$, it was observed that the surface area of the raw grafted material was much more smaller than the Fenton's treated material and this affected the percentage methylene blue removal of the sample.

4.3 OPTIMIZATION OF ADSORPTION PARAMETERS

4.3.1 Methyl violet (MV)

4.3.1.1 Optimization of solution pH

The pH of the aqueous solution in which sorption is being conducted is an important controlling parameter in the sorption process. The magnitude of electrostatic charges imparted by the ionization metal ions and the functional groups on the adsorbent surface are primarily controlled by pH of the medium.

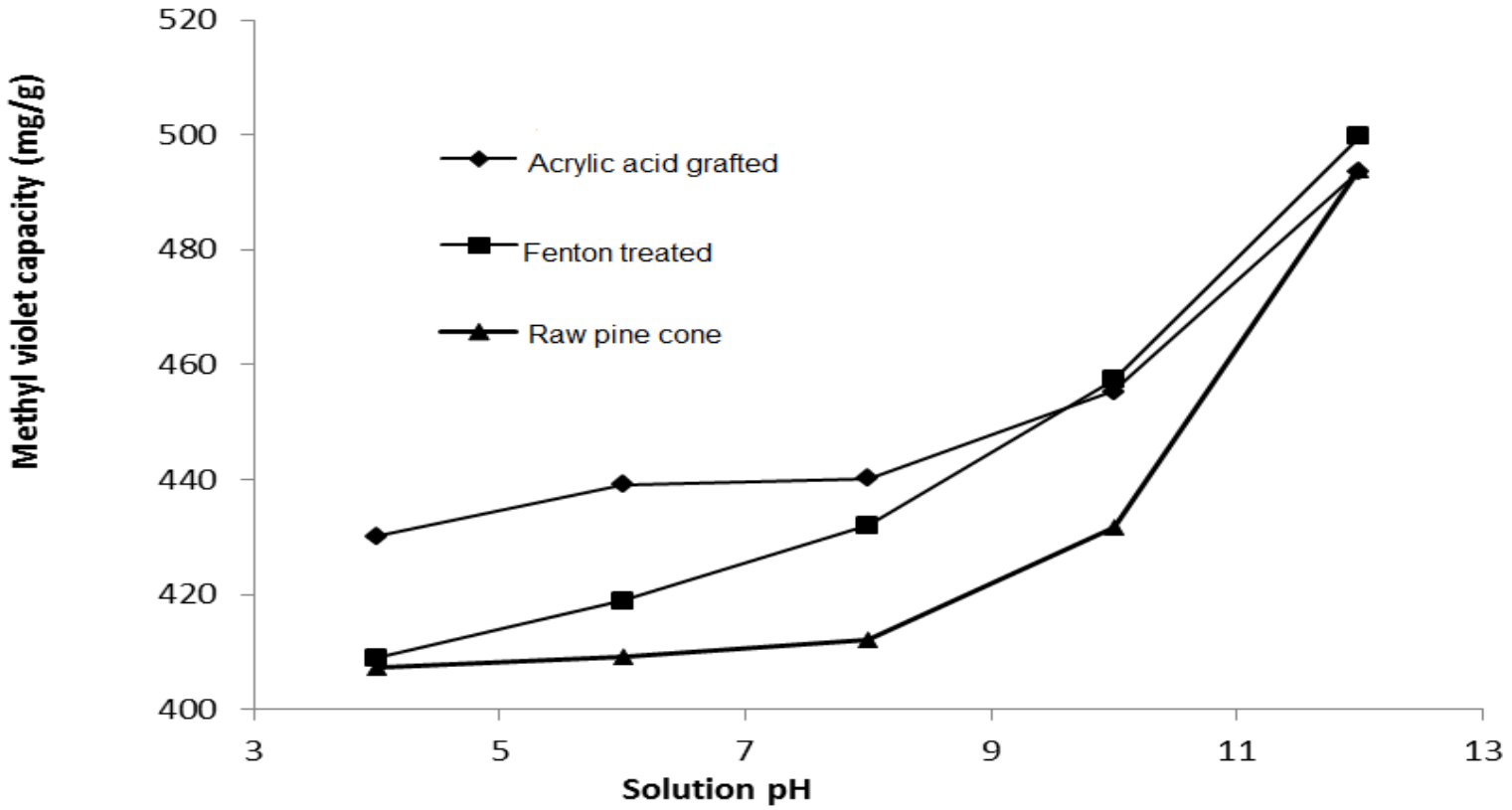

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Fig.4.3.1.: Plot of methyl violet capacity verses pH, for the adsorption of methyl violet onto raw, Fenton's treated and acrylic acid grafted pine cone.

Fig 4.3.1. shows the relationship between methyl violet capacity verses solution pH for raw, Fenton's treated and acrylic acid grafted. It was observed that, the increasing percentage removal with pH is attributed to the fact that decreasing solution pH increases H+ concentration in solution which will coordinate with OH groups to form $–OH_2^+$ and will reduce the number of negative sides on the adsorbent.

On the other hand, increasing pH reduces the amount of H^+ in solution and promotes ionization of –OH groups, thus increasing cation exchange capacity. In Fig 4.3.1; it is observed that increase in solution pH from 4 to 12 increased the pH removal, experienced in the three experiments. Raw pine cone as expected has the lowest percentage removal than the two, as it has all the organic compounds, there is high competition for the negative side on adsorbent for H^+ and MV^+. The slight difference between raw and Fenton treated pine cone is that Fenton treated pine cone has a longer surface area. Acrylic acid treated has the highest percentage removal as there is less competition for MV^+ to be adsorbed and more acrylic acid due to drafting. Low pH means high concentration of H^+ in solution, while high pH means high concentration of H^+ and higher concentration of OH^-.At pH 12 , precipitation occurred, thus pH 10 is the best optimum pH.

4.3.1.2 Optimization of adsorbent mass

The effect of varying the adsorbent mass, m_s is shown in Figs. 4.3.2 a-c. Figs. 4.3.2 a-c show the plots of percentage removal and adsorption capacity verses mass of raw, Fenton's treated and acrylic acid grafted pine cone, respectively.

The figures all show that the percentage methyl violet removal increased as the adsorbent mass increased from 0.05 to 0.3 g, while the adsorbent capacity of methyl violet decreased as the adsorbent mass increased. It was observed that the percentage methyl violet removal from aqueous solution using 0.3 g of the adsorbent was highest for the acrylic acid grafted pine cone (99.85 %), Fenton's reagent treated pine cone removed 91.20 %, while the raw pine cone at the same adsorbent mass removed only 90.89 % of the methyl violet dye from aqueous solution.

The adsorbent mass on the other hand, reduced from 1622.36 to 727.66 mg/g for the raw pine cone, from 1629.66 to 273.6 mg/g for the Fenton's treated pine cone and

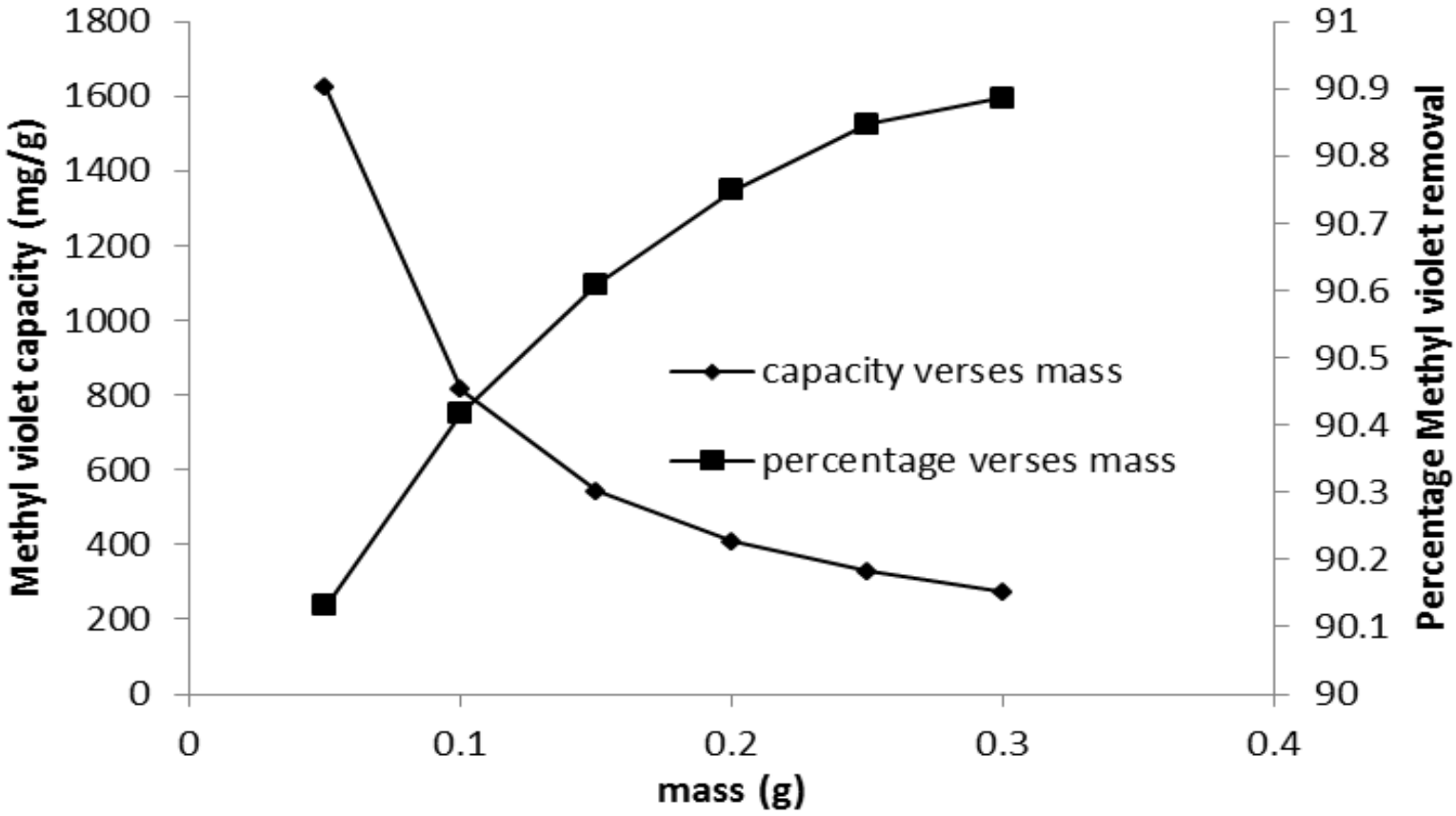

Fig. 4.3.2a: Effect of increasing raw pine cone mass on the adsorption capacity and percentage removal of methyl violet.

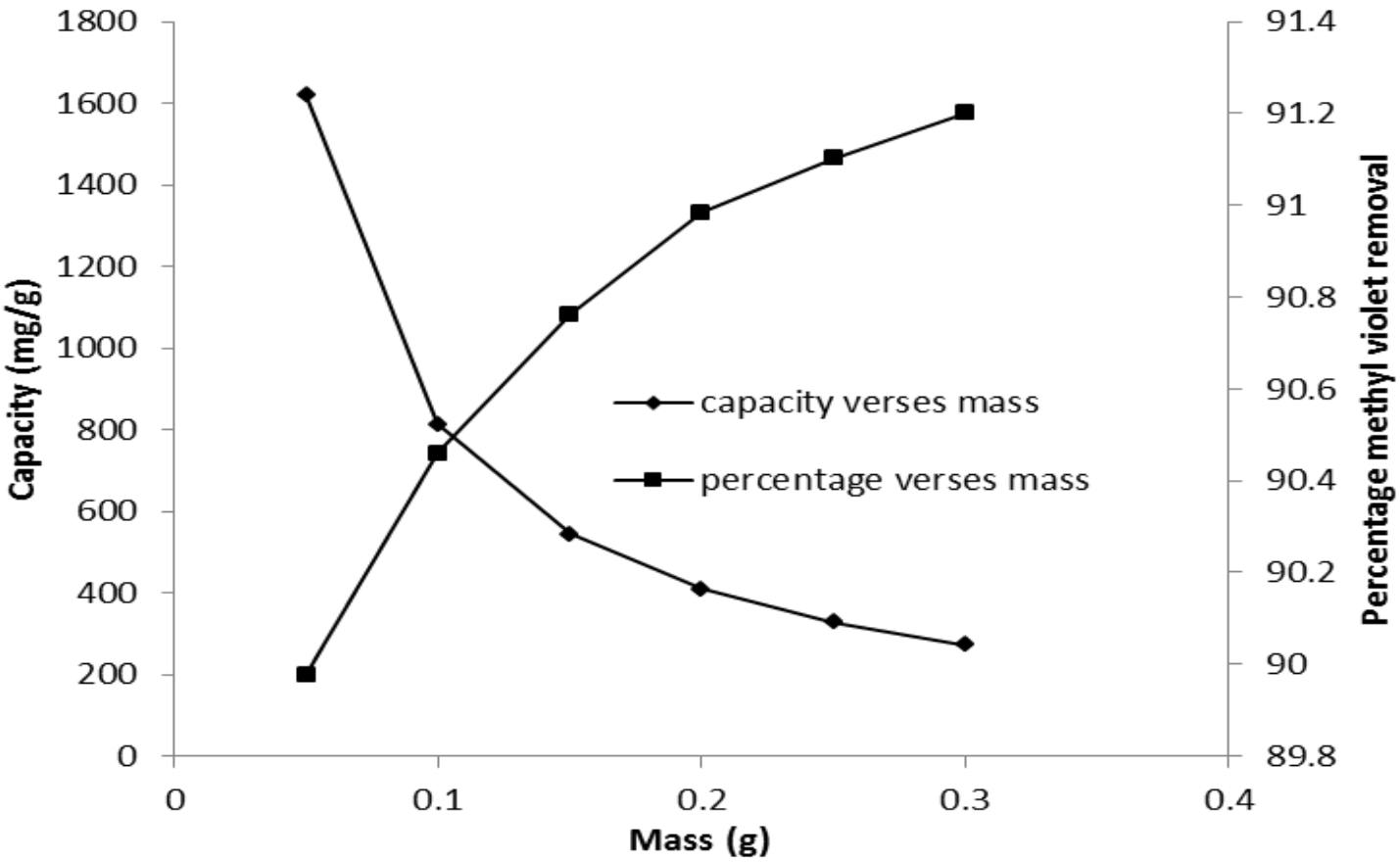

Fig. 4.3.2b: Effect of increasing Fenton's treated pine cone mass on the adsorption capacity and percentage removal of methyl violet.

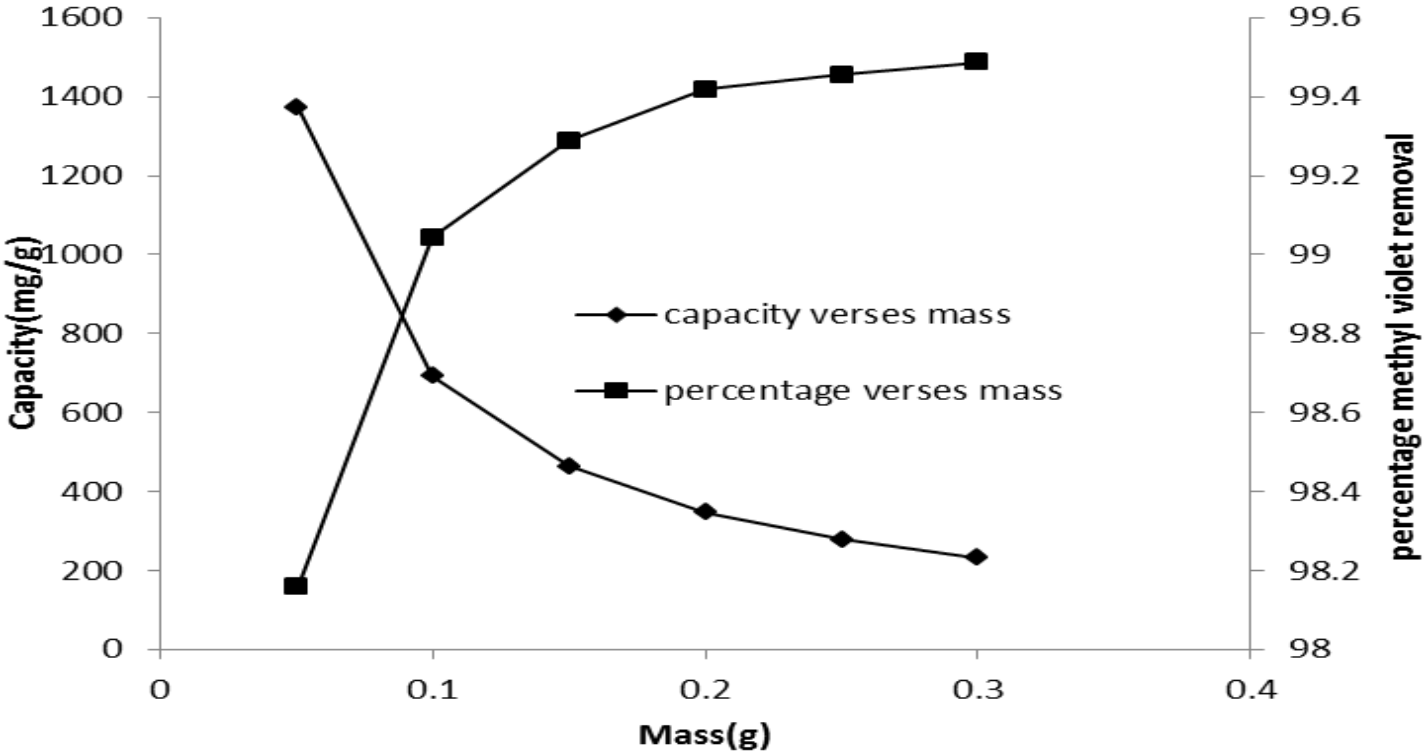

Fig. 4.3.2c: Effect of increasing acrylic acid grafted pine cone mass on the adsorption capacity and percentage removal of methyl violet.

from 1374.2 to 232.14 mg/g for the acrylic acid grafted pine cone powder. The decrease in sorbent capacity, i.e. amount of dye sorbed per unit mass of adsorbent with increase in pine cone dose, may be attributed to two reasons. The increase in sorbent dose at constant dye concentration and volume will lead to saturation of sorption sides through the sorption process and secondly may be due to particular interaction such as aggregation resulting from high sorbent dose. Such aggregation would lead to decrease in total surface area of the sorbent and an increase in diffusional path length. In Fig. 4.3.2a; b and c, from 0.05 to 0.3 g, there is a high increase, as from 0.15 to 0.3 g, it is constant, thus making 0.15 g the optimum mass.

4.3.1.3 Percentage Methyl violet removals from aqueous solution

The graphs in Figs. 4.3.3 a-c show the percentage Methyl violet removal from aqueous solution verses time. It was observed that as the time of contact increased, the percentage Methyl violet removal also increased rapidly at the initial stage and gradually reduced until it came to an almost steady state. Two sections were observed in the plots; at contact times 0.5 to 3 min, there is a sharp increase, while from 10 to 60 min there is a slow increase in percentage removal. For the initial contact time, for example at 0.5 minutes of contact using the raw pine cone, it is observed that there was a percentage removal of 89.95, 88.28, 87.12 and 86.95 % of methyl violet from solutions of methyl violet of concentrations of 150, 200, 500, 700 and 900 mg/dm^3 respectively. With Fenton treated and acrylic acid treated the same was observed.

The plots in Fig. 4.3.4 show the percentage methyl removal verses time (min) at 900 mg/dm^3 for raw pine, Fenton's treated and acrylic acid grafted pine cone. It was observed that raw pine cone had the least percentage removal, because of its smaller surface area due the presence of plant components occupying pore spaces and the limited amounts of acidic functional groups. Fenton's treated pine cone on the other hand had a higher percentage methyl violet percentage removal than the raw pine cone because on extraction of plant organic components, the surface area of the pine increased, while the acrylic acid grafted pine cone sample displayed the highest methyl violet percentage removal due to the increase in carboxylic acid function grafted onto the pine cone material.

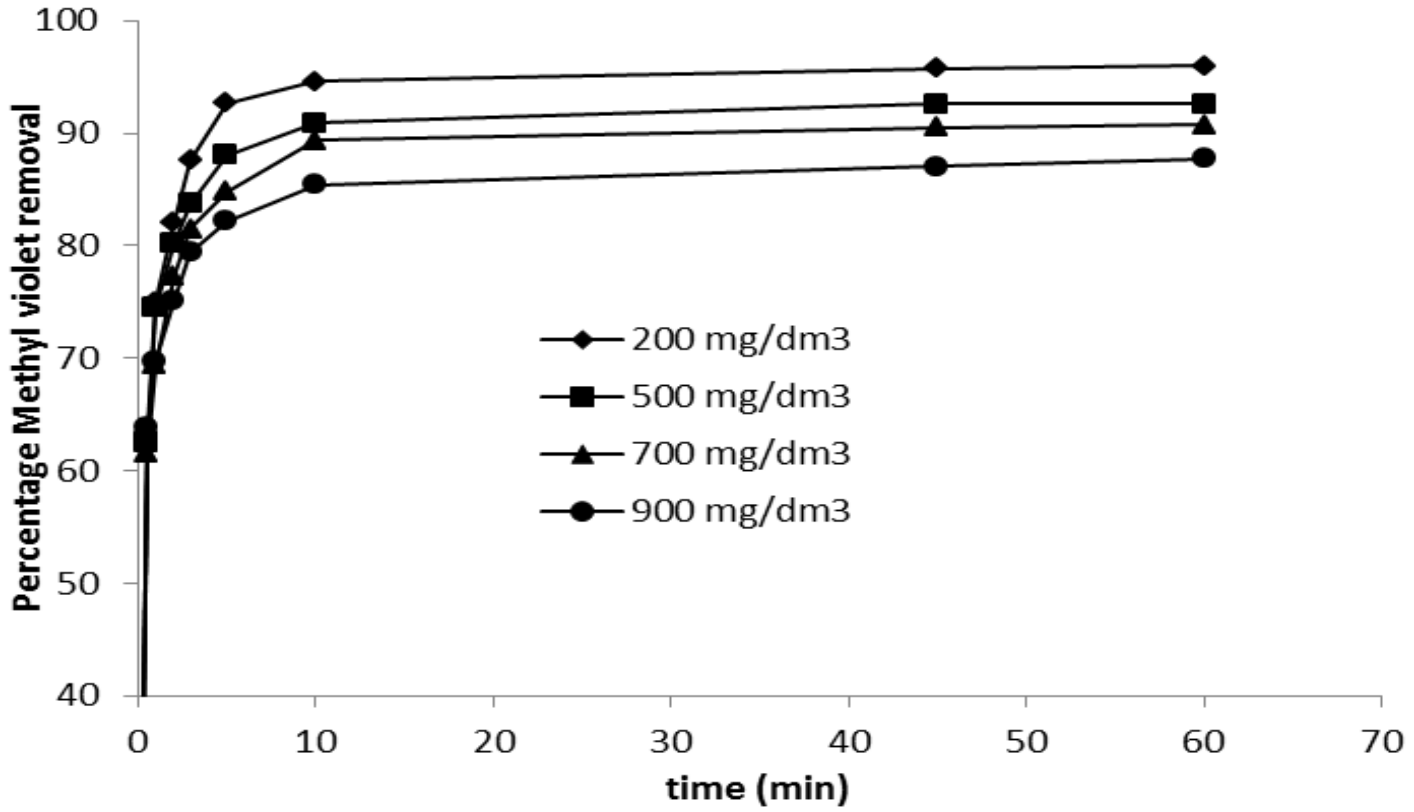

Fig. 4.3.3a: Plot of percentage methyl violet removal at different time of contact using raw pine cone.

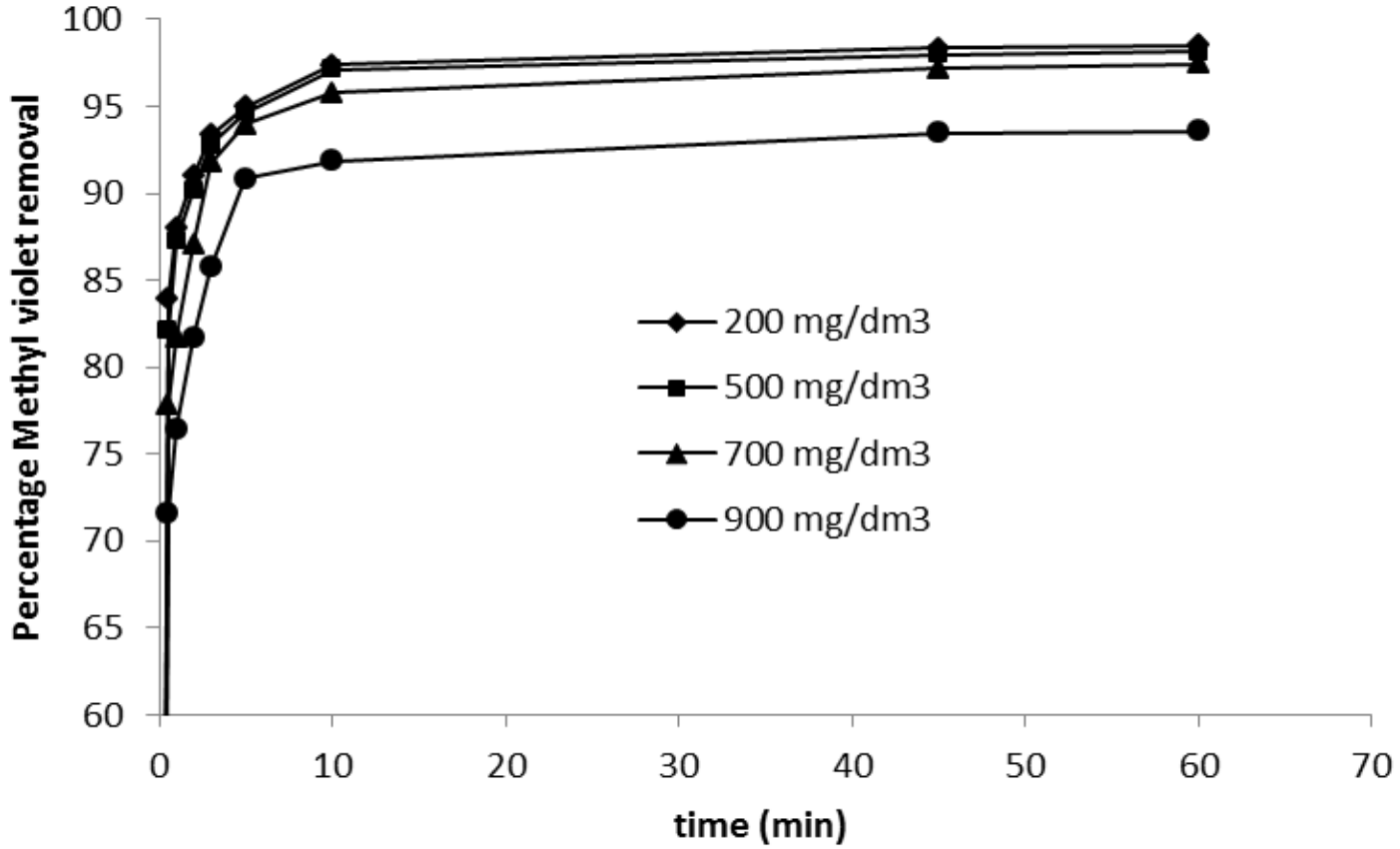

Fig.4. 3.3b: Plot of percentage methyl violet removal at different time of contact using Fenton's reagent treated pine cone.

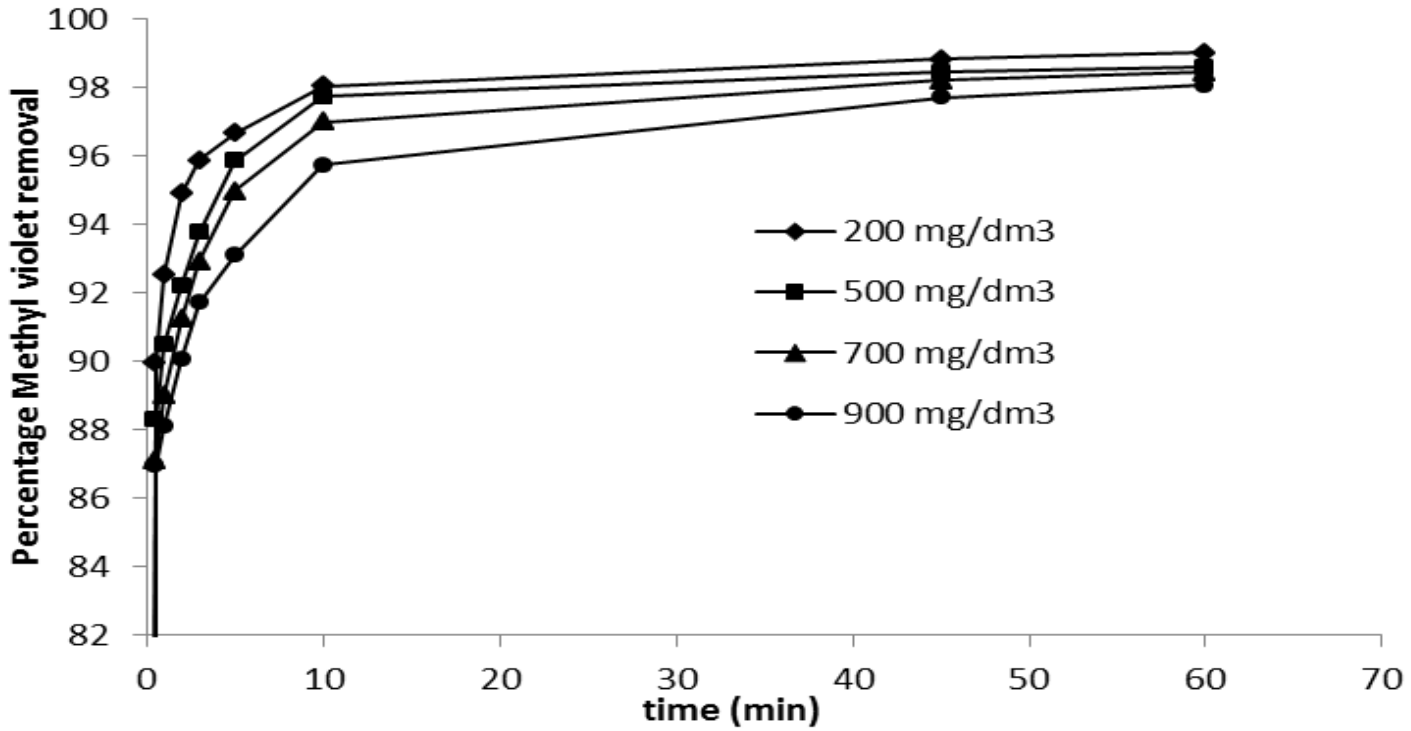

Fig.4.3.3c: Plot of percentage methyl violet removal at different time of contact using acrylic acid grafted pine cone.

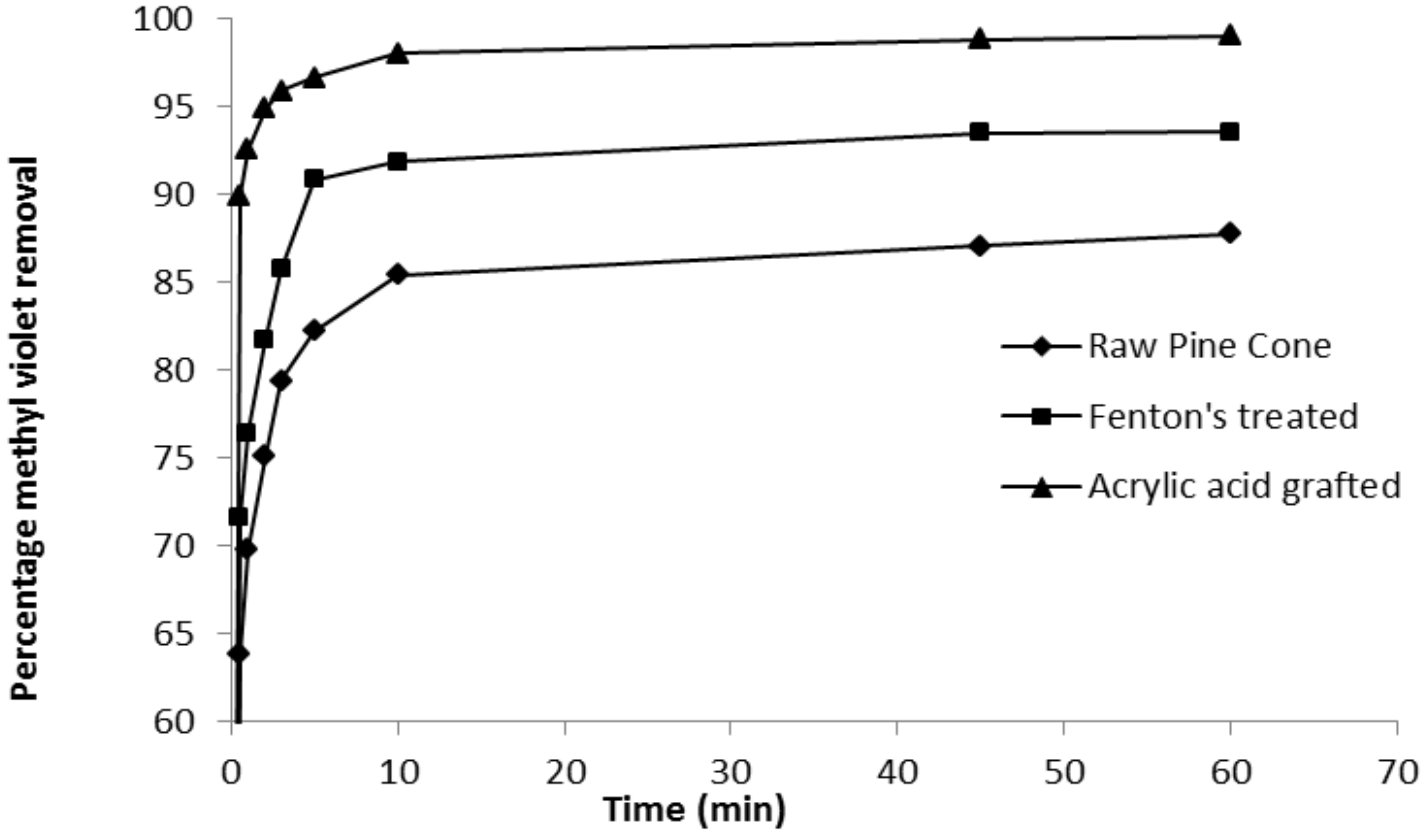

Fig.4.3.4: Comparison of methyl violet percentage removal from a 900 mg/dm^3 of methyl violet using raw pine, Fenton's treated and acrylic acid grafted pine cone.

4.3.2 Methylene blue (MB)

4.3.2.1 Optimization of solution pH

The pH of the aqueous solution in which sorption is being conducted is an important controlling parameter in the sorption process. The magnitude of electrostatic charges imparted by the ionization of metal ions and the functional groups on the adsorbent surface are primarily controlled by pH of the medium. Fig. 4.3.5a shows the relationship between adsorption capacity of adsorbent verse solution pH for raw, Fenton's treated and acrylic acid grafted pine cone. It was observed that, the increasing percentage removal with pH is attributed to the fact that decreasing solution pH increases H^+ concentration in solution which will coordinate with OH groups to form $–OH_2^+$ and will reduce the number of negative sides on the adsorbent. On the other hand, increasing pH reduces the amount of H^+ in solution and promotes ionization of –OH groups, thus increasing cation exchange capacity. In Fig 4.3.5a; it is observed that increase in pH of the solution from 4 to 12 increased the percentage removal as observed in the three experiments. Raw pine cone, as expected has the lowest percentage removal than the two, as it has all the organic compounds, there is high competition for the negative side on adsorbent for H^+ and MB^+. The slight difference between raw and Fenton treated pine cone is that, Fenton treated pine cone has a wider surface area. Acrylic acid treated pine cone has the highest percentage removal as there is less competition for MB^+ to be adsorbed than H^+. Low pH means high concentration of H^+ in solution, while high pH means low concentration of H^+ and higher concentration of OH^- on the adsorbent surface. At pH 12, we observed that for MB, there is a high percentage removal compared to any pH value.

4.3.2.2 Optimization of adsorbent mass

The effect of varying the adsorbent mass, m_s is shown in Figs. 4.3.6 a-c. Figs. 4.3.6 a-c shows the plots of percentage removal and adsorption capacity verse mass of raw, Fenton's treated and acrylic acid grafted pine cone, respectively.

The graphs show that the percentage methylene blue removal increased as the adsorbent mass increased from 0.05 to 0.3 g, while the adsorbent capacity of methyl violet decreased as the adsorbent mass increased. It was observed that the percentage methylene blue removal from aqueous solution using 0.3 g of the adsorbent was highest for the acrylic acid grafted pine cone (99.44 %), Fenton's reagent treated pine

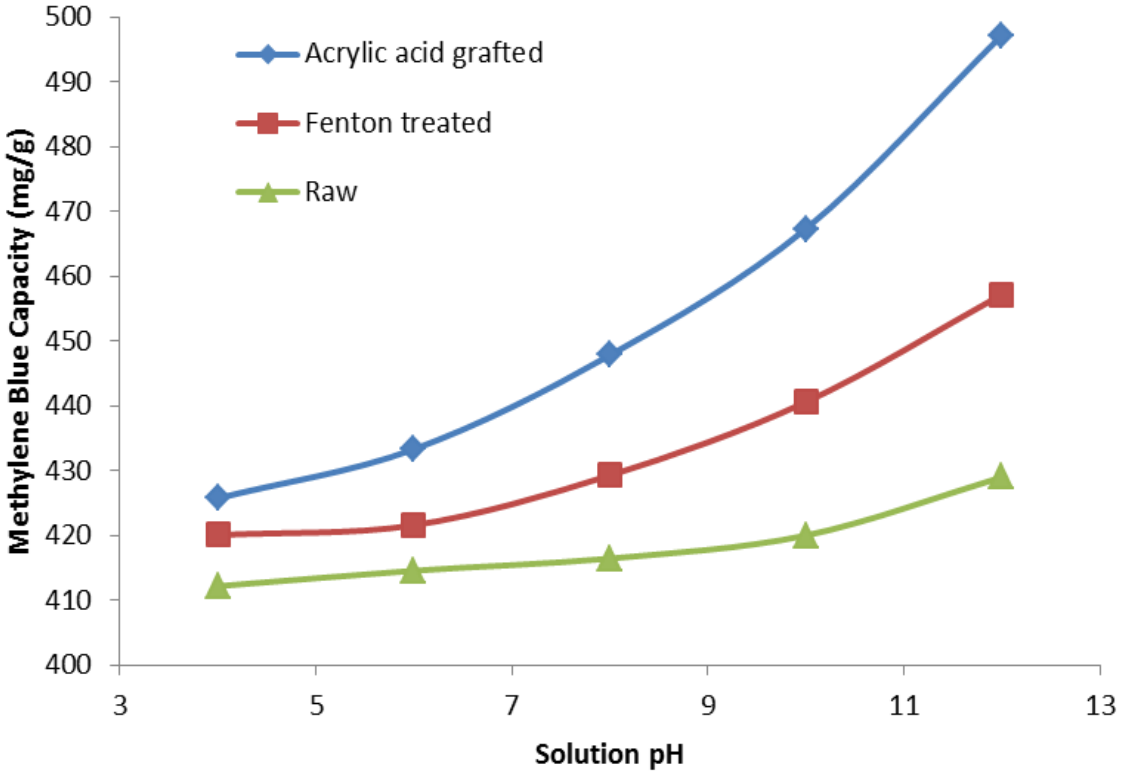

Fig. 4.3.5a: Plot of methylene blue percentage verses pH, for the adsorption of methylene blue onto raw, Fenton's treated and acrylic acid grafted pine cone.

cone (91.44 %) and raw pine cone (90.65 %) of the methyl blue dye from aqueous solution.

The adsorbent mass on the other hand, reduced from 1632.72 to 625.66 mg/g for the raw pine, from 1672 to 297.60 mg/g for the Fenton's treated pine and from 882 to164.72 mg/g for the acrylic acid grafted pine cone powder.

4.3.2.3 Percentage MB removals from aqueous solution

The graphs in Figs. 4.3.7a-c show the percentage Methylene blue removal from aqueous solution verse time. It was observed that as the time of contact increased, the percentage Methylene blue removal also increased rapidly at the initial stage and gradually reduced onto until equilibrium was established. Two sections were observed in the plots; at contact times from 0.5 to 3 min, there is a sharp increase, while from 10 to 60 min there is a slow increase in percentage removal. For the initial contact time, for example at 0.5 min of contact using the raw pine cone, it is observed that there was a percentage removal of 67.52 % to 97.1 % removal of methylene blue removed from solutions of methylene blue of concentrations of 150, 200, 500, 700 and 900 mg/dm^3 respectively. With Fenton treated and acrylic acid treated adsorbent trend the same was observed.

The plots in Figs. 4.3.7a-c shows the percentage methylene blue versus time in (min) at 900 mg/dm^3 for raw pine, Fenton's treated and acrylic acid grafted. It is observed that raw pine had the least percentage removal, because of its smaller surface area due the presence of plant components occupying pore spaces and the limited amounts of acidic functional groups. Fenton's treated pine on the other hand a higher percentage methylene blue percentage removal than the raw pine because on extraction of plant organic components, the surface area of the pine increased, while the acrylic acid grafted sample displayed the highest methylene blue percentage removal due to the increase in carboxylic acid function grafted onto the pine material.

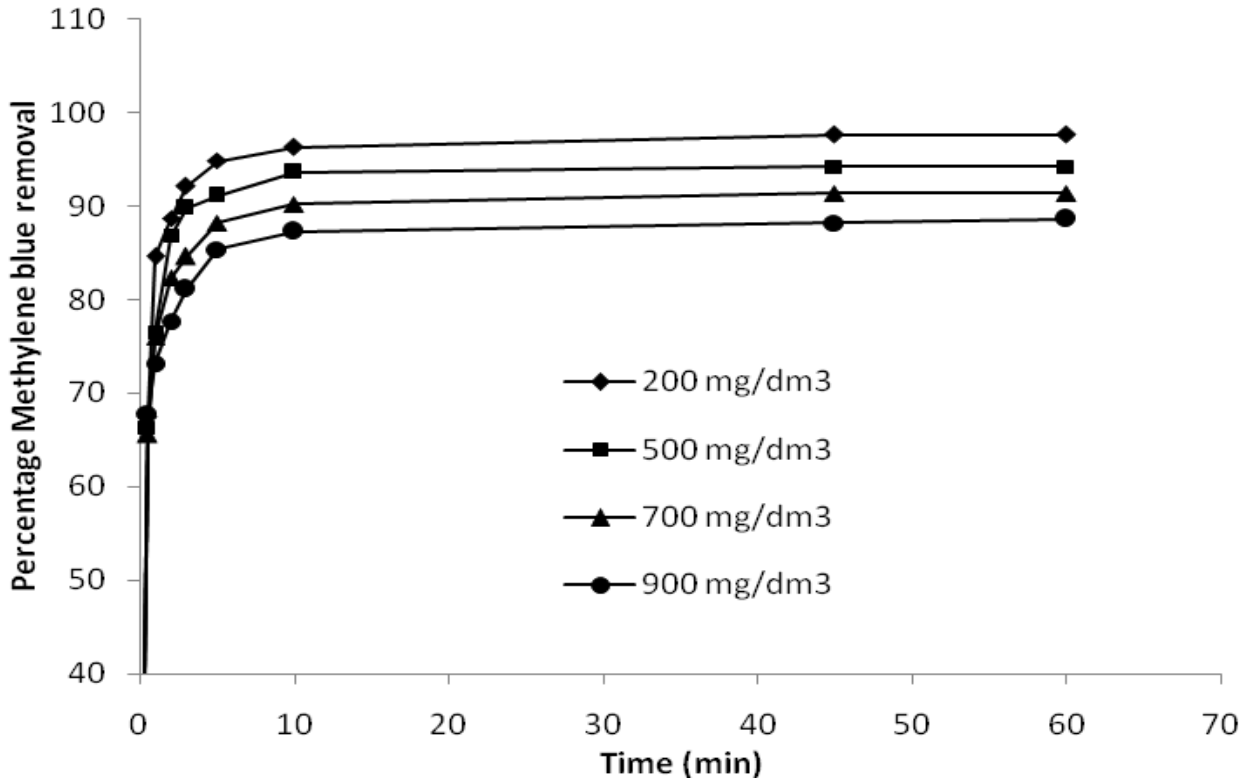

Fig. 4.3.7a: Plot of percentage MB removal at different time of contact using raw pine cone.

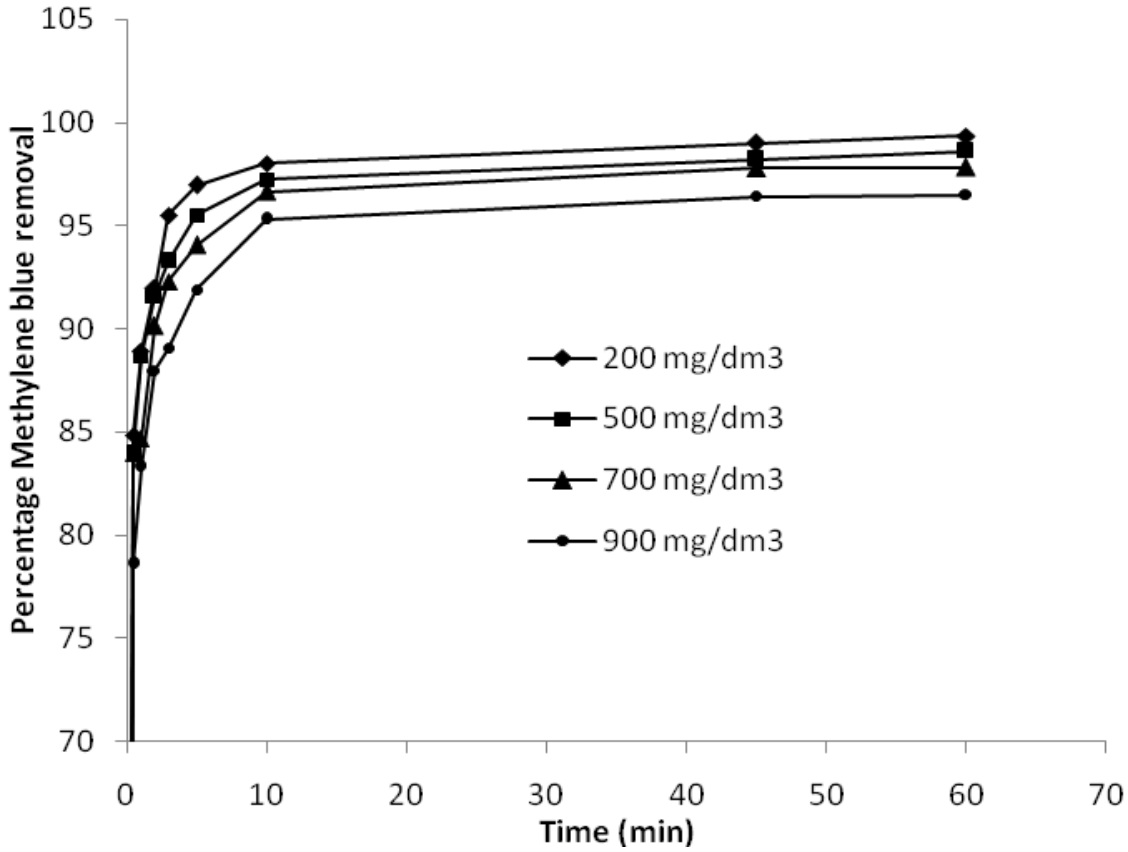

Fig.4.3.7b: Plot of percentage MB removal at different time of contact using Fenton's reagent treated pine cone.

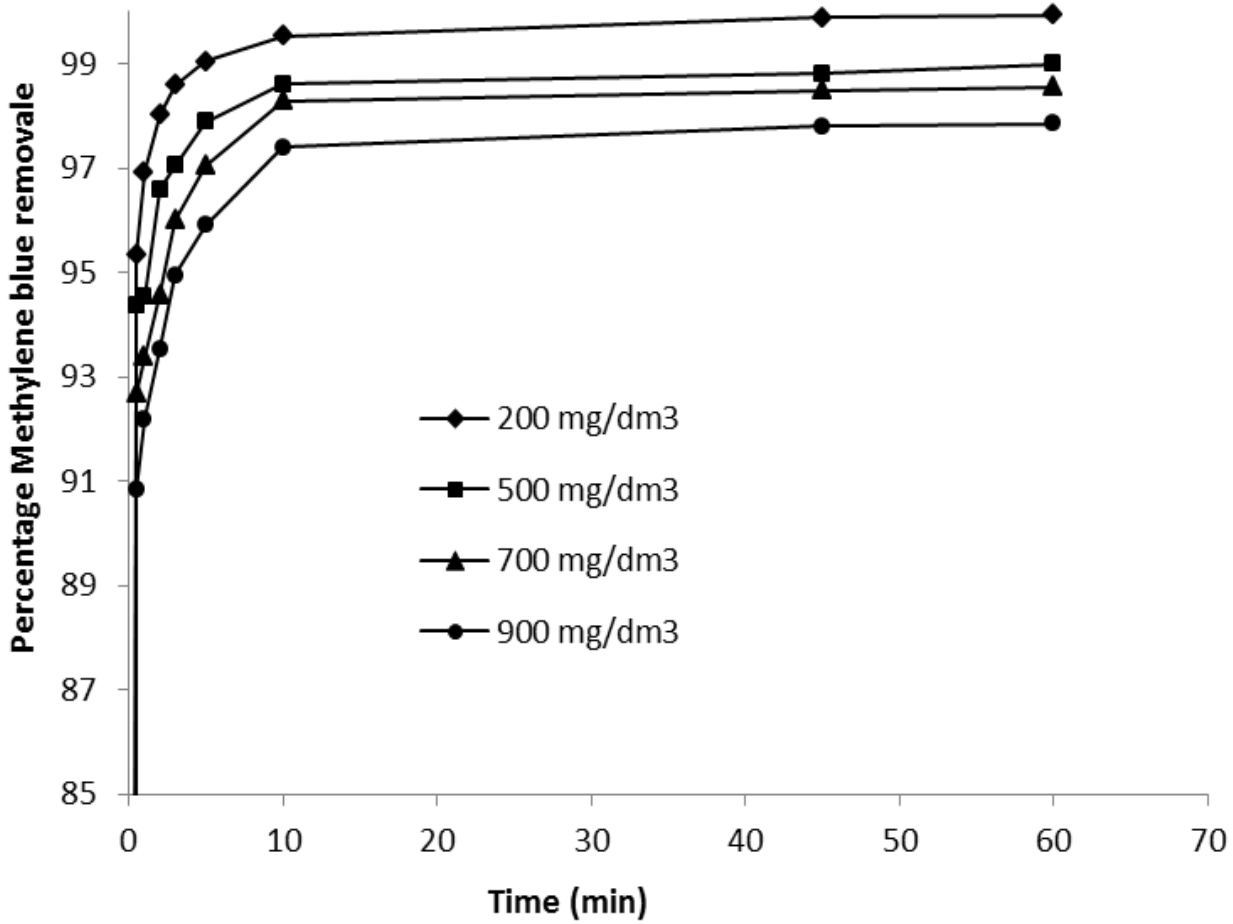

Fig.4. 3.7c: Plot of percentage MB removal at different time of contact using acrylic acid grafted pine cone.

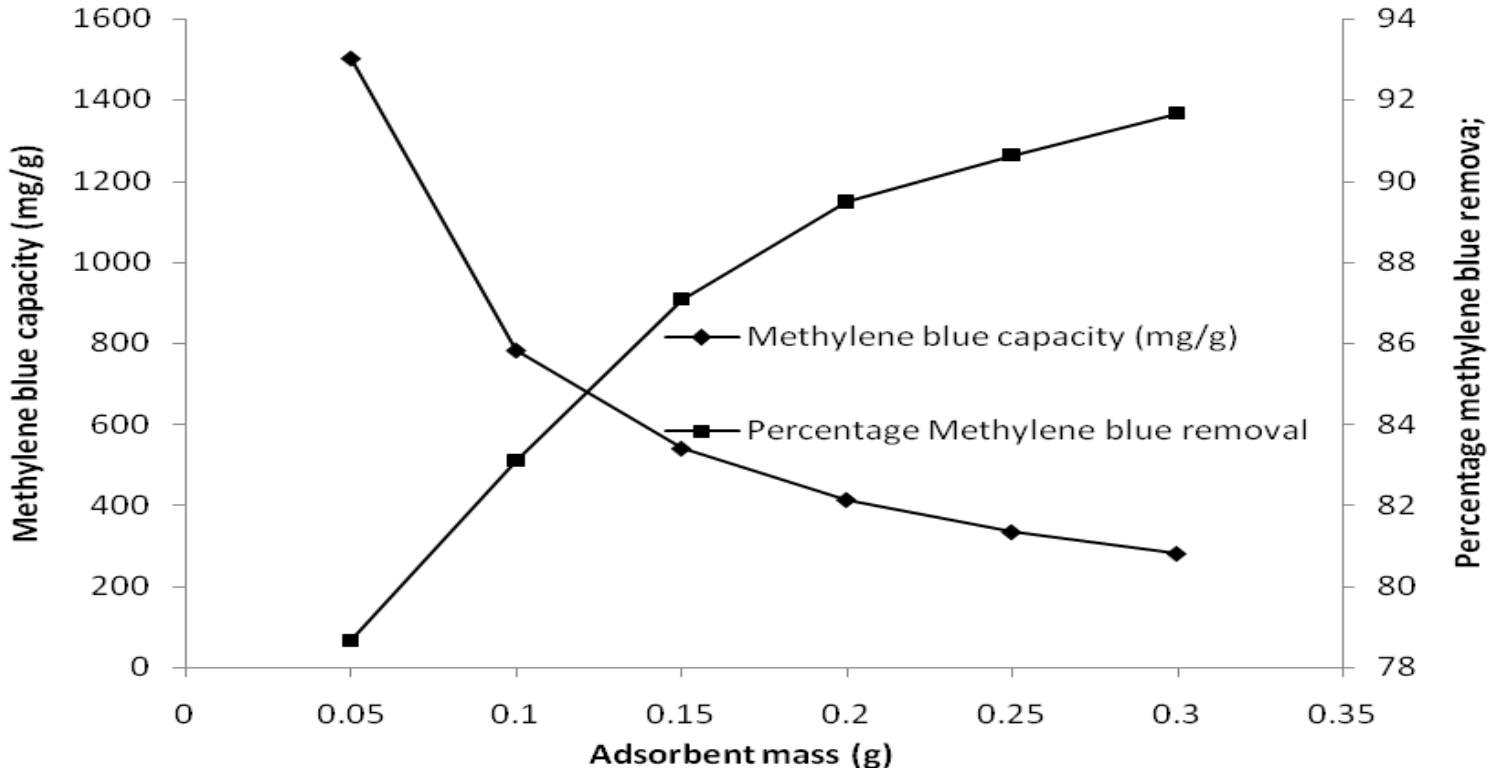

Fig. 4.3.8a: Effect of increasing raw pine cone mass on the adsorption capacity and percentage removal of methylene blue.

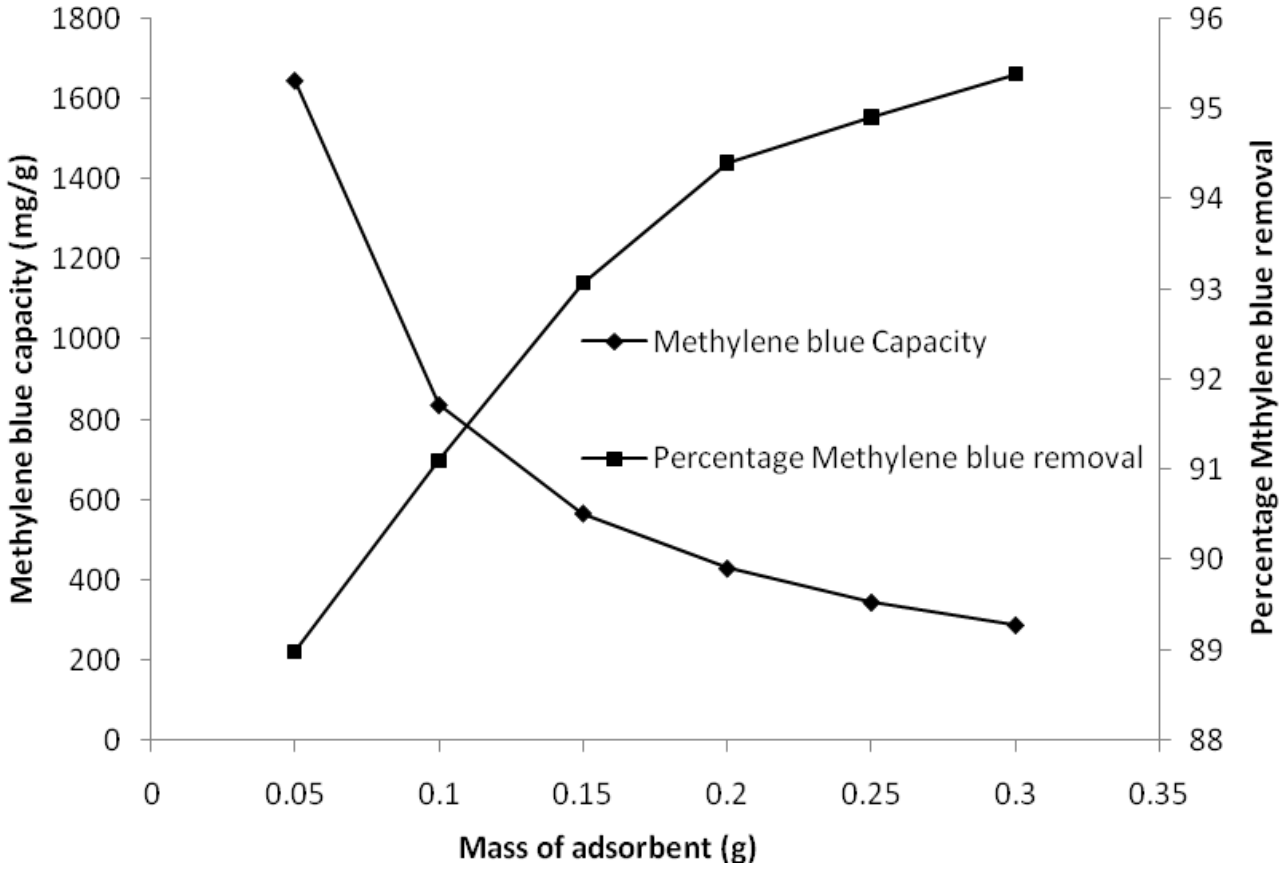

Fig. 4.3.8b: Effect of increasing Fenton's treated pine cone mass on the adsorption capacity and percentage removal of methylene blue.

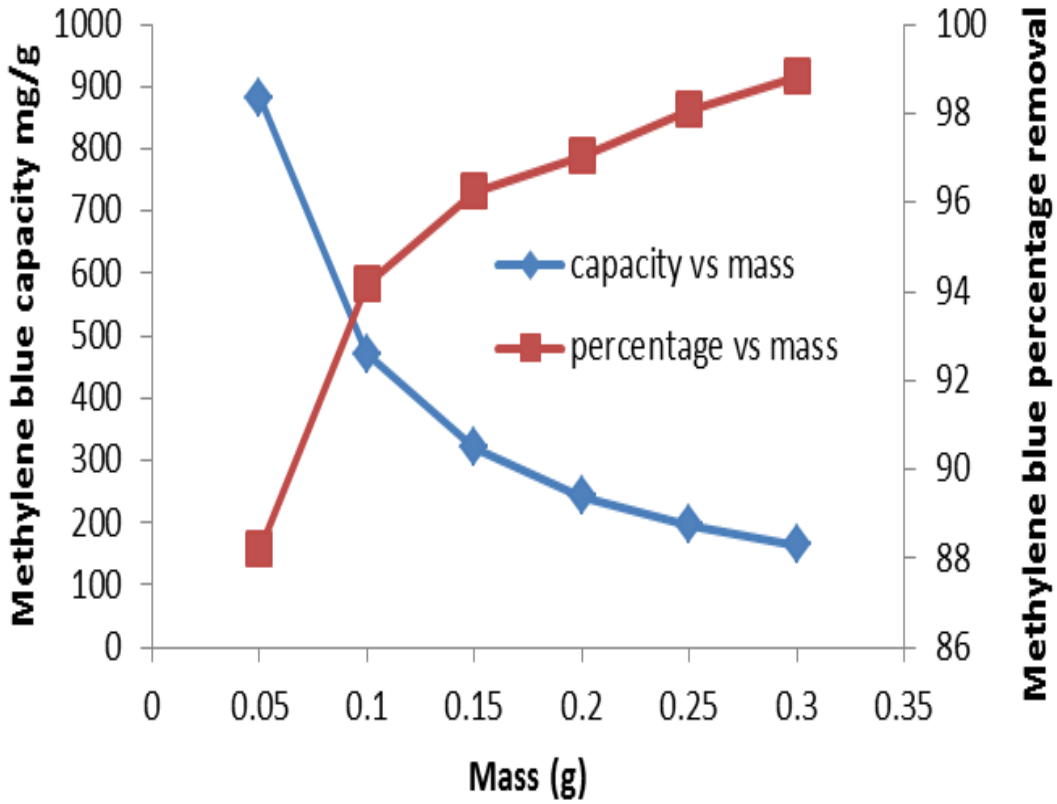

Fig. 4.3.8c: Effect of increasing acrylic acid grafted pine cone mass on the adsorption capacity and percentage removal of methylene blue.

4.4 ADSORPTION KINETICS

Kinetic data obtained from batch kinetic experiments of the adsorption of Methyl violet and Methylene blue onto raw, Fenton's treated and acrylic acid grafted pine cone was analyzed using the pseudo-first and pseudo-second order kinetic model.

4.4.1. Methyl violet (MV)

4.4.1.1 Pseudo-first order kinetic model

The pseudo first order kinetics data for adsorption of methyl violet onto treated pine cone, shown in Figs. 4.4.1. a-c. Figs. 4.4.1.a-c represents the relationship of log (q_e-q_t) verses time in minutes.

From Figs. 4.4.1. a-c, it was observed that the experimental data all lie on the straight line for 0.5 to 3 min of contact for all initial methyl violet concentrations and after 3 min of contact time i.e. from 10-60 min, the experimental data deviated from a straight line. Within this time period, it is believed that there is a switch in mechanism from film transfer diffusion control and pore diffusion control (Ofomaja and Ho, 2007). Thus pseudo first order is not appropriate to predict the experimental data.

Table 4.4.1 show the applicability of the pseudo-first order kinetic model to the experimental data generated for the adsorption removal of methyl violet onto raw, Fenton's treated and acrylic acid treated pine cone. Concentration ranged from 200 to 900mg/dm^3.The initial adsorption rate, h, pseudo-second order rate constant, k_2,amount of dyes adsorption at equilibrium, q_e, and the corresponding linear regression r^2 are given in Table 4.4.1. From the table it can be observed that increase in initial dye concentration caused an increase in the equilibrium adsorption capacity, q_e , and initial adsorption rate, h, but reduces the sorption rate, k_2. It is also observed from Table 4.4.1, that the values of r^2 for raw pine cone were found to range from 0.9695 to 0.9935 mg/g, which is relatively low. The plot show that there is a deviation from the straight line after the first 3min of adsorption for all initial methyl violet

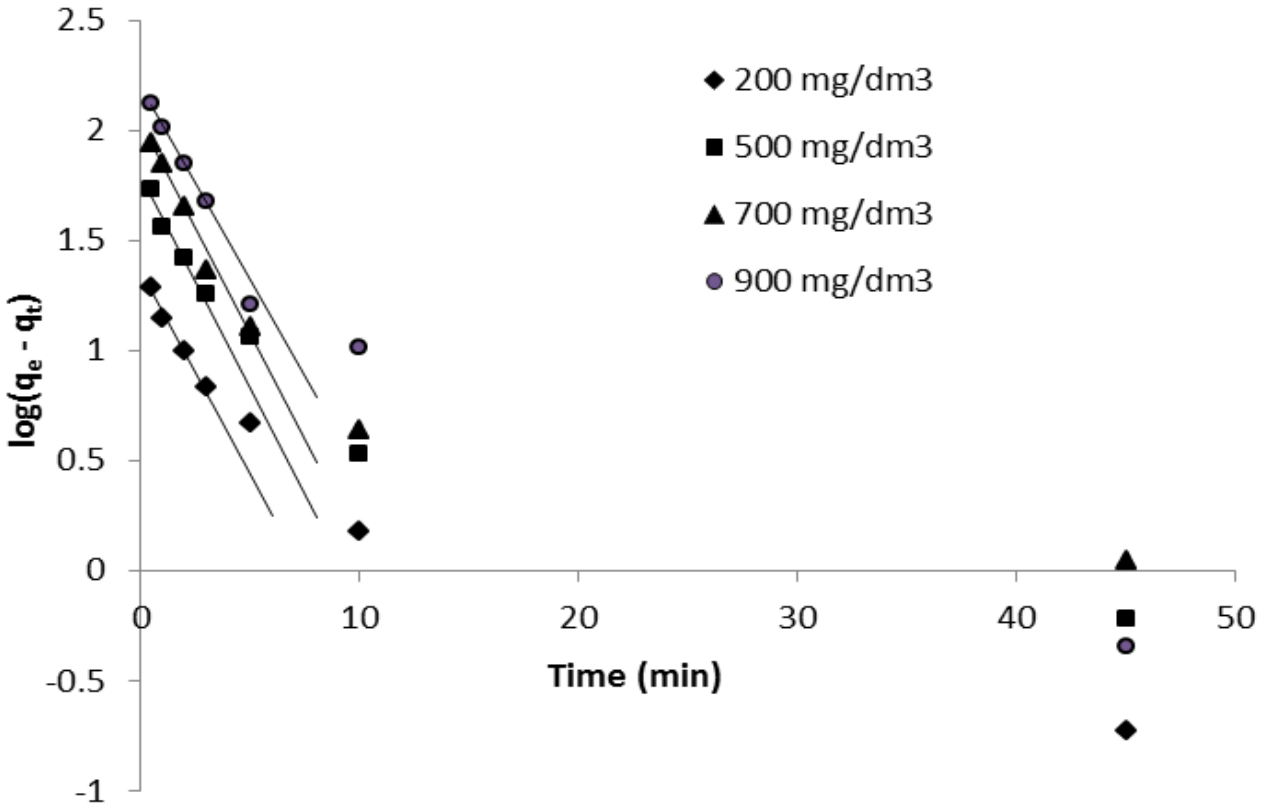

Fig.4.4.1.a: Pseudo first order kinetics data for adsorption of methyl violet onto raw pine, pine cone.

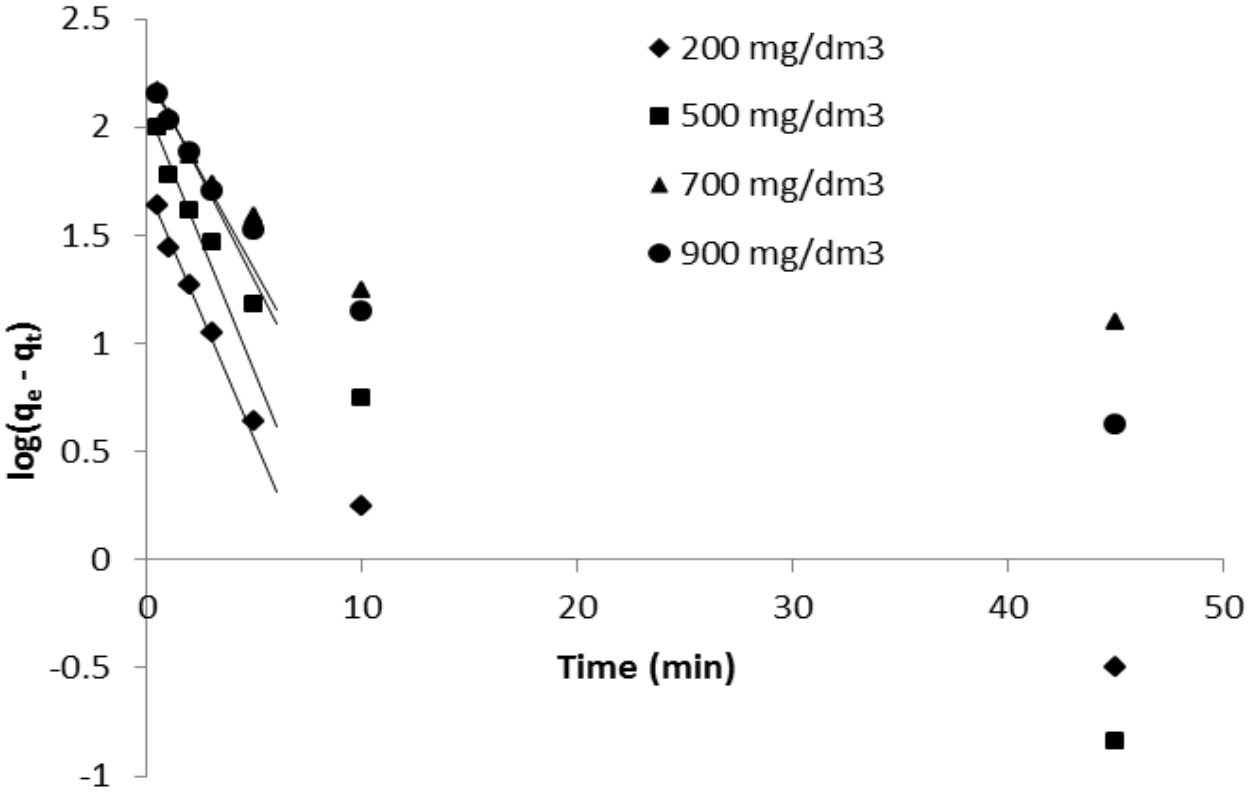

Fig.4.4.1b: Pseudo first order kinetics data for adsorption of methyl violet onto Fenton's reagent treated pine cone.

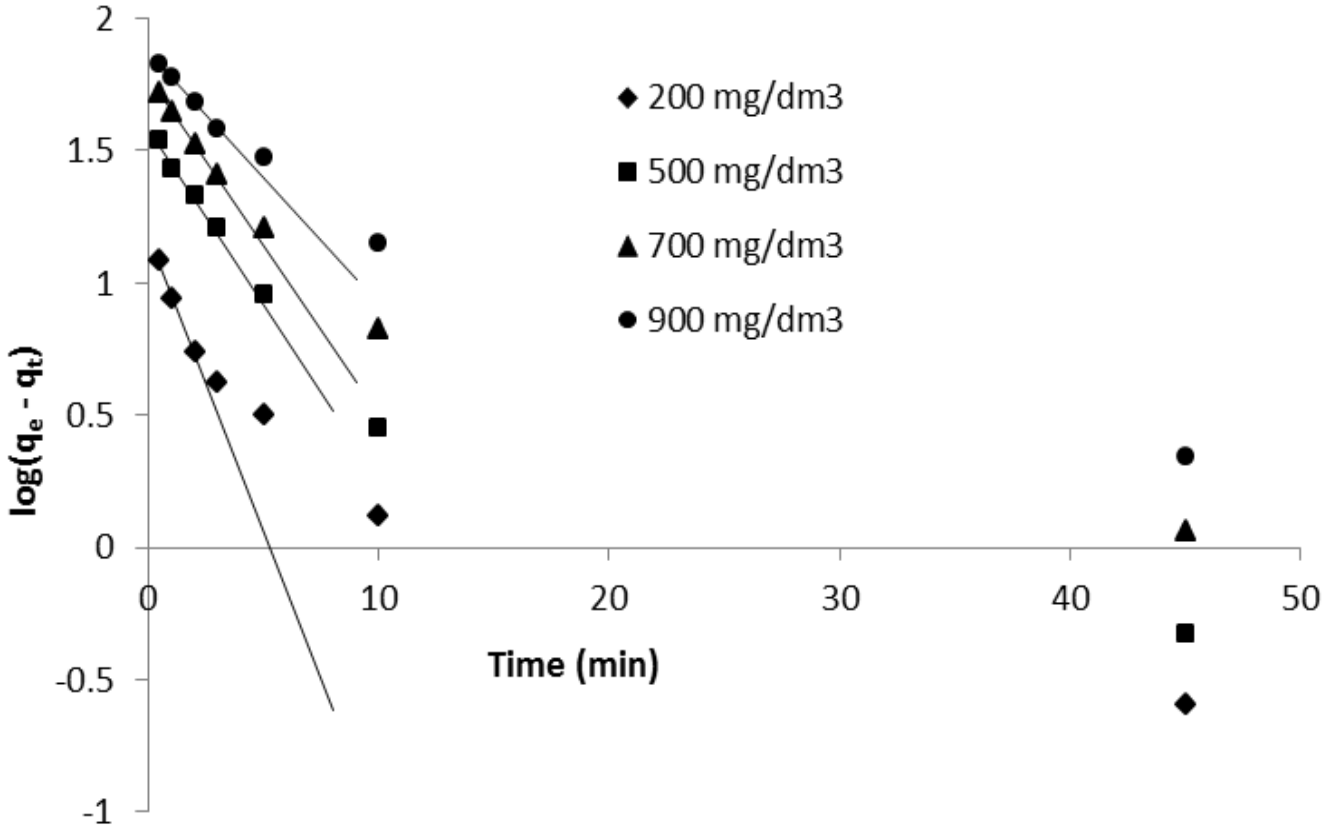

Fig.4.4.1c: Pseudo first order kinetics data for adsorption of methyl violet onto acrylic acid grafted pine cone grafted.

Table 4.4.1: Pseudo-first order parameters of adsorption of Methyl violet onto pine cone.

Sample	200 mg/dm^3	500 mg/dm	700 mg/dm^3	900 mg/dm^3
Raw pine				
q_e (mg/g) (*exp*)	127.96	308.68	423.38	526.44
q_e (mg/g)	50.16	93.54	183.19	151.43
k_1 (min^{-1})	0.4917	0.3938	0.2883	0.3222
r^2	0.9935	0.9905	0.9856	0.9695
χ^2	296.50	688.20	2426.70	928.50
Fenton's treated pine				
q_e (mg/g) (*exp*)	131.36	327.15	454.71	560.05
q_e (mg/g)	19.76	53.96	77.98	158.20
k_1 (min^{-1})	0.3072	0.3270	0.3374	0.4042
r^2	0.9578	0.9605	0.9793	0.9902
χ^2	965.60	2078.30	2619.70	2455.60
Acrylic acid grafted pine				
q_e (mg/g) (*exp*)	132.03	328.62	459.41	588.45
q_e (mg/g)	11.62	37.85	61.70	79.25
k_1 (min^{-1})	0.2895	0.2863	0.2761	0.2086
r^2	0.9998	0.9956	0.9865	0.9623
χ^2	1944.60	7088.50	4671.60	2297.00

concentrations, signifying that the pseudo-first order kinetics is not applicable for the first 3 min of adsorption. The calculated $q_{e\ exp}$ is far greater than the q_e, for example in acrylic acid grafted pine q_e (exp) increases from 132.03 to 588.45 mg/g, while q_e increases from 11.62 to 79.25 mg/g.

4.4.1.2 Pseudo-second order kinetic model

The pseudo second order kinetics data for adsorption of methyl violet onto raw, Fenton's treated and acrylic acid treated pine cone is shown in Fig 4.4.2a-c.Fig 4.4.2a-c represents the relationship of t/q_t verses time in min.

From the Figs 4.4.2a-c it was observed that the experimental data all lie on the straight line for 0.5-60 min with all the concentrations, thus the adsorption mechanisms obeys pseudo-second order kinetics. Table 4.4.2, shows the kinetic value calculated for the effect of adsorption removal of methyl violet onto raw, Fenton's treated and acrylic acid pine cone concentration ranging from 200 to 900 mg/dm^3.The initial adsorption rate, *h*, pseudo-second order rate constant, k_2 and amount of dye adsorbed at equilibrium, q_e , are given in Table 4.4.2. It is also observed that the values of r^2 were all close to 0.9999, which is much higher than r_2 for pseudo first order values. From the table it can be observed that increase in initial dye concentration caused an increase in equilibrium adsorption capacity, q_e and initial adsorption rate, *h*, but reduced the adsorption rate k_2 .It is observed that raw pine cone has the lowest increases, that is from 480.42 to 1414.19 mg/g (initial adsorption rate, *h*),while acrylic treated had the highest increases, that is 1432.15 to 3269.52 mg/g (initial adsorption rate).

The model values of equilibrium sorption, q_e, were found to be very close to the experimental values of equilibrium sorption, $q_{e\ exp}$, indicating the pseudo-second sufficiently describes the adsorption of methyl violet onto treated and untreated pine cone.The correlation coefficient, r^2 were all higher than 0.9999,which is much higher than r^2 (for pseudo-first order) values .The higher values of r_2 and the calculated values of equilibrium sorption capacity, q_e which is very much in agreement with experimental data for all initial methyl violet concentrations,confirms that the adsorption process follows a pseudo-second order mechanism.

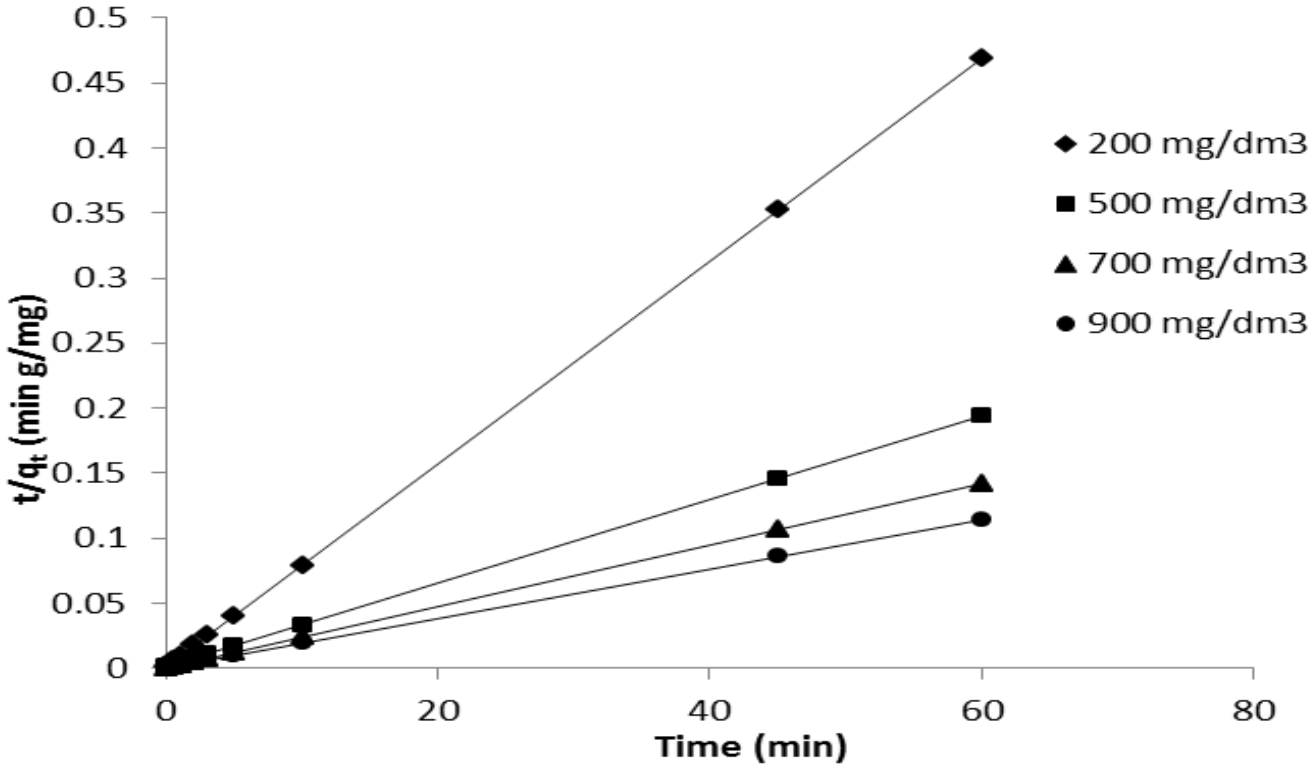

Fig.4.4.2a: Pseudo second order kinetics data for adsorption of methyl violet onto Raw pine cone.

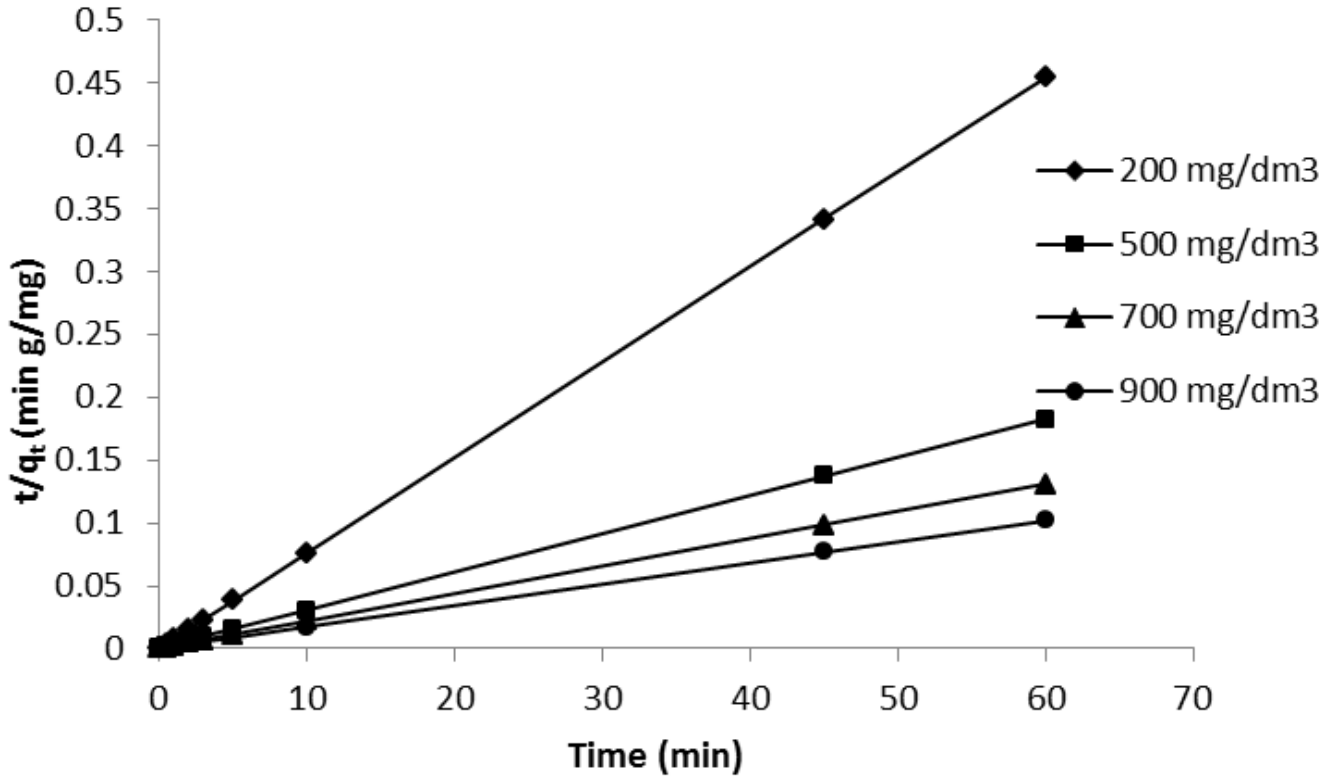

Fig.4.4.2b: Pseudo first order kinetics data for adsorption of methyl violet onto Fenton's treated pine cone grafted.

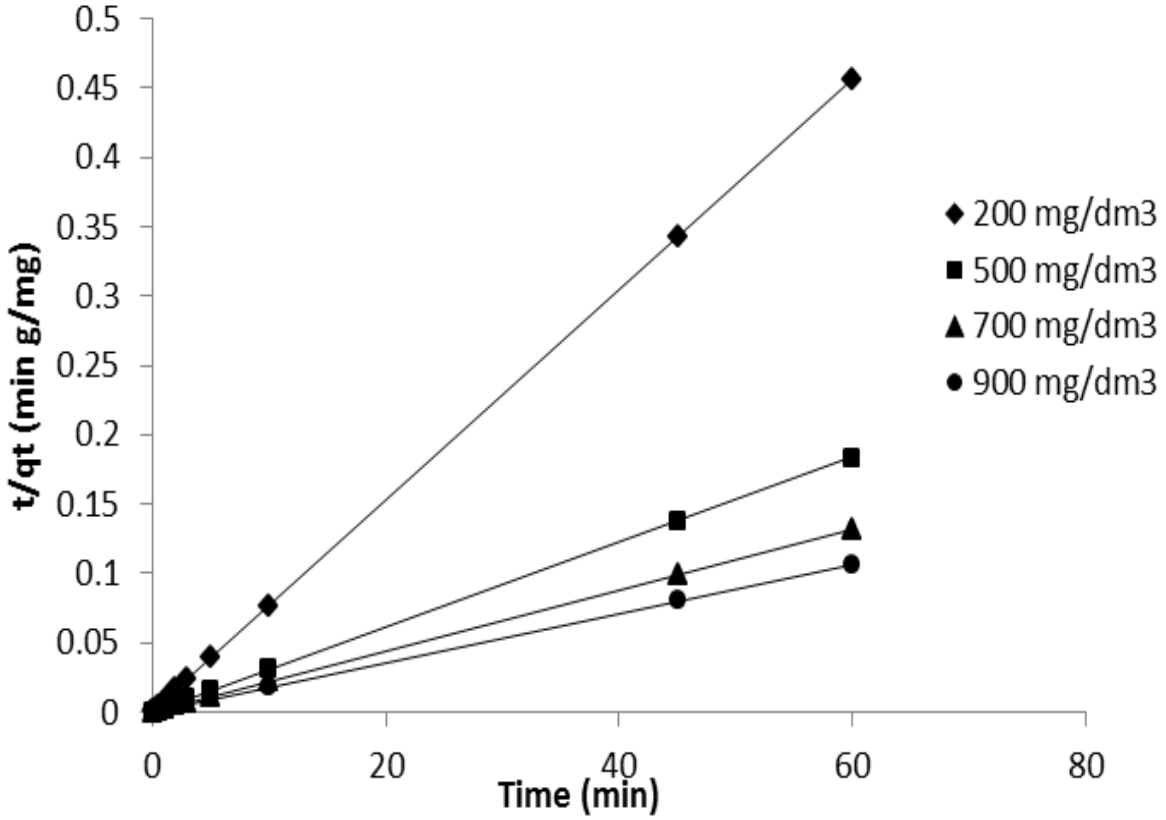

Fig.4.4.2c: Pseudo second order kinetics data for adsorption of methyl violet onto acrylic acid grafted pine cone grafted.

Table 4.4.2
Kinetic value calculated for the effect of initial concentration of methyl violet adsorption onto pine, Fenton's treated and acrylic acid pine cone,concentration of 200 to 900ppm at 10 pH.

Sample	200 mg/dm^3	500 mg/dm^3	700 mg/dm^3	900 mg/dm^3
Pseudo-second order				
Raw pine				
q_e (mg/g) (*exp*)	127.96	308.68	423.38	526.40
q_e (mg/g)	128.50	310.24	425.47	527.86
k_2 (g /mg min)	0.0291	0.0162	0.0076	0.0063
h (mg/g min)	480.42	1118.46	1368.98	1414.79
Fenton treated pine				
q_e (mg/g) (*exp*)	131.36	327.15	454.71	560.05
q_e (mg/g)	131.65	327.86	455.95	562.60
k_2 (g /mg min)	0.0513	0.0200	0.0113	0.0078
h (mg/g min)	888.89	2147.05	2346.10	2479.10
Acrylic acid grafted pine				
q_e (mg/g) (*exp*)	132.03	328.62	459.41	588.45
q_e (mg/g)	132.15	329.17	460.21	589.37
k_2 (g /mg min)	0.0820	0.0257	0.0148	0.0098
h (mg/g min)	1432.15	2780.32	3130.2	3269.52

4.4.2 Methylene blue

4.4.2.1 Pseudo-first order kinetic model

From Figure 4.4.3 a-c, it was observed that the experimental data all lie on the straight line from 0.5 to 3 min of contact for all initial methylene blue concentrations and after 3 min of contact i.e. from 10-60 min, the experimental data deviated from a straight line.

Within this time period, it is believed that there is a switch between film transfer diffusion control and pore diffusion control (Ofomaja and Ho, 2007). Thus pseudo first order is not fit to predict the experimental data. Table 4.4.2 shows the applicability of the pseudo-first order kinetic model to the experimental data generated for the adsorption removal of methylene blue onto raw, Fenton's treated and acrylic acid treated pine cone. Concentration ranging from 200 to 900 mg/dm^3.The initial adsorption rate, h, pseudo-second order rate constant ,k_2,amount of dyes adsorption at equilibrium, q_e, and the corresponding linear regression r_2 are given in Table 4.4.3

From table 4.4.2.1a it can be observed that increase in initial dye concentration caused an increase in the equilibrium adsorption capacity, q_e and initial adsorption rate, h, but reduces the sorption rate, k_2. It is also observed from Table 4.4.2.1, that the values of r^2 for raw pine cone were found to range from 0.9368 to 0.9975 mg/g, which is relatively low. The plot show that there is a deviation from the straight line after the first 3 min of adsorption for all initial methylene blue concentration, signifying that the pseudo-first order kinetics is not applicable for the first 3 min of adsorption. The calculated q_e (experimental) is far greater than the q_e, for example in acrylic acid grafted pine q_e (exp) increases from 133.25 to 587.11 mg/g, while q_e increases from 5.96 to 47.91 mg/g.

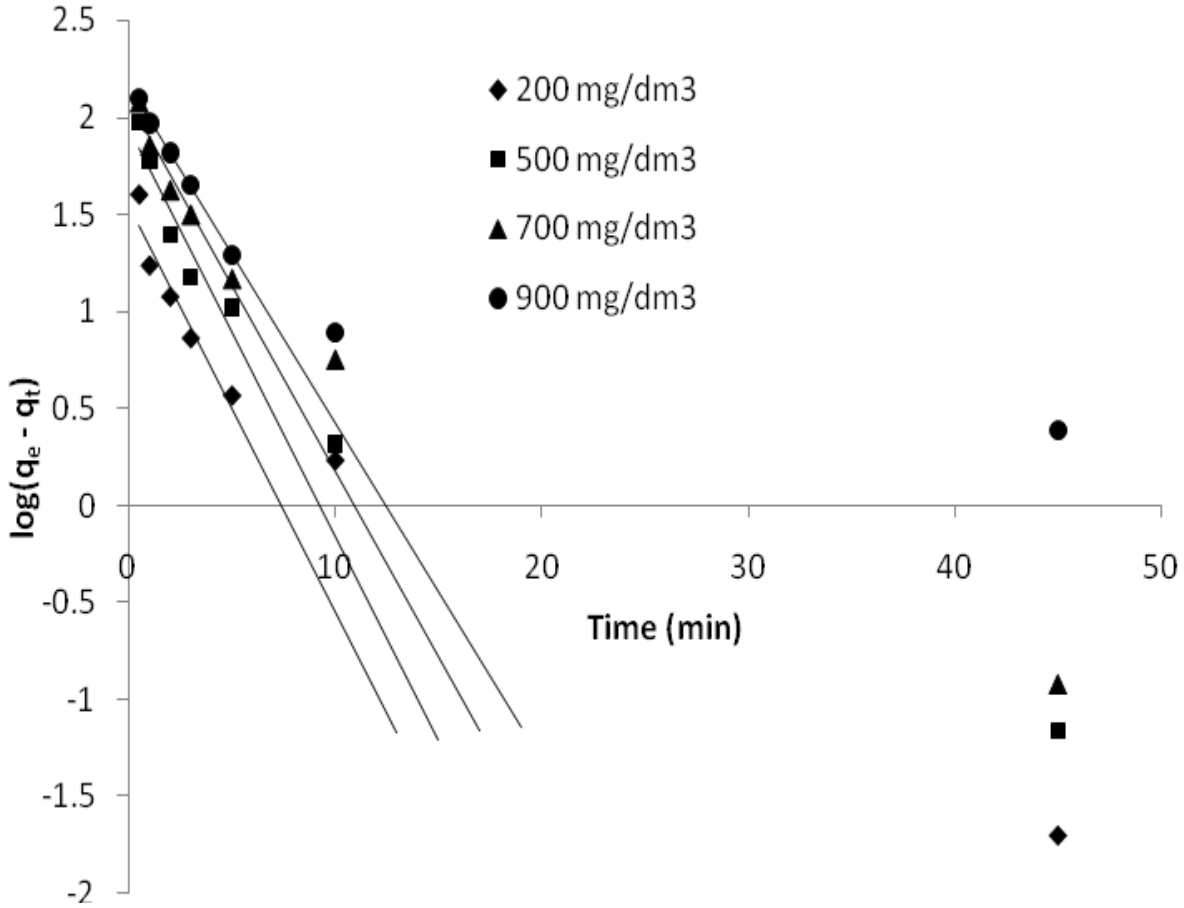

Fig.4.4.3.a: Pseudo first order kinetics data for adsorption of methylene blue onto raw pine, pine cone.

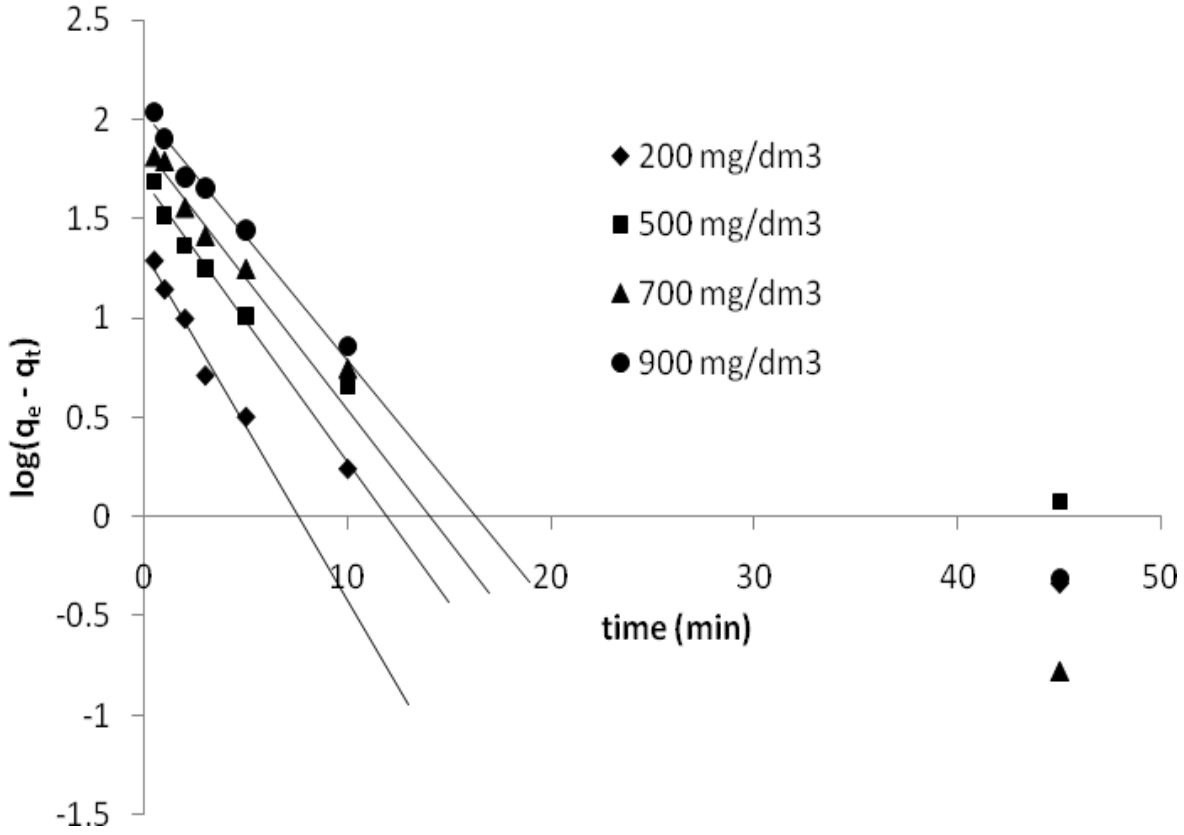

Fig.4.4.3b: Pseudo first order kinetics data for adsorption of methylene blue onto Fenton's reagent treated pine cone.

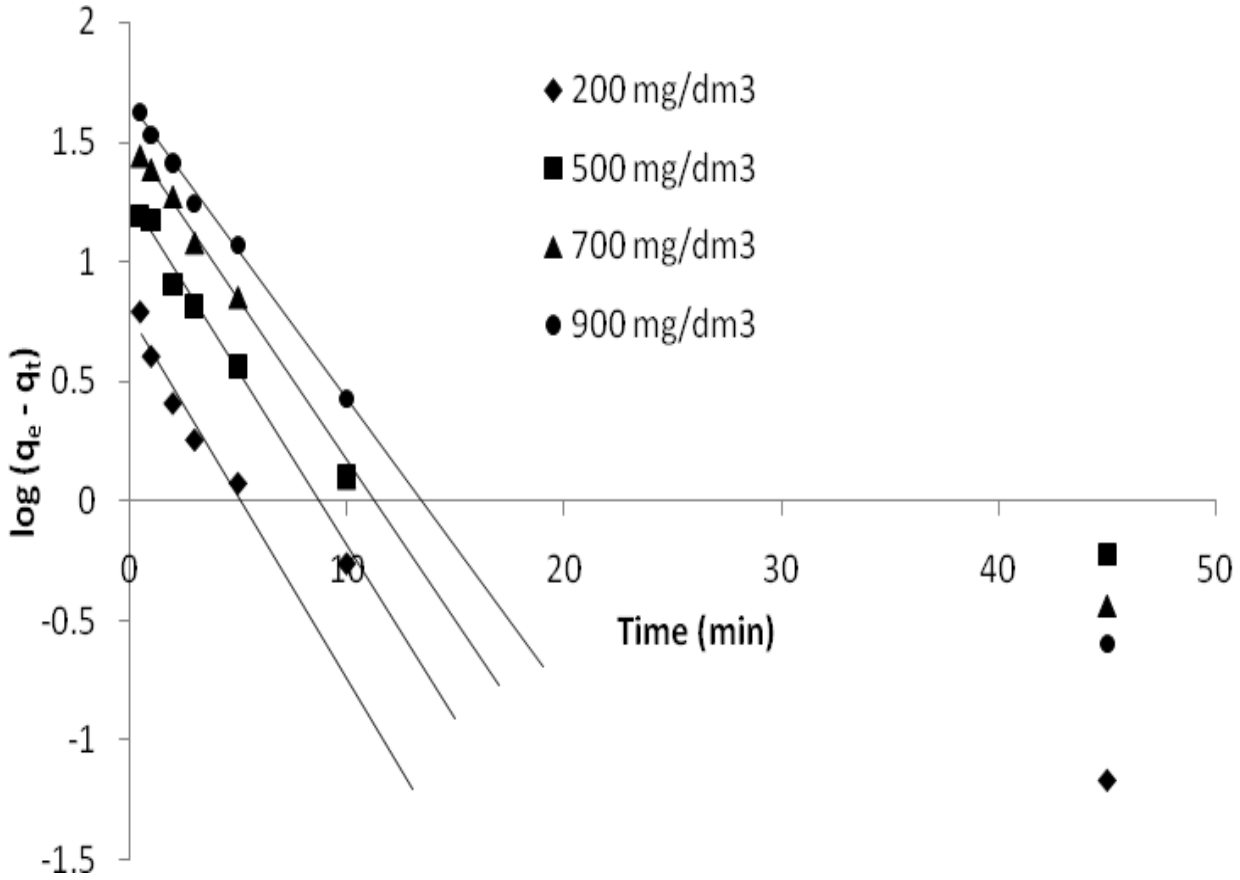

Fig.4.4.3c: Pseudo first order kinetics data for adsorption of methylene blue onto acrylic acid grafted pine cone grafted.

Table 4.4.3.
Pseudo-first order parameters of adsorption of Methylene blue onto pine cone.

	200 mg/dm^3	500 mg/dm	700 mg/dm3	900mg/dm^3
Pseudo-first order				
Raw pine				
q_e (mg/g) (*exp*)	130.15	314.15	426.59	531.69
q_e (mg/g)	35.95	89.07	121.80	146.22
k_1 (min^{-1})	0.5219	0.4851	0.4390	0.4004
r^2	0.9368	0.889	0.9649	0.9975
x^2	321.328	759.32	2824.91	1442.12
Fenton treated pine				
Pseudo-first order				
q_e (mg/g) (*exp*)	132.45	328.63	456.54	578.98
q_e (mg/g)	21.45	49.11	73.65	107.49
k_1 (min^{-1})	0.3912	0.3250	0.3050	0.2861
r^2	0.9666	0.9697	0.9566	0.9865
x^2	1222.36	2002.77	8746.17	3236.79
Acrylic acid grafted pine				
Pseudo-first order				
q_e (mg/g) (*exp*)	133.25	329.97	459.96	587.11
q_e (mg/g)	5.96	18.19	32.57	45.71
k_1 (min^{-1})	0.3501	0.3324	0.3093	0.2846
r^2	0.9366	0.9686	0.9922	0.9816
x^2	4077.95	8014.6	32398.45	10074.99

4.4.2.2 Pseudo-second order model

The pseudo second order kinetics data for adsorption of methylene blue onto raw, Fenton's treated and acrylic acid treated pine cone is shown in Fig 4.4.4a-c.Fig 4.4.4a-c represents the relationship of t/q_t verses time in min.

From the Fig 4.4.4a-c it was observed that the experimental data all lie on the straight line from 0.5-60 min with all the concentrations, thus the adsorption mechanisms obeys pseudo-second order kinetics. Table 4.4.4, shows the kinetic value calculated for the effect of adsorption removal of methylene blue onto raw, Fenton's treated and acrylic acid pine cone concentration ranging from 200 to 900 mg/dm^3.The initial adsorption rate, *h*, pseudo-second order rate constant, k_2 and amount of dye adsorbed at equilibrium, q_e , are given in Table 4.4.4. It is also observed that the values of r^2 were all close to 1, which is much higher than r^2 for pseudo first order values. From the table it can be observed that increase in initial dye concentration caused an increase in equilibrium adsorption capacity, q_e ,and initial adsorption rate ,*h*, but reduces the adsorption rate k_2. It is observed that raw pine cone has the lowest increases, that is 702.00 to 2360 mg/g (initial adsorption rate, *h*),while acrylic treated has the highest increases, that is 3449.85 to 7690.21 mg/g (initial adsorption rate ,*h*).

The model values of equilibrium sorption, q_e, were found to be very close to the experimental values of equilibrium sorption, $q_{e\ exp}$, indicating the pseudo-second order sufficiently describes the adsorption of methylene blue onto treated and untreated pine cone.The correlation coefficient, r^2 were all higher than 0.9999 (Table 4.4.2b), which is much higher than r^2 (for pseudo-first order) values .The higher values of r^2 and the calculated values of equilibrium sorption capacity ,q_e, which is very much in agreement with experimental data for all initial methylene blue concentrations, confirms that the adsorption process follows a pseudo-second order mechanism.

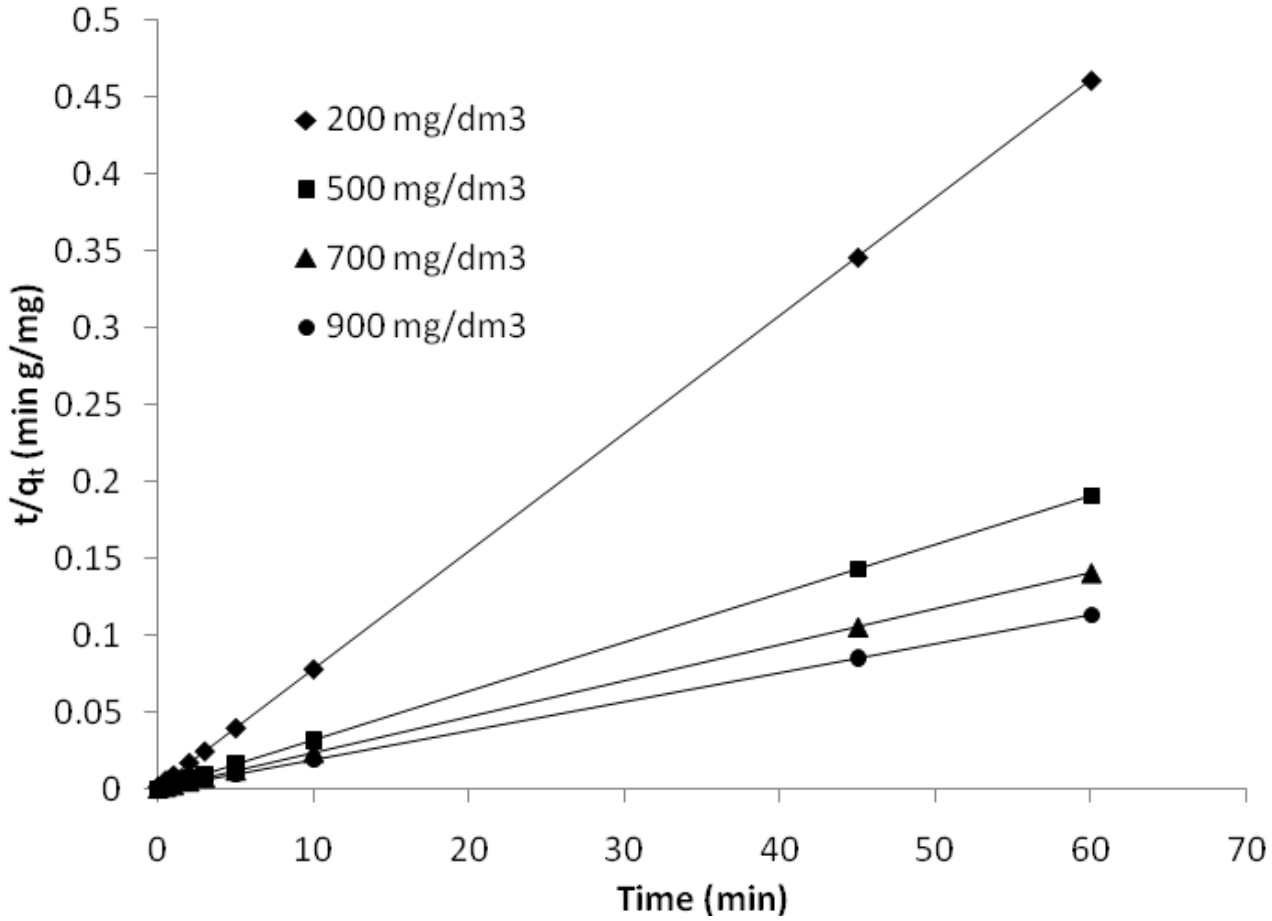

Fig.4.4.4a: Pseudo second order kinetics data for adsorption of MB onto Raw pine cone.

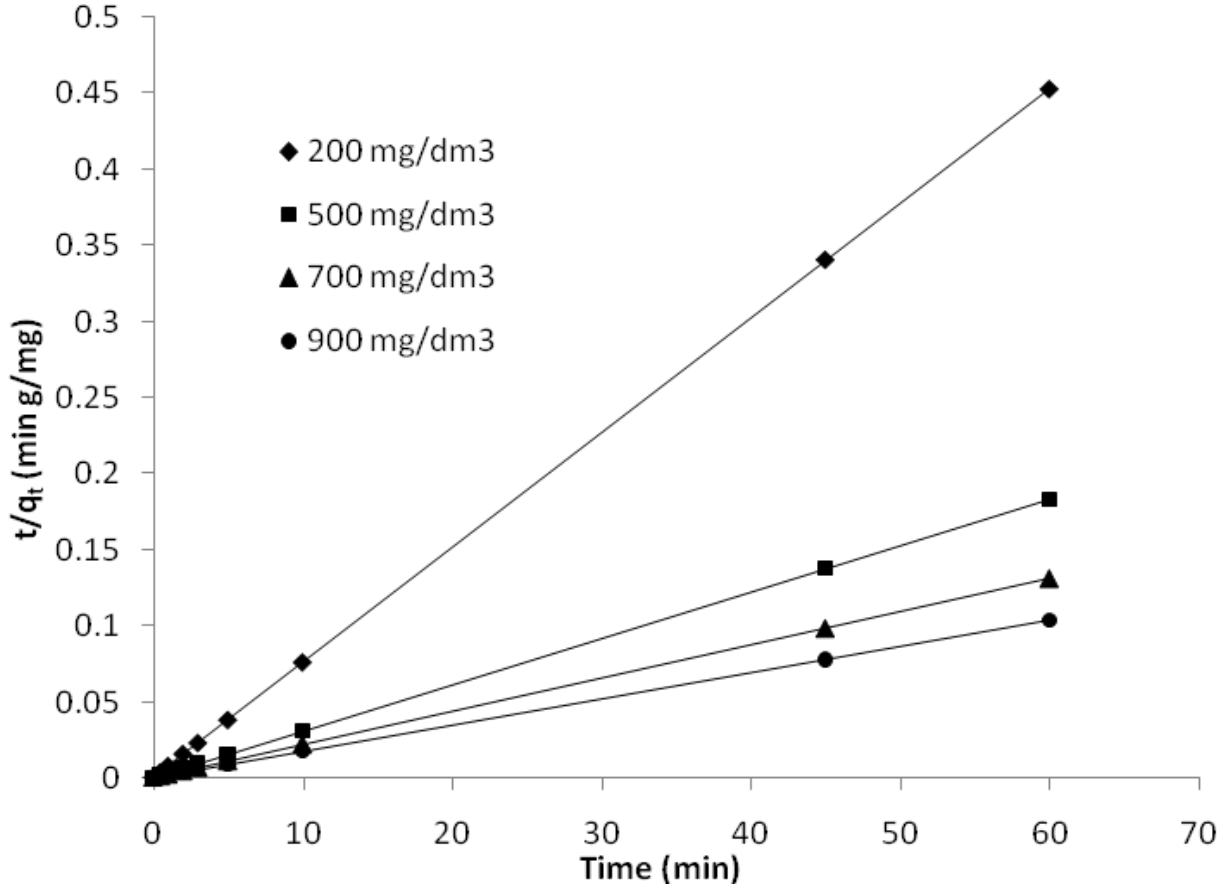

Fig.4.4.4b: Pseudo first order kinetics data for adsorption of MB onto Fenton's treated pine cone grafted.

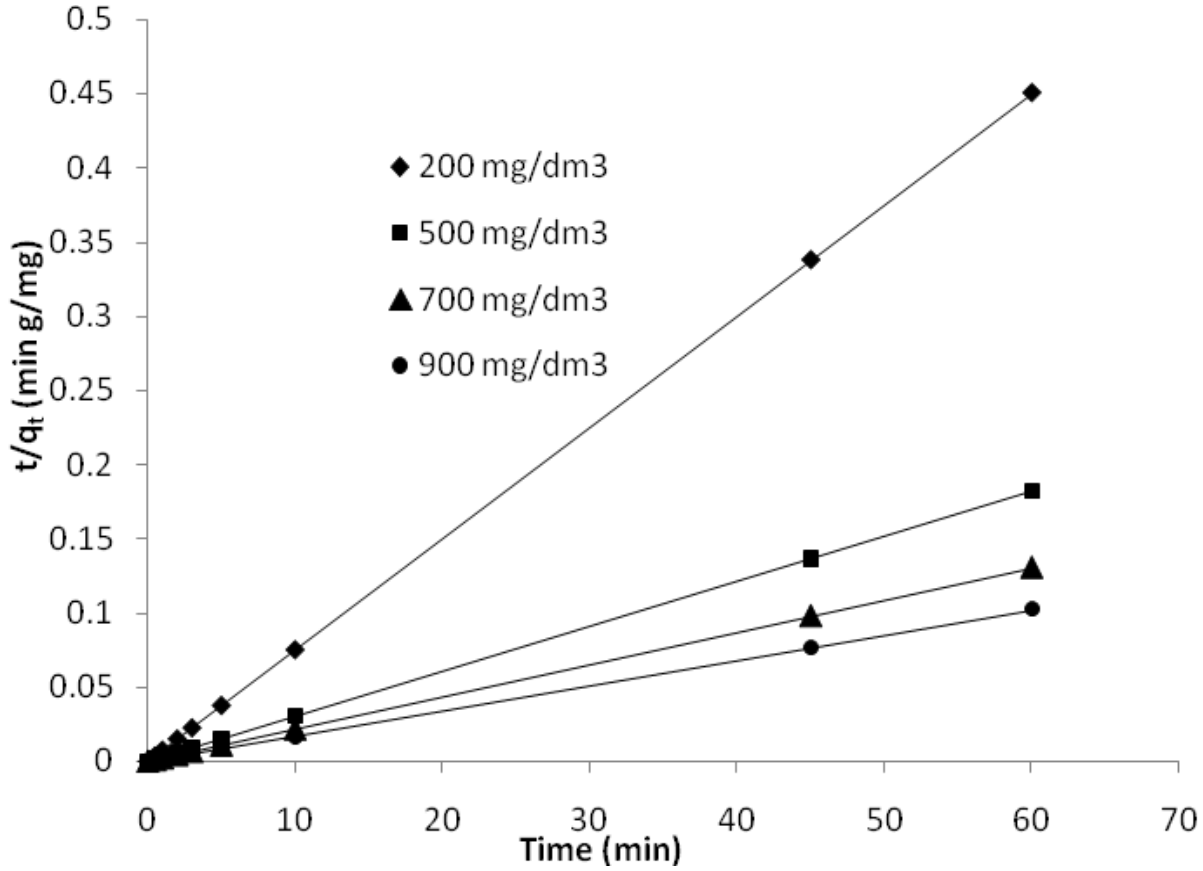

Fig.4.4.4c: Pseudo second order kinetics data for adsorption of MB onto acrylic acid grafted pine cone grafted.

Table 4.4.4: Kinetic value calculated for the effect of initial concentration of methylene blue adsorption onto pine, Fenton's treated and acrylic acid pine cone, concentration of 200 to 900ppm at 12 pH.

	200 mg/dm^3	500 mg/dm	700 mg/dm3	900mg/dm^3
Pseudo-second order				
Raw pine				
q_e (mg/g) (*exp*)	130.15	314.15	426.59	531.69
q_e (mg/g)	130.59	315.23	428.24	533.07
k_2 (g /mg min)	0.0413	0.0175	0.0111	0.0083
h (mg/g min)	702.00	1739.68	2036.18	2360.57
r^2	1.000	1.000	1.000	1.000
x^2	0.0385	0.1120	0.0208	0.9879
Fenton treated pine				
Pseudo-second order				
q_e (mg/g) (*exp*)	132.45	328.63	456.54	578.98
q_e (mg/g)	132.60	329.65	457.83	580.88
k_2 (g /mg min)	0.0577	0.0209	0.0135	0.0089
h (mg/g min)	1015.04	2264.32	2838.21	3000.10
r^2	1.000	1.000	1.000	1.000
x^2	0.0359	0.2922	0.6259	0.7434
Acrylic acid pine				
Pseudo-second order				
q_e (mg/g) (*exp*)	133.25	329.97	459.96	587.11
q_e (mg/g)	132.35	330.05	460.38	587.85
k_2 (g /mg min)	0.1941	0.0621	0.0341	0.0223
h (mg/g min)	3449.85	6760.43	7227.52	7690.21
r^2	1.000	1.000	1.000	1.000
x^2	0.6116	0.0751	0.1756	0.2942

4.5 EQUILIBRUIM BIOSORPTION

4.5.1 Methyl violet

4.5.1.1 Langmuir and Freundlich isotherm

Tables 4.5.1 a-c shows the Langmuir's parameters for raw, Fenton treated and acrylic acid grafted pine cone. From Tables 4.5.1 a-c it was observed that, the capacities for each sample increase as the temperature of the experiment increases. Comparing the raw with the Fenton treated and acrylic grafted pine cone, the raw pine cone has a lower capacity than Fenton treated and acrylic acid grafted pine cone. Acrylic acid grafted pine cone has more sites to hold the adsorbate as compared to the raw pine cone and Fenton treated. For each sample, the constant equilibrium increases as the temperature of the experiment increases. It is also observed that the raw pine cone has lower equilibrium constant than Fenton treated and acrylic acid grafted pine cone. This is due to strong bonds formed between acrylic acid grafted pine cone with the adsorbate as compared to raw pine cone and Fenton's reagent. The r^2 values of all three experiments are close to 1.0 and the x^2 values are lower. For raw pine cone, the x^2 values were between 0.2861 to 0.6516,while for r^2 ,they were between 0.9945 to 0.9982. For Acrylic acid treated pine cone, the x^2 values were between, 0.0542 to 0.3669 and r^2 were between 0.9974 to 0.9994,thus showing that the Langmuir isotherm properly describes the experimental data and that the sample surfaces are homogeneous.

Table 4.5.1.a-c, the Freundlich isotherm constants, 1/n and K_F, were calculated for methyl violet adsorption according to Eq.

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (4.5.1)$$

The Freundlich constant K_F indicate the adsorption capacity of the adsorbent while Freundlich constant *n* is a measure of the deviation from linearity of the adsorption or the adsorption affinity of the adsorbent for the adsorbate. The values of 1/*n* for methyl violet adsorption on to adsorbent for all samples were between $0.1 < 1/n < 1$, indicating that methyl violet adsorption onto all samples is favourable at 299 K. The value of K_f for the adsorption of methyl violet using acrylic acid was found to be higher than that of raw and Fenton's reagent treated pine cone. The value of K_f is indicative of the adsorption capacity.

Table 4.5.1. a:
Isotherm parameters for the adsorption of methyl violet onto raw pine cone at different temperatures.

Isotherm	Parameters	*T (K)*	289	303	308	313	318
Langmuir	q_m, mg/g		620.65	630.69	640.15	651.01	657.93
	K_a, dm^3/mg		0.0367	0.0382	0.0395	0.0425	0.0436
	r^2		0.9982	0.9968	0.9947	0.9960	0.9945
	χ^2		0.2861	0.4587	0.6903	0.4509	0.6515
Freundlich							
	n		2.1199	2.1125	2.1059	2.0828	2.0711
	K_F		57.494	59.2896	60.9295	63.0282	64.0044
	r^2		0.9776	0.9823	0.9850	0.9880	0.9884
	χ^2		2.9137	2.3288	1.5592	1.5838	1.3828

Table 4.5.1.b:
Isotherm parameters for the adsorption of methyl violet onto Fenton's reagent treated pine cone at different temperatures.

Isotherm	Parameters	*T (K)*	289	303	308	313	318
Langmuir	q_m, mg/g		661.45	667.43	674.18	680.41	690.03
	K_a, dm^3/mg		0.0972	0.1047	0.1036	0.1092	0.1217
	r^2		0.9922	0.9988	0.9982	0.9992	0.9961
	χ^2		0.2467	0.2444	0.3093	0.1371	0.5691
Freundlich							
	n		2.1484	2.1500	2.1237	2.0929	2.0896
	K_F		96.961	101.404	100.85	102.83	110.03
	r^2		0.9472	0.9613	0.9647	0.9776	0.9718
	χ^2		6.2154	4.6806	4.0788	5.2845	5.1022

Table 4.5.1.c:
Isotherm parameters for the adsorption of methyl violet onto acrylic acid grafted pine cone at different temperatures.

Isotherm	Parameters	*T(K)*	289	303	308	313	318
Langmuir	q_m, mg/g		815.60	820.88	835.59	843.30	856.25
	K_a, dm^3/mg		0.1487	0.1608	0.1642	0.1673	0.1714
	r^2		0.9974	0.9994	0.9990	0.9994	0.9977
	χ^2		0.3669	0.0865	0.0542	0.1815	0.1048
Freundlich							
	n		1.7101	1.7112	1.6910	1.6484	1.6686
	K_F		122.88	129.61	132.59	135.05	138.39
	r^2		0.9656	0.9741	0.9776	0.9776	0.9835
	χ^2		5.3480	4.1911	3.4555	2.5087	1.8599

4.5.1.2 Thermodynamics studies

Thermodynamic considerations of a biosorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG*, is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Also, both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occurs spontaneously at a given temperature if ΔG* is a negative quantity. The free energy of a biosorption reaction, considering the biosorption equilibrium constant K_a is given by the following equation:

$$\Delta G^* = -RT \ln K_a \tag{4.5.2}$$

where ΔG* is the standard free energy change, J/mol; R is the universal gas constant, 8.314 J/mol K, and T is absolute temperature, K.

Considering the relationship between free energy and equilibrium constant, change in equilibrium constant with temperature can be obtained in the differential form as follows:

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^*}{RT^2} \tag{4.5.3}$$

After integration, the integrated form of Eq. (4.5.3) becomes

$$\ln K_a = -\frac{\Delta H^*}{RT} + Y \tag{4.5.4}$$

where Y is a constant. Eq. (4.5.4) can be rearranged to obtain

$$\Delta S^* = RY \tag{4.5.5}$$

Substituting Eqs. (4.5.2) and (4.5.5), the Gibbs free energy change, ΔG*, can be represented as follows:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (4.5.6)$$

The biosorption equilibrium constant, Ka, obtained from non-linear method were analysis using Eqs. (4.5.5 and 4.5.6). A plot of Gibbs free energy change, ΔG^*, versus temperature, K, will be linear and the values of ΔH^* and ΔS^* determined from the slope and intercept of the plot. The parameter Gibbs free energy, ΔG^*, for the biosorption process using the biosorption equilibrium constant, K_a, from the Langmuir-1 forms is shown in Table 4.5.2a-c.

Table's 4.5.2 a-c shows the thermodynamic parameters for all the samples. It was observe that the free energy of all samples is negative meaning that the adsorption is spontaneous. This suggests that the reaction is likely to be chemisorption as it is activated by high temperature. A negative enthalpy signifies that the reaction is exdothermic and is favored by the increase of temperature for all samples. The enthalpy of acrylic acid grafted pine cone was higher than those for raw and Fenton's reagent sample. This suggests that entropy which suggests that the methyl violet motion is fixed at the surface of the adsorbent and the bond formed is strong.

4.5.2 Methylene blue

4.5.2.1 Langmuir and Freundlich isotherm

Figures 4.5.2 a-c shows the equilibrium isotherms of methylene blue adsorbed on raw pine, Fenton's reagent pine cone and acrylic acid treated pine cone. The figures reveal that the adsorption of MB onto the different adsorbent is exothermic in nature.

Table 4.5.3 a-c shows the Langmuir's parameters for raw, Fenton's reagent and acrylic acid grafted pine cone. From the tables, we observed that, for each sample, the capacities increases as the temperature of the experiment is increased. Comparing each sample, the raw pine cone capacity is observed to have lower capacity than Fenton's reagent and acrylic acid grafted pine cone. In conclusion, acrylic acid grafted pine cone has more adsorption sites to hold the adsorbate as compared with raw pine cone and Fenton's reagent modified samples, the r^2 values were close to 1 and the x^2 values are lower, this shows that the Langmuir isotherm properly describes the experimental data and also concludes that the sample surfaces are homogeneous.

Table 4.5.1a: Thermodynamic parameters for the adsorption of MV onto raw pine cone at different temperatures.

Parameter	Temperature (K)	289	303	308	313	318
ΔG^* (*kJ/mol*)		-23.82	-24.32	-24.81	-25.40	-25.87
ΔH^* (*kJ/mol*)			-103.71			
ΔS^* (*J/K mol*)			7.099			

Table 4.5.1b: Thermodynamic parameters for the adsorption of MV onto Fenton's treated pine cone at different temperatures.

Parameter	Temperature (K)	289	303	308	313	318
ΔG^* (*kJ/mol*)		-26.23	-26.68	-27.28	-27.86	-27.59
ΔH^* (*kJ/mol*)			-114.11			
ΔS^* (*J/K mol*)			7.785			

Table 4.5.1c: Thermodynamic parameters for the adsorption of MV onto acrylic acid treated pine at different temperatures.

Parameter	Temperature (K)	289	303	308	313	318
ΔG^* (*kJ/mol*)		-27.29	-27.94	-28.46	-28.97	-29.49
ΔH^* (*kJ/mol*)			-108.78			
ΔS^* (*J/K mol*)			5.076			

Table 4.5.2.a:
Isotherm parameters for the adsorption of methylene blue onto raw pine cone at different temperatures.

Isotherm	Parameters	*T(K)*	289	303	308	313	318
Langmuir	q_m, mg/g		627.48	635.55	644.35	653.23	660.84
	K_a, dm^3/mg		0.0483	0.0491	0.0507	0.0515	0.0518
	r^2		0.9989	0.9992	0.9971	0.9920	0.9912
	χ^2		0.2576	0.1723	0.3611	0.8241	0.9912
Freundlich							
	n		2.1389	2.1289	2.1246	2.1239	2.1014
	K_F		66.5546	67.1160	69.4422	71.0836	71.2197
	r^2		0.9465	0.9543	0.9737	0.9845	0.9847
	χ^2		5.1520	4.6356	3.4836	1.5070	1.3969

Table 4.5.2b:

Isotherm parameters for the adsorption of methylene blue onto Fenton's reagent treated pine cone at different temperatures.

Isotherm	Parameters	*T(K)*	289	303	308	313	318
Langmuir	q_m, mg/g		679.55	648.86	691.24	700.73	707.38
	K_a, dm^3/mg		0.1153	0.1182	0.1186	0.1233	0.1235
	r^2		0.9922	0.9989	0.9988	0.9957	0.9943
	χ^2		0.1094	0.1511	1.3561	0.4764	0.5726
Freundlich							
	n		2.1070	2.0972	2.0722	2.0648	2.0444
	K_F		106.01	107.760	107.80	111.38	111.70
	r^2		0.9673	0.9613	0.9730	0.9841	0.9858
	χ^2		5.1802	4.3414	3.1866	2.3243	1.9757

Table 4.5.2.c:

Isotherm parameters for the adsorption of methylene blue onto acrylic acid grafted pine cone at different temperatures.

Isotherm	Parameters	*T(K)*	289	303	308	313	318
Langmuir	q_m, mg/g		834.54	841.49	847.71	854.71	861.95
	K_a, dm^3/mg		0.2031	0.2107	0.2235	0.2356	0.2401
	r^2		0.9944	0.9973	0.9980	0.9957	0.9910
	χ^2		0.3743	0.1587	0.1336	0.2793	0.5124
Freundlich							
	n		1.6830	1.6791	1.6763	1.6734	1.6652
	K_F		149.69	154.12	160.68	167.31	170.48
	r^2		0.9591	0.9690	0.9750	0.9830	0.9868
	χ^2		5.3455	3.9865	3.6337	1.7490	1.2206

4.5.2.2 Thermodynamics studies

Table's 4.5.3 a-c shows the thermodynamic parameters for all the samples. From these tables it was observed that the free energy of all samples is negative meaning that the adsorption is spontaneous. This concludes that the reaction is likely to be chemisorption as it is activated by high temperature. The enthalpy that is negative signifies that the reaction is exothermic and is favored by the increase of temperature for all samples. The enthalpy of acrylic acid grafted pine cone is higher as compared to raw and Fenton's reagent so as the entropy which suggests that the MB motion is fixed at the surface of the adsorbent and that the bond formed is strong.

4.6 SIMULTANEOUS ANALYSIS OF CATIONIC DYES IN A SINGLE AND BINARY SOLUTIONS

4.6.1 Wavelength of dye measurement in single and mixed solutions

In the analysis of dyes in solution using UV/VIS spectroscopy, it is usual to scan the dye solution to obtain the maximum wavelength i.e. the wavelength at which the dye absorbs the more of the radiation. Figs. 4.5.1 and 4.5.2 shows a scan of the solutions of methyl violet and methylene blue and the optimum wavelengths observed were 592.19 nm for methyl violet and 660.17 nm for methylene blue. However, when the two dyes were mixed in ratio 1:1, as shown in Figs. 4.5.3, it was observed that the peaks of the absorption maximum for both dyes were found to merge and the wavelength maximum shifted to 601.50 and 676.70 nm. This means that in trying to determine the concentration of one dye, there will be interference by the second dye. This problem with interference was resolved using the second derivative scan. The wavelength maximum was chosen at points where the absorbance of one component is maximum and the other is at zero. For example in Fig. 4.5.4, at 572.75 nm the absorbance of methylene blue is zero while that of methyl violet is maximum, and at 693.94 nm the absorbance of methyl violet is zero while methylene blue is maximum. Therefore, these maximum wavelengths were applied for the dye concentration analysis.

4.6.2 Percentage removal of methyl violet and methylene blue from single and mixed solution

In this study, raw, Fenton's treated and acrylic acid grafted pine cone where applied for methyl violet and methylene blue removal from aqueous solution. Figs. 4.5.5a and

Table 4.5.3a:

Thermodynamic parameters for the adsorption of MB onto raw pine cone at different temperatures.

Parameter	Temperature (K)	289	303	308	313	318
ΔG^* (*kJ/mol*)		-23.90	-24.34	-24.82	-25.27	-25.69
ΔH^* (*kJ/mol*)			-90.10			
ΔS^* (*J/K mol*)			2.948			

Table 4.5.3b:

Thermodynamic parameters for the adsorption of MB onto Fenton's reagent treated pine cone at different temperatures.

Parameter	Temperature (K)	289	303	308	313	318
ΔG^* (*kJ/mol*)		-26.05	-26.44	-27.00	-27.54	-27.98
ΔH^* (*kJ/mol*)			-96.93			
ΔS^* (*J/K mol*)			2.829			

Table 4.5.3c: Thermodynamic parameters for the adsorption of MB onto acrylic acid grafted pine cone at different temperatures.

Parameter	Temperature (K)	289	303	308	313	318
ΔG^* (*kJ/mol*)		-27.46	-28.01	-28.62	-29.22	-29.74
ΔH^* (*kJ/mol*)			-115.71			
ΔS^* (*J/K mol*)			7.027			

b, Figs. 4.5.6 a and b and Figs. 4.5.7 a and b show the plots of the percentage removal of methyl violet and methylene blue from aqueous solution at different time intervals onto the various biomaterial surfaces. The plots can be divided to two sections, the initial rapid section in which the percentage methyl violet and methylene blue removal is high and the second section in which the percentage removal slows down to an almost constant rate. From the Figures it can also be seen that the percentage removal is higher for methyl violet than for methylene blue, meaning that all the biomaterials have higher capacities for methyl violet than for methylene blue.

It was also observed that the acrylic acid grafted pine removed more of the dyes from aqueous solution than the Fenton's reagent treated and raw pine cone. This is due to the higher number of carboxylic acid groups on the biomaterial surface due to acrylic acid grafting. The higher adsorption of the Fenton's reagent sample over the raw pine can be attributed to the extraction of plant organic components from the pine cone which leads to an increase in surface area.

When the methyl violet and methylene blue dyes were mixed together in a ratio of 1:1 (500 mg/dm^3) and the concentration of each dye measured using the wavelength obtained from the derivative scan, the percentage removal of both dyes changes. The change in percentage removal can be attributed to competition between the methyl violet and the methylene blue for adsorption sites on the biomaterials. Figs. 4.5.9 a and b, Figs. 4.5.10 a and b and Figs. 4.5.11c a and b shows the comparison of the removal of methyl violet and methylene blue dyes from single and mixed solutions.

From the figures above, it was observed that there was a difference in percentage removal when the dyes were mixed. The difference was found to be higher for the raw, than the Fenton's and smaller for the acrylic acid grafted pine. These results indicate that the effect of completion was reduced for the treated samples as compared with the untreated samples.

4.6.3 ADSORPTION KINETICS

4.6.3.1 Pseudo-first order and pseudo-second order kinetic model

From tables 4.6.3.1a and b (raw pine cone), Tables 4.6.3.2 a and b (Fenton's treated pine cone) and Table 4.6.3.3a and b (acrylic acid grafted pine cone). It will be observed that the experimentally determined equilibrium capacities were found to be very different from that predicted by the pseudo-first order model for both the single

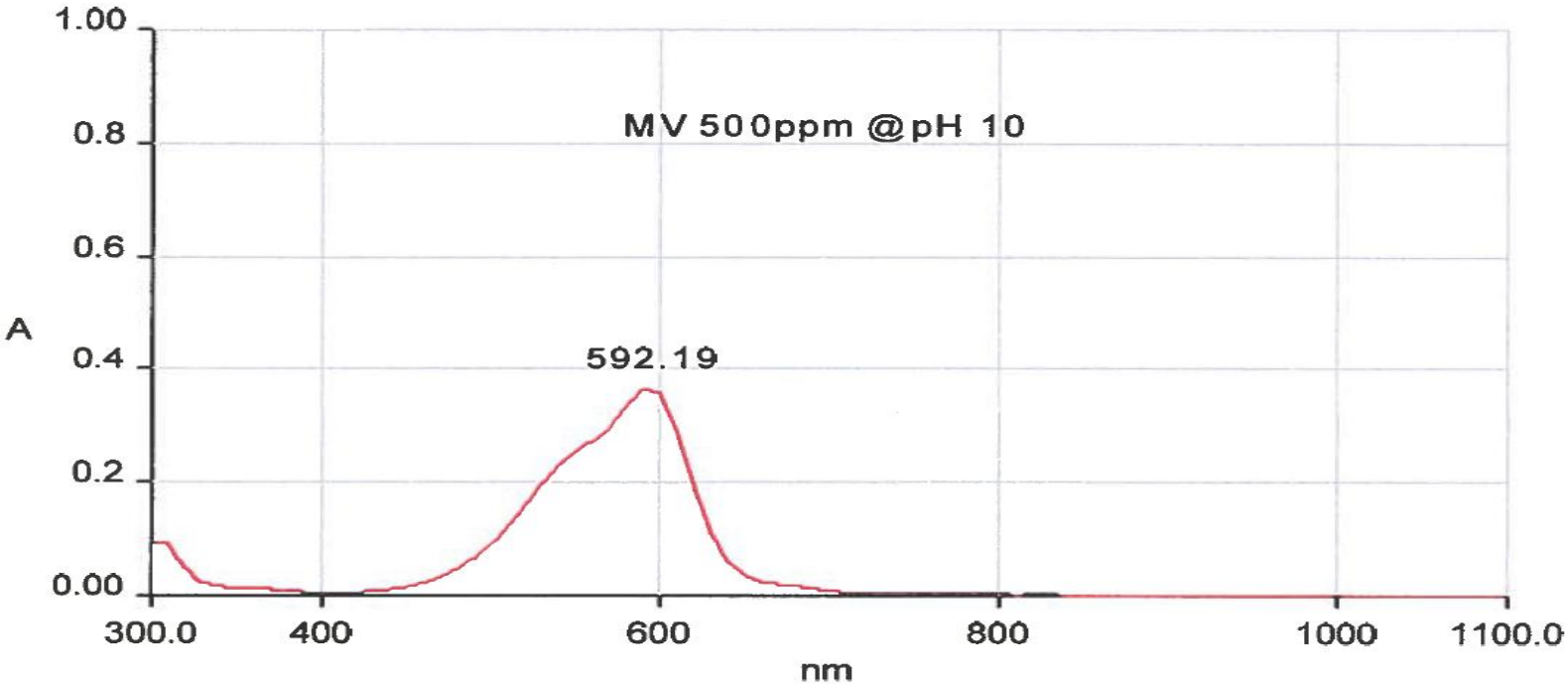

Fig. 4.5.1.: Wavelength scan for methyl violet in single dye solution.

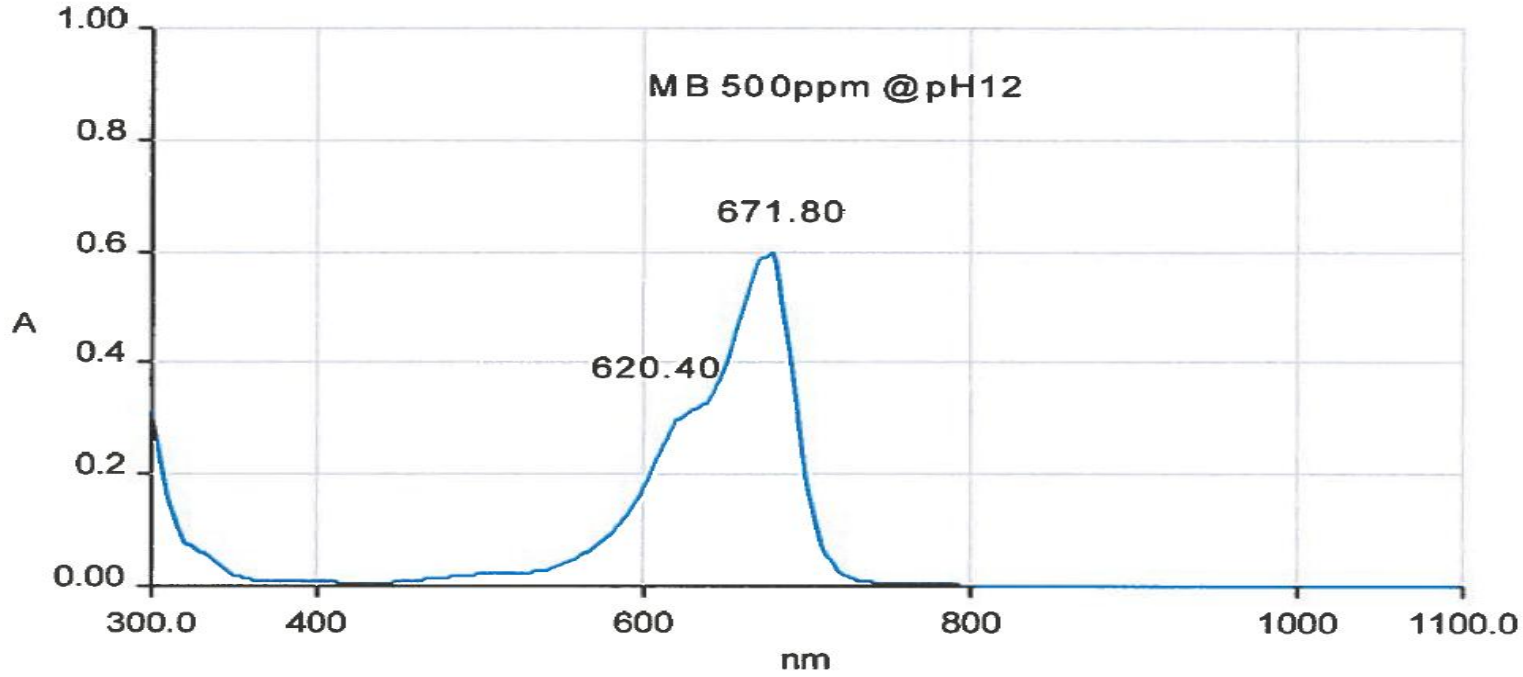

Fig. 4.5.2: Showing UV/Vis wavelength scans for the mixture of methyl violet and methylene blue.

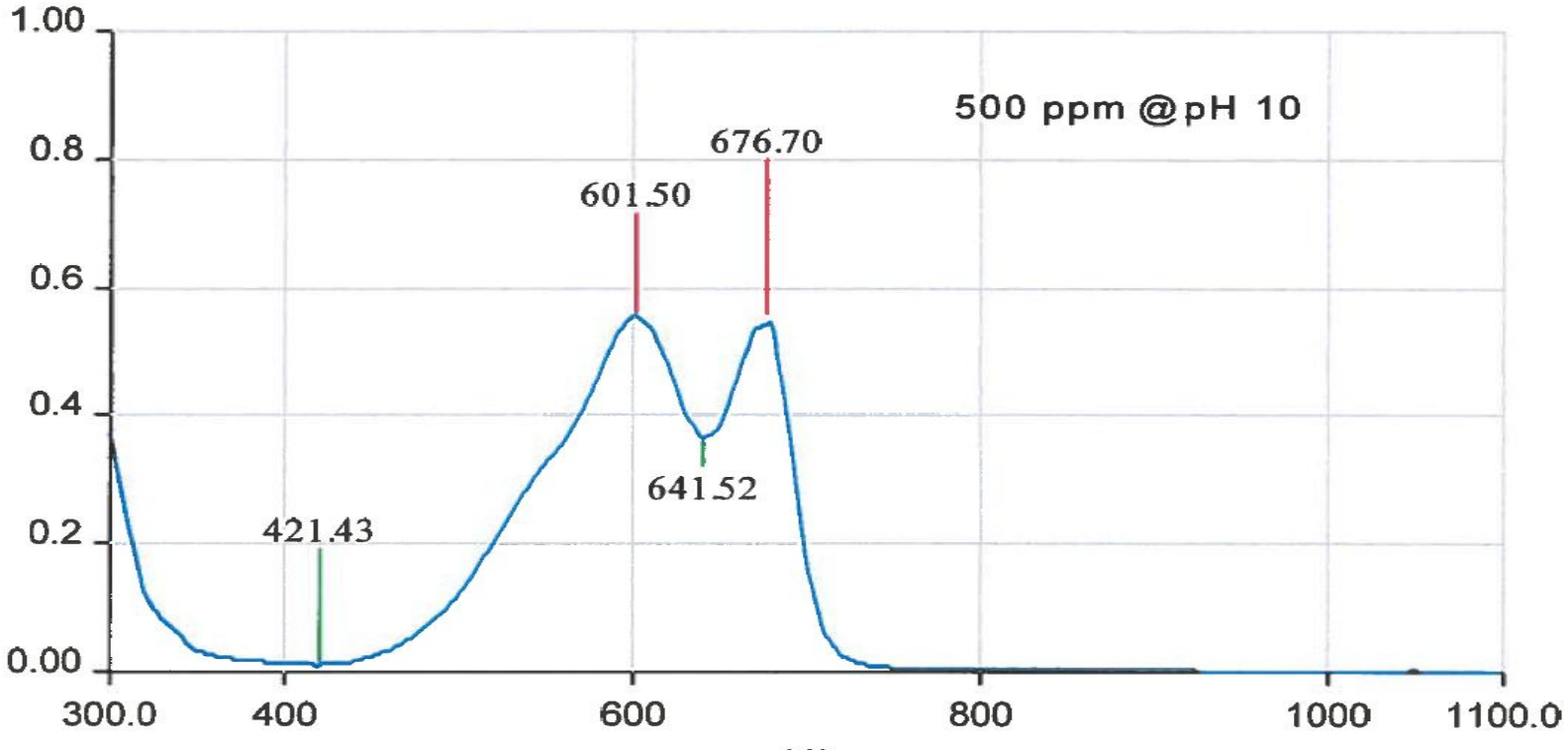

Fig. 4.5.3: Showing UV/Vis wavelength scans for the mixture of methyl violet and methylene blue.

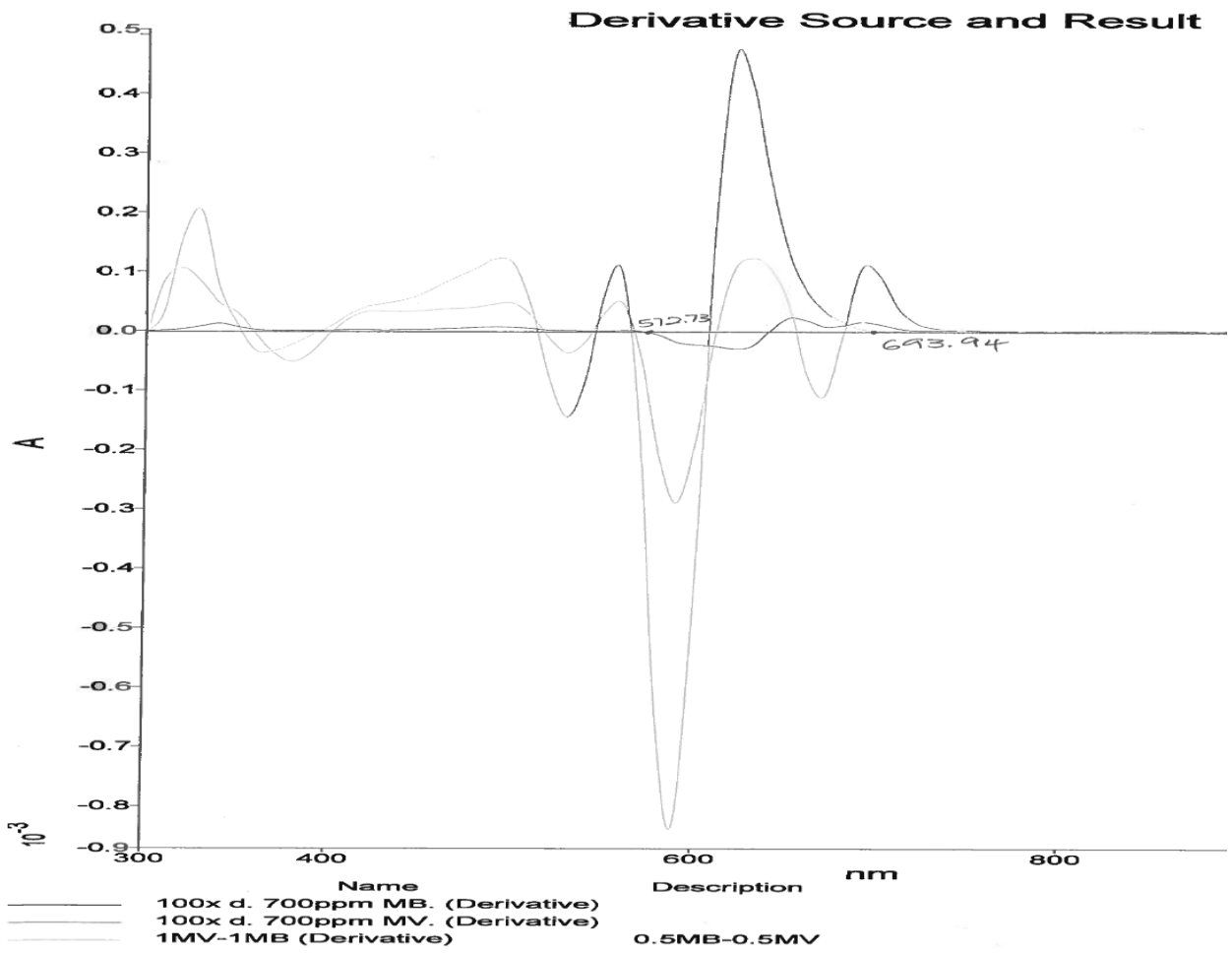

Fig. 4.5.4: Derivative plots for the scanning of methyl violet + methylene blue mixture.

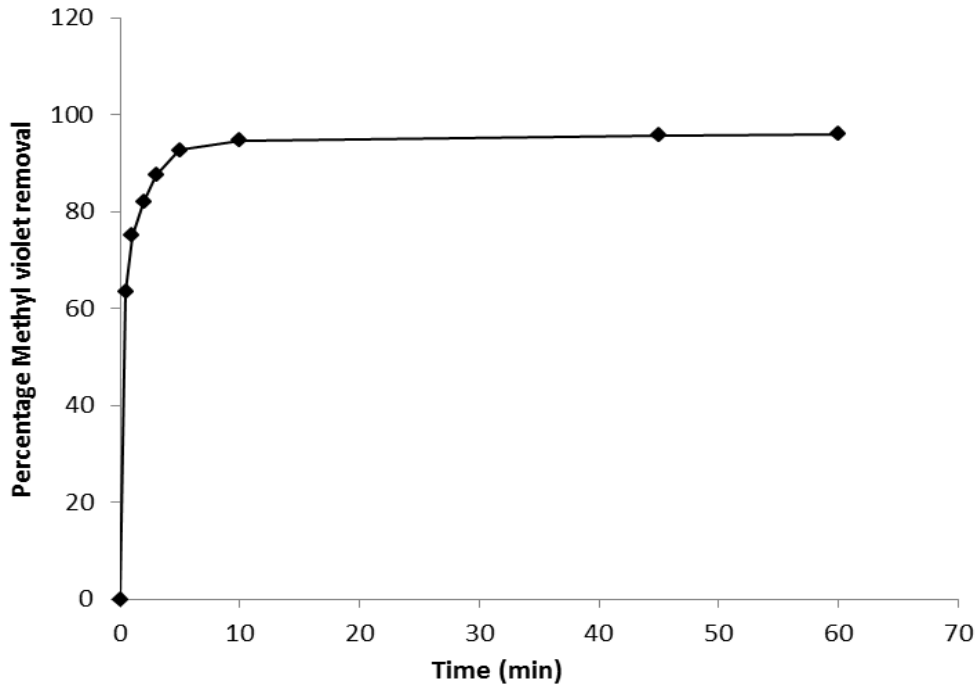

Fig. 4.5.5 a: Percentage removal of Methyl violet from single dye solution onto raw pine.

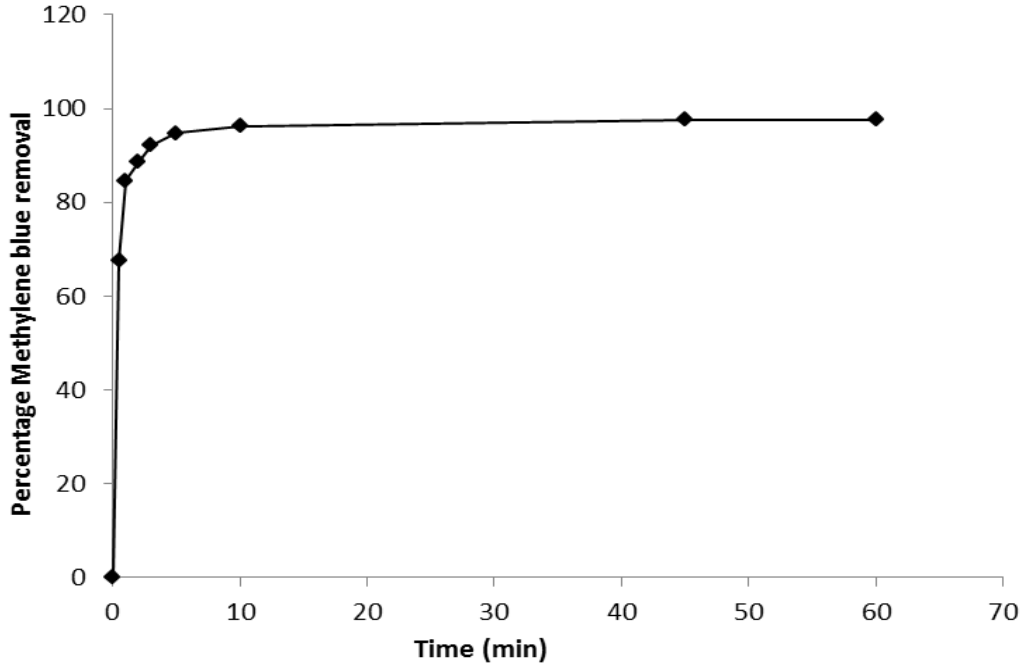

Fig. 4.5.5 b: Percentage removal of Methylene blue from single dye solution onto raw pine.

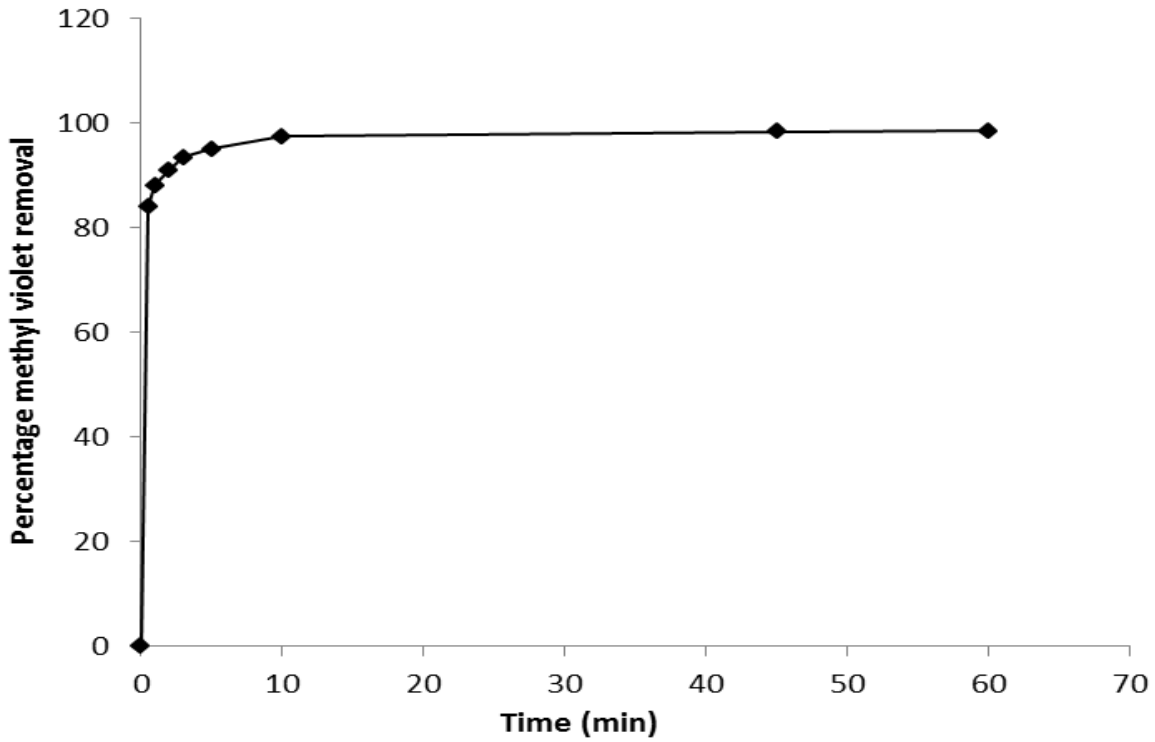

Fig. 4.5.6 a: Percentage removal of Methyl violet from single dye solution onto Fenton's reagent.

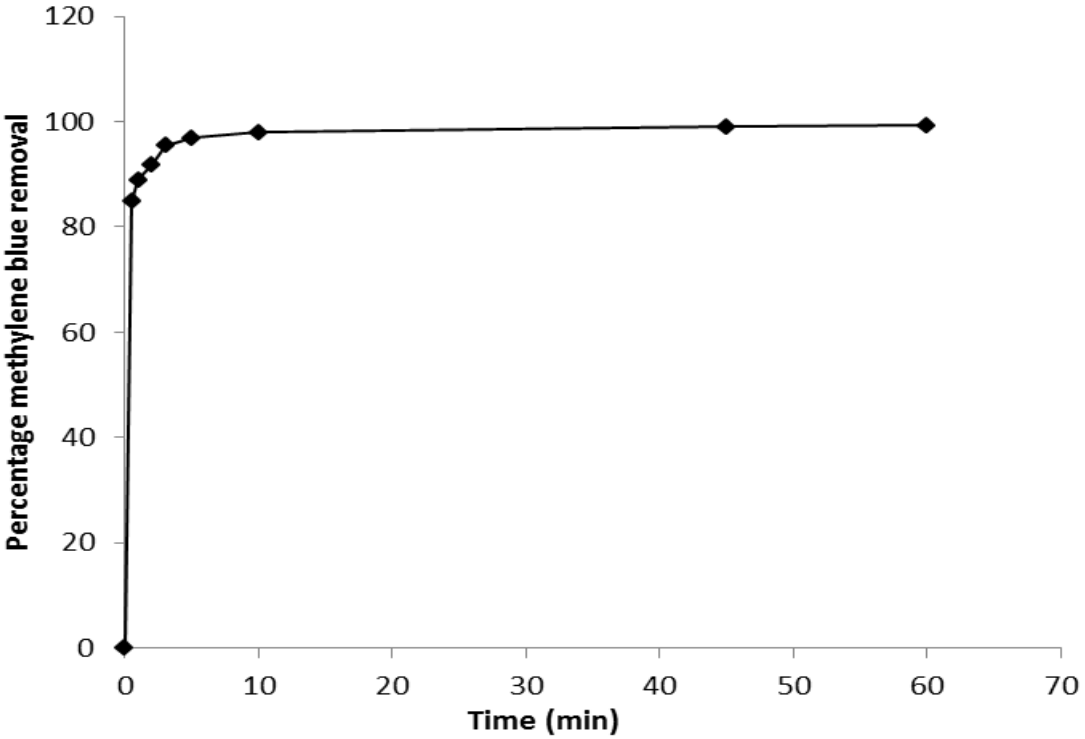

Fig. 4.5.6 b: Percentage removal of Methylene blue from single dye solution onto Fenton's reagent.

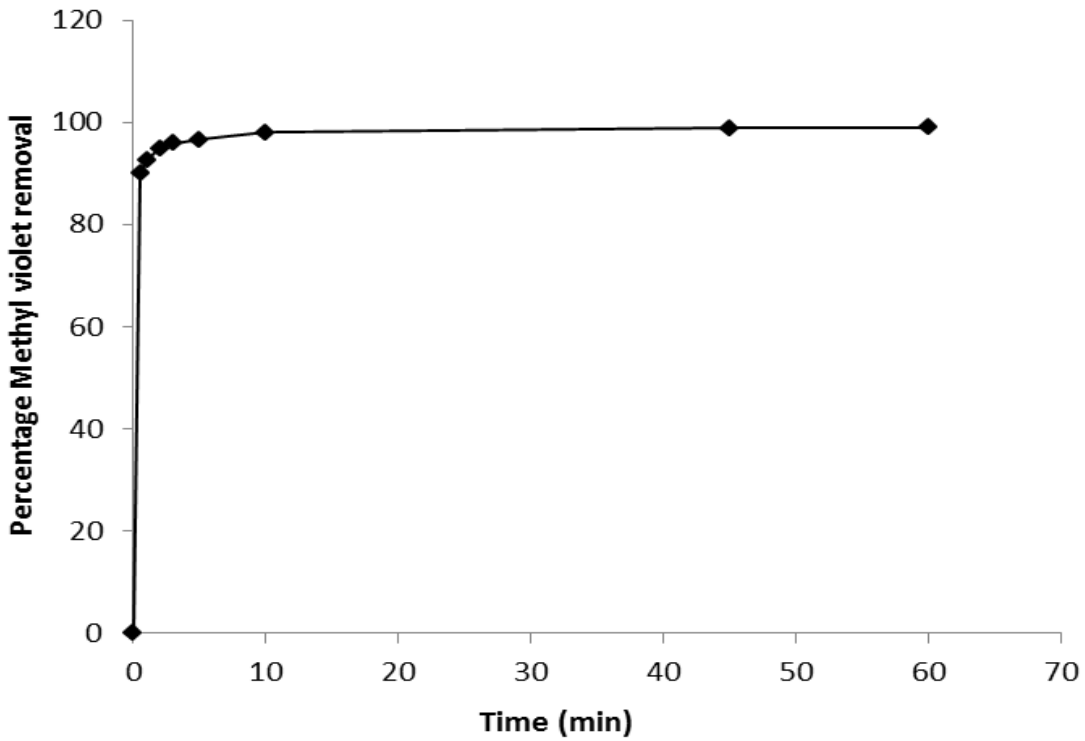

Fig. 4.5.7 a: Percentage removal of Methyl violet from single dye solution onto Fenton's reagent.

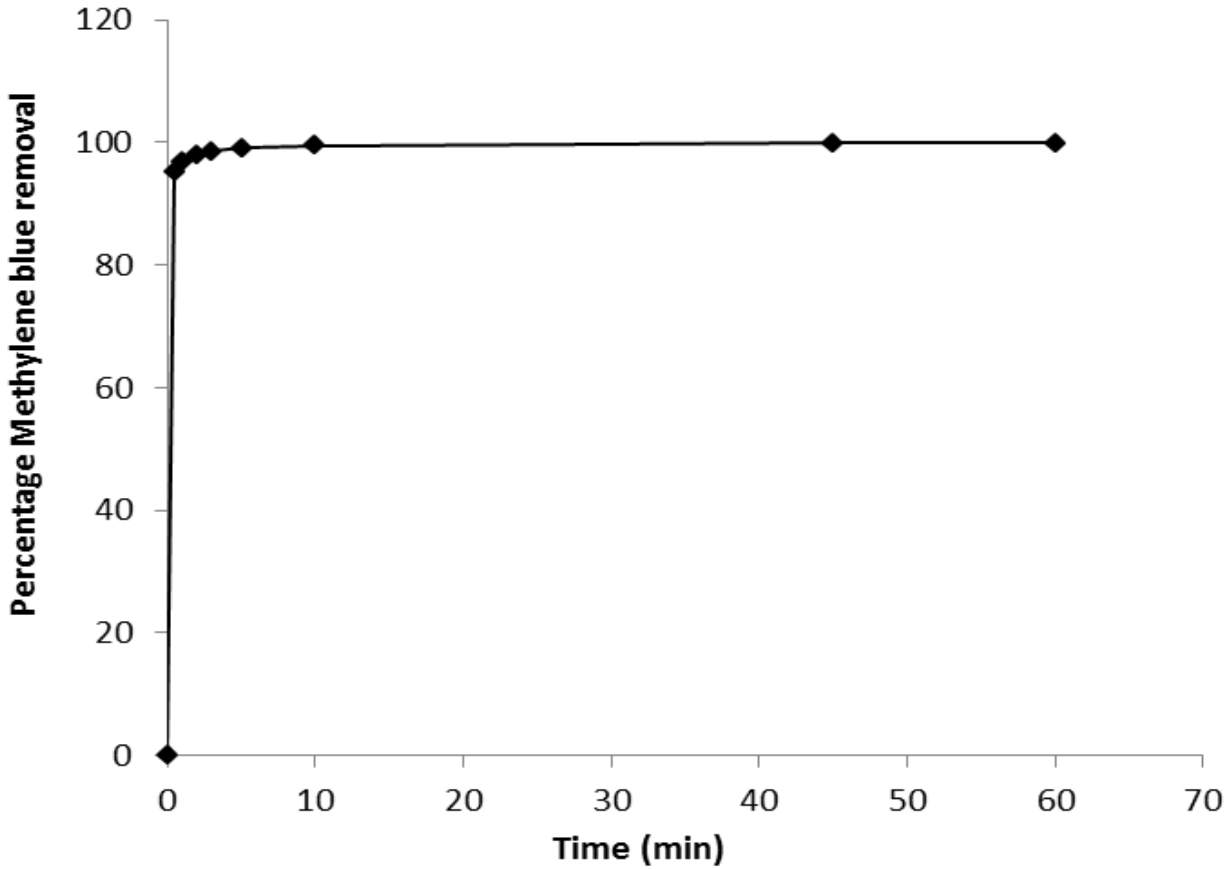

Fig. 4.5.7 b: Percentage removal of Methylene blue from single dye solution onto Fenton's reagent.

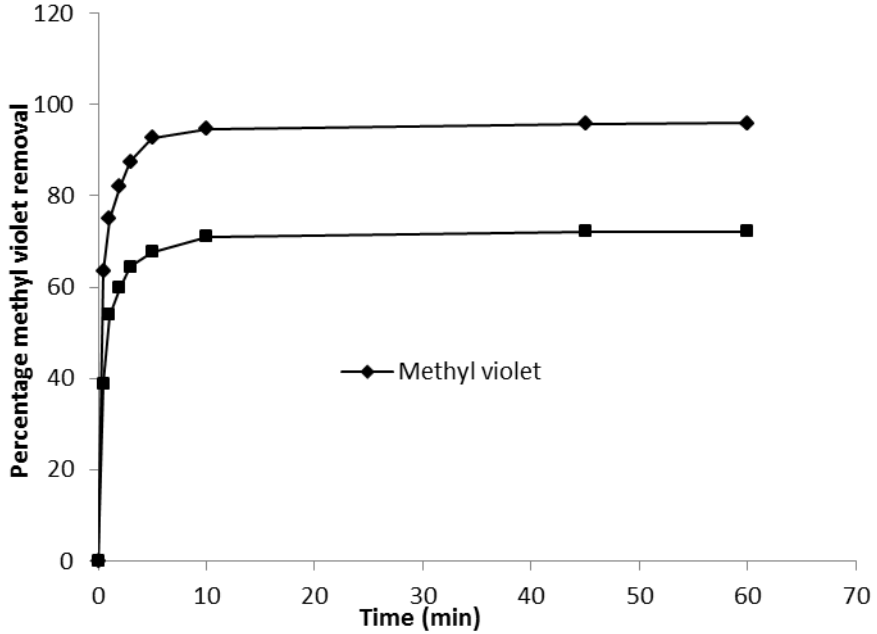

Fig. 4.5.9a: Comparison of methyl violet removal from a 500 mg/dm^3 solution of single and mixed methyl violet and methylene blue (1:1) onto raw pine

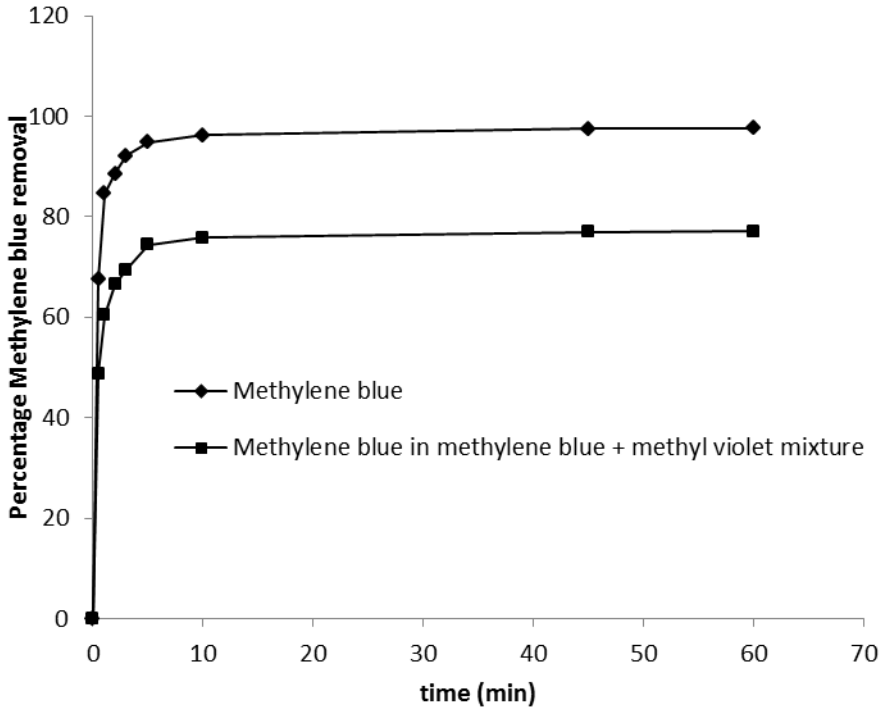

Fig. 4.5.9 b: Comparison of methylene blue removal from a 500 mg/dm^3 solution of single and mixed methyl violet and methylene blue (1:1) onto raw pine.

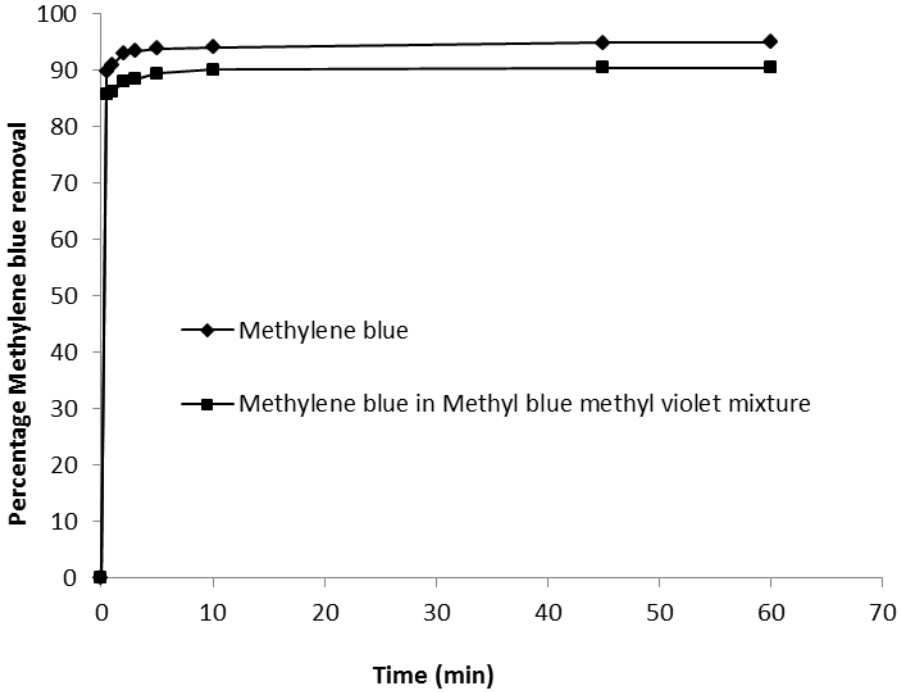

Fig. 4.5.10a: Comparison of methyl violet removal from a 500 mg/dm^3 solution of single and mixed methyl violet and methylene blue (1:1) Fenton's treated pine

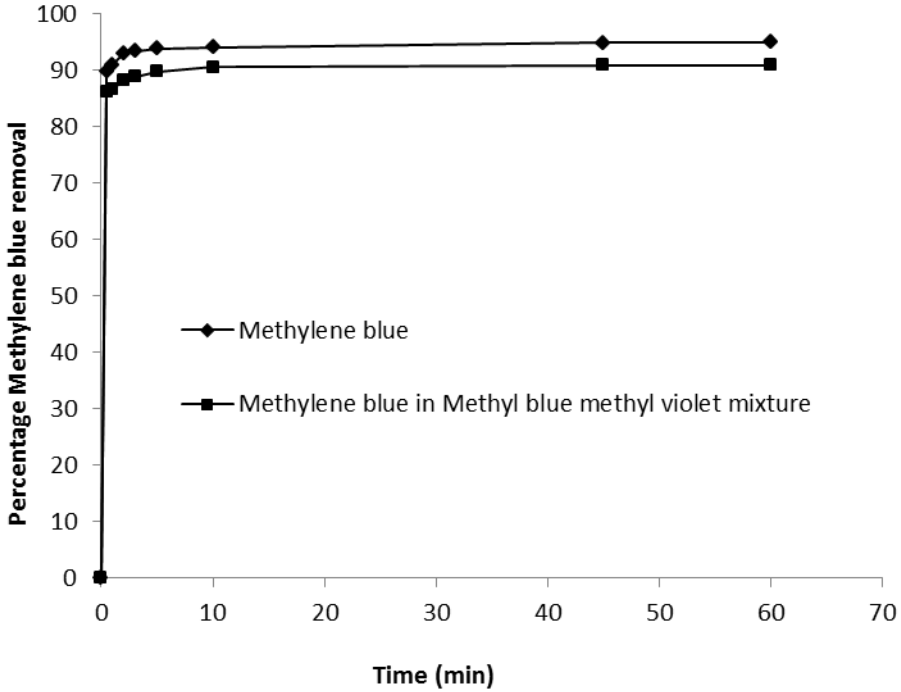

Fig. 4.5.10 b: Comparison of methylene blue removal from a 500 mg/dm^3 solution of single and mixed methyl violet and methylene blue (1:1) Fenton's treated.

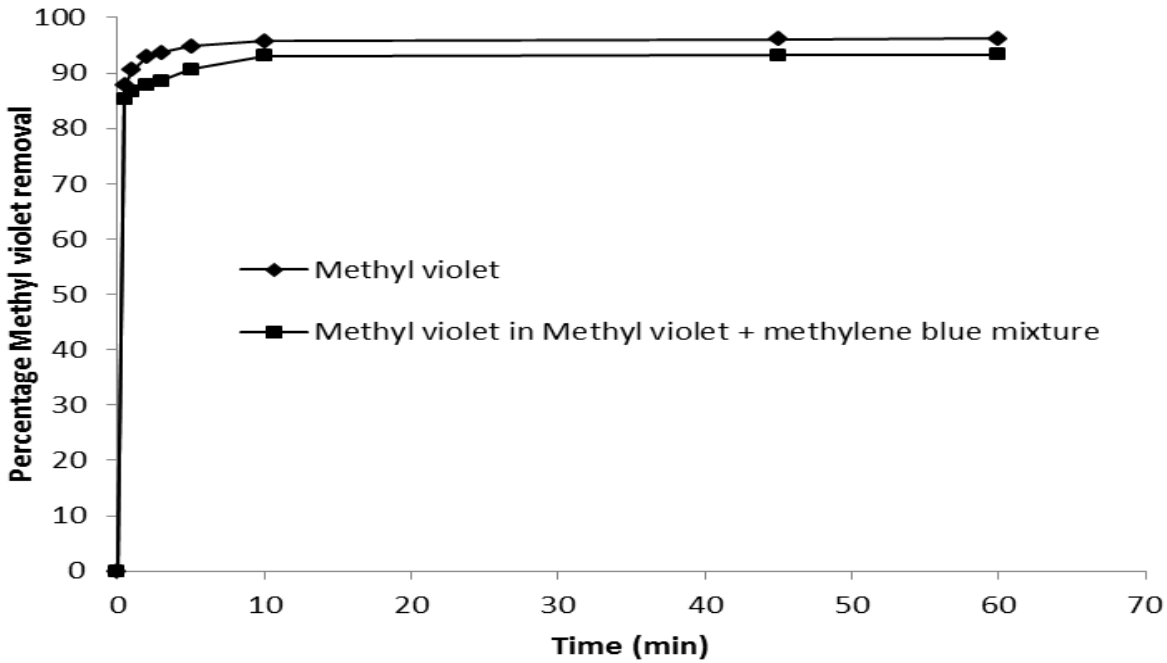

Fig. 4.5.11a: Comparison of methyl violet removal from a 500 mg/dm^3 solution of single and mixed methyl violet and methylene blue (1:1) acrylic acid grafted pine.

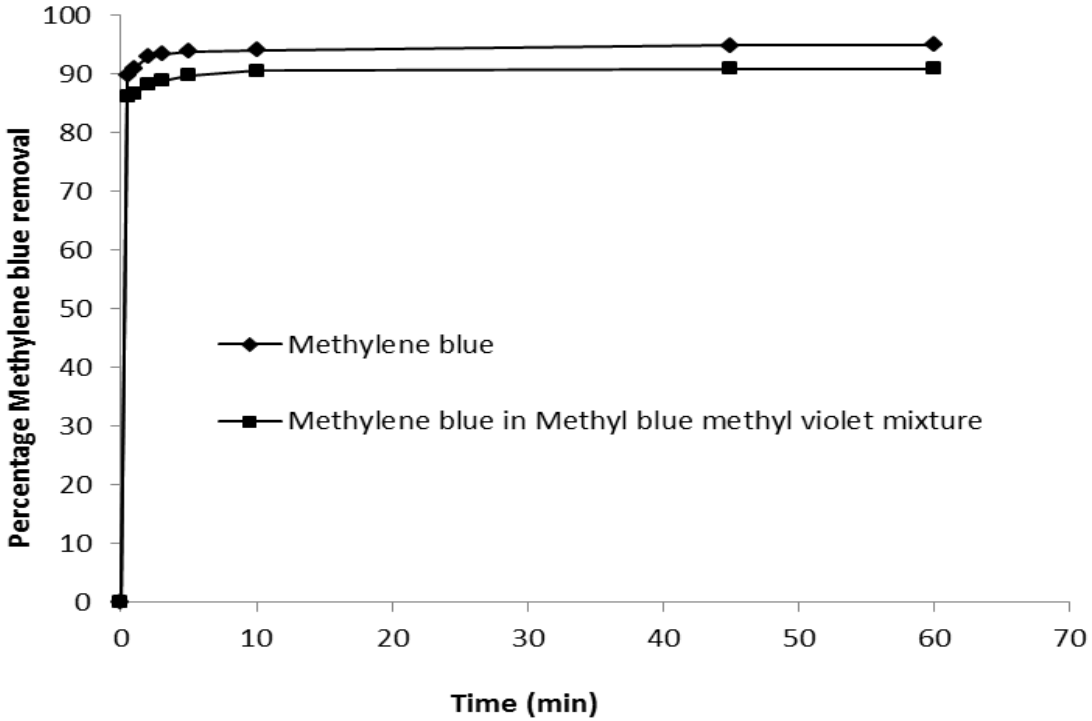

Fig. 4.5.11b: Comparison of methylene blue removal from a 500 mg/dm^3 solution of single and mixed methyl violet and methylene blue (1:1) acrylic acid grafted pine.

and mixed dye solutions. This result suggests that the pseudo-first order model cannot be used to predict the experimental data. On the other hand, the predicted values of the pseudo- second order. From the tables below, it was observed that there was a reduction in the experimentally determined equilibrium capacity for the single and mixed dye solutions signifying the presence of competition for adsorption sites. As expected, the difference between the single and mixed solutions increased in the order of Raw < Fenton's treated < Acrylic acid grafted. The percentage reduction for the methyl violet adsorption in the mixed solution was higher as compared with the methylene blue and the percentage reduction reduces in the order of Raw < Fenton's treated < Acrylic acid grafted. For all the samples the h, was found to reduce from the single dye solution to mixed dye solution, while k_2 increased from single dye solution to mixed dye solution. For all samples, the values of k_2 were found to decrease as the solution concentration was increasing, while the values for h were found to increase as the solution concentration was increasing.

Table 4.6.3.1a.
Kinetic parameters for the effect of Methylene blue concentration on the uptake of Methyl violet from dye mixture by Raw pine cone.

Methyl violet	200 mg/dm^3	500 mg/dm^3
Pseudo-first order		
q_e (mg/g) (*exp*)	127.96	308.68
q_e (mg/g)	50.16	93.54
k_1 (min^{-1})	0.4917	0.3938
Pseudo-second order		
q_e (mg/g) (*exp*)	127.96	308.68
q_e (mg/g)	128.50	310.24
k_2 (g /mg min)	0.0291	0.0162
h (mg/g min)	480.42	118.46
Methyl violet + Methylene blue (1:1 mixture)		
Pseudo-first order		
q_e (mg/g) (*exp*)	96.31	196.57
q_e (mg/g)	42.20	165.20
k_1 (min^{-1})	0.4142	0.4488
Pseudo-second order		
q_e (mg/g) (*exp*)	96.31	195.53
q_e (mg/g)	96.95	199.08
k_2 (g /mg min)	0.0278	0.0042
h (mg/g min)	261.26	184.81

Table 4.6.3.1b.
Kinetic parameters for the effect of methyl violet concentration on the uptake of Methylene blue from dye mixture by raw pine cone.

Methylene blue	200 mg/dm^3	500 mg/dm^3
Pseudo-first order		
q_e (mg/g) (*exp*)	130.15	314.15
q_e (mg/g)	35.62	89.07
k_1 (min^{-1})	0.4824	0.4851
Pseudo-second order		
q_e (mg/g) (*exp*)	130.15	314.15
q_e (mg/g)	130.66	315.23
k_2 (g /mg min)	0.0413	0.0175
h (mg/g min)	705.00	1739.68
Methylene blue + Methyl violet (1:1 mixture)		
Pseudo-first order		
q_e (mg/g) (*exp*)	102.86	243.08
q_e (mg/g)	41.47	86.31
k_1 (min^{-1})	0.4881	0.3983
Pseudo-second order		
q_e (mg/g) (*exp*)	102.86	243.08
q_e (mg/g)	103.37	244.44
k_2 (g /mg min)	0.0341	0.0125
h (mg/g min)	364.00	743.98

Table 4.6.3.2a.
Kinetic parameters for the effect of Methylene blue concentration on the uptake Methyl violet of from dye mixture by Fenton treated pine cone.

Methyl violet	200 mg/dm^3	500 mg/dm^3
Pseudo-first order		
q_e (mg/g) (*exp*)	131.36	327.15
q_e (mg/g)	19.76	53.16
k_1 (min^{-1})	0.3072	0.3271
Pseudo-second order		
q_e (mg/g) (*exp*)	131.36	327.15
q_e (mg/g)	131.65	327.86
k_2 (g /mg min)	0.0513	0.0200
h (mg/g min)	888.88	2147.65
Methyl violet + Methylene blue (1:1 mixture)		
Pseudo-first order		
q_e (mg/g) (*exp*)	118.45	297.82
q_e (mg/g)	18.02	59.22
k_1 (min^{-1})	0.2712	0.3302
Pseudo-second order		
q_e (mg/g) (*exp*)	118.45	297.82
q_e (mg/g)	118.65	298.36
k_2 (g /mg min)	0.0476	0.0172
h (mg/g min)	669.67	1524.59

Table 4.6.3.2b.
Kinetic parameters for the effect of methyl violet concentration on the uptake of Methylene blue from dye mixture by Fenton treated pine cone.

Methylene blue	200 mg/dm^3	500 mg/dm^3
Pseudo-first order		
q_e (mg/g) (*exp*)	132.45	328.63
q_e (mg/g)	21.40	49.11
k_1 (min^{-1})	0.4039	0.3260
Pseudo-second order		
q_e (mg/g) (*exp*)	132.45	328.63
q_e (mg/g)	132.66	329.05
k_2 (g /mg min)	0.0577	0.0209
h (mg/g min)	1015.04	2264.32
Methylene blue + Methyl violet (1:1 mixture)		
Pseudo-first order		
q_e (mg/g) (*exp*)	126.54	321.93
q_e (mg/g)	21.64	66.75
k_1 (min^{-1})	0.3473	0.1831
Pseudo-second order		
q_e (mg/g) (*exp*)	126.54	321.93
q_e (mg/g)	126.63	323.52
k_2 (g /mg min)	0.0491	0.0090
h (mg/g min)	787.81	945.26

Table 4.6.3.3a.
Kinetic parameters for the effect of Methylene blue concentration on the uptake Methyl violet of from dye mixture by Acrylic acid grafted pine cone.

Methyl violet	200 mg/dm^3	500 mg/dm^3
Pseudo-first order		
q_e (mg/g) (*exp*)	133.25	320.00
q_e (mg/g)	5.96	18.20
k_1 (min^{-1})	0.3501	0.3324
Pseudo-second order		
q_e (mg/g) (*exp*)	133.25	320.00
q_e (mg/g)	132.32	330.05
k_2 (g /mg min)	0.1941	0.0621
h (mg/g min)	3449.86	6760.43
Methylene blue + Methyl violet (1:1 mixture)		
Pseudo-first order		
q_e (mg/g) (*exp*)	126.63	304.35
q_e (mg/g)	6.87	18.39
k_1 (min^{-1})	0.3521	0.32572
Pseudo-second order		
q_e (mg/g) (*exp*)	126.63	304.35
q_e (mg/g)	126.71	304.61
k_2 (g /mg min)	0.1483	0.0603
h (mg/g min)	2380.93	5592.67

Table 4.6.3.3b.
Kinetic parameters for the effect of Methylene blue concentration on the uptake of Methylene blue uptake by Acrylic acid grafted pine cone.

Methylene blue	200 mg/dm^3	500 mg/dm^3
Pseudo-first order		
q_e (mg/g) (*exp*)	132.63	328.63
q_e (mg/g)	11.62	37.85
k_1 (min^{-1})	0.2894	0.2863
Pseudo-second order		
q_e (mg/g) (*exp*)	132.63	328.63
q_e (mg/g)	132.15	329.17
k_2 (g /mg min)	0.0820	0.0257
h (mg/g min)	1432.15	2780.32
Methyl violet + Methylene blue (1:1 mixture)		
Pseudo-first order		
q_e (mg/g) (*exp*)	128.35	311.03
q_e (mg/g)	14.23	29.84
k_1 (min^{-1})	0.2075	0.2362
Pseudo-second order		
q_e (mg/g) (*exp*)	128.35	311.03
q_e (mg/g)	128.46	311.57
k_2 (g /mg min)	0.1119	0.0307
h (mg/g min)	1846.21	2679.20

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CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

This study was successfully done and the following conclusions have been drawn from the results obtained:

The results for this thesis shows that surface properties of the treated and the untreated sample were successfully measured using different techniques. The use of Fenton's reagent as a pre-treatment step which followed by biological treatment processes achieved lower cost and sufficient organic compounds removal.

The optimization and removal of the organic plant component using Fenton's Reagent from pine cone powder has been achieved. The results obtained from this research show that plant components have been extracted from the raw pine cone powder which was monitored by the bulk density measurements and BET surface area. The bulk density for the raw pine cone powder was higher (0.6457 g/cm^3) than the Fenton treated pine cone powder (0.2480 g/cm^3). The surface area for the Fenton treated pine cone powder is higher (27.45 m^2/g) than the raw pine cone powder (4.39 m^2/g). This shows that treating raw pine cone with Fenton's reagent enhanced the removal of organic plant component. Graft copolymerization of acrylic acid onto pine cone at different temperature (50 – 90 °C) has beendone using various $KMnO_4$ concentrations as the initiator. The results obtained shows that the cause of the initiator stage can be followed by monitoring the ORP, the change in solution pH and the MnO_2 deposited. At 0.0005 mol/dm^3 $KMnO_4$ concentrations highest ORP, maximum change in solution pH, less MnO_2 deposited were obtained. A decrease in the MnO_2 results in a high conversion of Mn^{4+} to Mn^{3+} in the bulk solution.

Temperature increased between 289-318 K produced an increase in equilibrium for raw, Fenton treated and acrylic acid grafted for both cationic dyes. The pseudo-second order model best described the sorption of methyl violet and methylene blue. The isotherm data obtained at varying temperatures (289-318) were described by the

Langmuir equation. Increase in reaction temperature also increased the monolayer capacity for all the pine cone biomaterials. The equilibrium sorption capacities obtained by pseudo-second order were quite close to Langmuir capacity values.

The wavelengths maximum to determine the unknown concentrations of methyl violet and methylene blue dyes in binary solutions using second order derivatives (SODS) were found as 561.8 nm and 623.1 nm, respectively, while analysis of methyl violet and methylene blue were conducted at 572.75 nm and 693.94 nm, respectively. The percentage removal for all three experiments showed that the percentage removal is higher for methyl violet than for methylene blue, meaning that all the biomaterials have higher capacities for methylene blue than for methyl violet. It was also observed that the acrylic acid grafted pine removed more of the dyes from aqueous solution than the Fenton's reagent treated and raw pine cone. A change in the percentage removal for the methyl violet and methylene blue dyes mixture in a ratio of 1:1 (500 mg/dm^3) was observed due to the competition for the adsorption sites between the two dyes. Pseudo-second order suited the biosorption mechanism for both single and binary studies. A reduction in the experimentally determined equilibrium capacity for the single and mixed dye solutions was obtained

5.2 RECOMMENDATIONS

1. Further studies should be done on:
   - removing more than two cationic dyes from wastewater.
   - applying the modified and optimized pine cone powder for dye removal using tri- component systems,
   - determining the kinetics and the thermodynamics of the dye biosorption in tri-component systems and
   - applying derivative spectrophotometry to resolve the problems of overlapping spectra in the tri-component system.
   - chemically grafting two or more monomer onto the surface of pine cone powder and apply this product of grafting to dye removal.
   - performing and studying the efficiency of grafting at room temperature (25 °C).

2. To minimize time and speed up grafting reaction, eliminate sample wastage, achieve more product yield and higher percentage grafting, microwave technique should be used instead of conventional reflux distillation method.