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The grafting of acrylic acid onto biosorbents: Effect of plant components and initiator concentration

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ABSTRACT

Acrylic acid was grafted onto raw and Fenton's reagent treated pine cone using $KMnO_4$ as initiator to determine the effect of plant organic components on grafting process. Concentration of the $KMnO_4$ was varied between 0.0005 and 0.0200 mol/dm^3 and progress of the initiation process monitored using ORP and change in hydrogen ion concentration (ΔH^+).

The optimum ratio for Fenton's modification was $Fe^{2+}/H_2O_2 = 1/50$ which corresponds to the highest leaching of plant components and having the least bulk density, ORP and ΔH^+. It was observed that increasing $KMnO_4$ concentration, reduced the MnO_2 deposited on the pine surface, increased Mn^{3+} production in bulk solution while reducing grafting efficiency but increasing homopolymer formation. Radical formation on the raw pine cone was found to be lower as seen from the lower ORP and ΔH^+ values observed at similar grafting conditions.

Plant organic components was observed to affect the grafting efficiency and monomer conversion as observed from the weight increase, surface charge and FTIR analysis of the acrylic acid grafted Fenton's reagent treated pine and the raw pine.

Optimum dye removal did not correspond to highest grafting efficiency.

1. Introduction

The application of biological waste materials in the cleanup of wastewater is becoming a more attractive alternative as compared to the use of other expensive adsorbent systems. These materials are readily available, cheap and efficient for the sequestration of most known pollutants from aqueous solutions. Acidic organic functional groups present in the chemical structure of these materials provide sites to which pollutant sequestration can take place or which other moieties can be reacted for possible enhancement of the efficiency of pollutant uptake and/or the maximum pollutant loadings (Ho & Ofomaja, 2007). Chemically modifying biological wastes materials by these methods have lead to great promise in improving the cation exchange capacity of biological wastes in their application as adsorbents (Laszlo & Dimtsiz, 1994).

Several organic acids such as citric acid (Wing, 1997) and ethylenediaminetetraacetic acid (Torres, Faria, & Prado, 2006) have been incorporated into agricultural wastes using thermochemical esterification method. Amine functions have also been incorporated into agricultural waste materials by the modification of these cellulose containing materials with phosphorous oxychloride to give the precursor cellulose and finally, reacting the precursors with diamine compounds. The bonds formed between the biosorbent and modifying agent (ester linkage or C—N linkage) are usually subject to reversal under low pH conditions. This becomes a limitation in the use of this method since most industrial wastes are discharged at low solution pH values.

Chemical grafting using radical initiators is known to form covalent linkages between biosorbent and polymer molecules that are not reversible under low solution pH conditions (Feng, Guo, & Liang, 2009). The process involves radical formation on the hydroxyl functional groups of the biosorbent which then reacts with monomer molecules to eventually graft the particular polymer containing a specific functional group onto the biosorbent by electron coupling. For example, Sacak and Keles (2003) successfully grafted acrylic acid onto starch and Geay, Marchetti, Clément, Loubinoux, and Gérardin (2000) also grafted polyacrylic acid onto sawdust which was applied as a biosorbent for Ni^{2+}, Cu^{2+} and Cd^{2+} from aqueous solution.

Since raw plant materials are composed of a complex mixture of organic materials containing lignin and tannins which can resist chemical attack Pholosi, Ofomaja, and Naidoo (2011), radical formation on these materials may be hindered or be unevenly distributed throughout the matrix. Therefore, the presence of such plant components may determine the levels of polymer grafting

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that can take place on the biosorbent material and hence affect its ability to be modified by chemical grafting.

The aim of this study therefore is to optimize the removal of plant organic components from pine cone using Fenton's oxidation and to determine the effect of plant components and initiator concentration of the grafting of acrylic acid onto pine cone powder. The methylene blue biosorption capacities of the various materials produced will eventually be compared with grafting performance of the samples.

2. Materials and methods

2.1. Materials

2.1.1. Sample preparation

Pine tree cones were collected from a plantation in Sasolburg, Free State, South Africa. The cone was washed to remove impurities such as sand and leafs. The washed cones were then dried at 90 °C for 48 h in the oven. The scales on the cones were removed and crushed using a pulveriser. The pine cone powder was then sieved and particles between 90 and 45 μm were collected and used for analysis.

2.2. Methods

The method section is divided into two parts: the first section deals with the Fenton's oxidation treatment of raw pine cone and a comparison of the change in properties such as change in solution pH (ΔpH), oxidation/reduction potential (ORP), bulk density, functional groups (FTIR), acid number and BET surface area after Fenton's oxidation treatment.

The second section deals with the grafting of acrylic acid onto the raw and Fenton's treated pine along with a comparison of change in surface properties such as surface charge, MnO_2 deposited, ΔpH, ORP, functional groups (FTIR) and BET surface area of the two grafted samples.

2.2.1. Fenton's reagent modification

Accurately weighed and oven dried (20 g) cone material was added into 500 ml conical flask containing 250 ml 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 °C. The optimum values for Fe^{2+} and H_2O_2 ratio were determined by monitoring the oxidation and reduction potential (ORP), change in solution pH (ΔpH) before and after treatment and acid number (AN).

2.2.2. Bulk density determination

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.

2.2.3. Fourier transform infra-red (FTIR) analysis

A qualitative and preliminary analysis of the main functional groups that might be involved in metal uptake was analyzed with a FTIR/FT-NIR Spectrometer Perkin Elmer Spectrum Model. Spectrum of the monomer, pure and modified pine cone was measured within a range of 500–400 cm^{-1}.

2.2.4. 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 h at 90° and increased to 120° for 2 h. A mass of 0.2 g of pine cone was applied for analysis.

2.2.5. Acid number

The acid number (AN) before and after the modification process was determined using the method suggested by Matsuda (1987). Approximately 0.3 g of pine cone powder was 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 was added. The mixture was then be titrated using 0.1 mol/dm^3 aqueous solution of KOH in the presence of phenolphthalein as an indicator. The acid number was then determined from the following equation (1):

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

where V is the volume of 0.1 mol/dm^3 KOH used for the titration of the solution [ml], H is the 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 is the sample weight (g).

2.2.6. 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, and 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 10 cm^3 acrylic acid in 125 cm^3 of hexane. Graft co-polymerization was carried out by mechanical stirring for 2 h 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 h 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.

2.2.7. 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 °C and then titrated against a $KMnO_4$ solution of 0.05 mol/dm^3.

$$\text{The amount of } MnO_2 \text{ deposited} = \frac{V \times 0.2 \times 100}{W} (\text{meq}/100\,\text{g}) \qquad (2)$$

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.

2.2.8. 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 h 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.

2.2.9. 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 °C/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. Results and discussion

3.1. Theory of Fenton's oxidation

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 ($^{\bullet}OH$ 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 $HO^{\bullet}$ production and hydro peroxide in the process is:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\bullet} \tag{3}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \tag{4}$$

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \tag{5}$$

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

$$RH^{\bullet} + HO^{\bullet} \rightarrow H_2O + R^{\bullet} \tag{6}$$

Argun, Dursun, Karatas, and Gürü (2008) showed that the change in 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. (3)) by accounting for the dissociation water as

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \tag{7}$$

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. Eq. (7) 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, Choi, & Huang, 2005). Therefore, change in solution pH during the Fenton's oxidation process may also be applied to monitor the progress of the oxidation.

3.2. Fenton's modification

In this investigation, the optimum H_2O_2/Fe^{2+} ratio was determined by keeping the H_2O_2 concentration constant and varying the Fe^{2+} concentration. The initial pH of solution was fixed between 3.0 and 4.5 which have been shown to be optimum for Fenton's reaction from literature (Niaounakis & Halvadakis, 2006). The progress of the oxidation was monitored by measuring the ORP and the change in H^+ ion concentration at the end of the oxidation process.

Table 1
Changes in solution pH and ORP for the variation of Fe^{2+} concentration between 5000 and 50 mg/dm^3 at fixed concentration of H_2O_2 of 100,000 mg/dm^3 during Fenton's reagent treatment.

Fe^{2+} conc. (mg/dm^3)	Initial pH	Final pH	ΔH^+ ion (mmol/dm^3)	ORP (mV)
5000	2.38	2.61	1.714	251.9
2000	2.42	2.72	1.896	253.5
1000	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 1 (table not shown) 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:.

$$\Delta[H^+] = \Delta[H^+ \text{Final}] - \Delta[H^+ \text{Initial}] \tag{8}$$

and

$$pH = -\log[H^+] \tag{9}$$

When the H_2O_2 concentrations were kept constant at 100,000 mg/dm^3 and the concentration of Fe^{2+} varied between 5000 and 50 mg/dm^3, ΔH^+ increased initially. 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.

3.2.1. Bulk density measurement

The extraction of plant components such as soluble sugars, lignins and tannins has been successfully monitored by bulk density measurements by several authors (Marshall, Wartelle, Boler, Johns, & Toles, 1999; Ofomaja & Naidoo, 2011; Wartelle & Marshall, 2000). Pore spaces exposure on the extraction of these components within the plant matrix will cause the pine cone power bulk density to decrease as compared with the untreated material.

On treatment of pine cone powder with Fenton's reagent, oxidation and extraction of plant organic components occurs which was seen 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/cm^3. When concentration of Fe^{2+} was further increased to 5000 g/cm^3 the value for bulk density increased slightly rather than decreasing. The decreasing values of bulk density may therefore be explained by

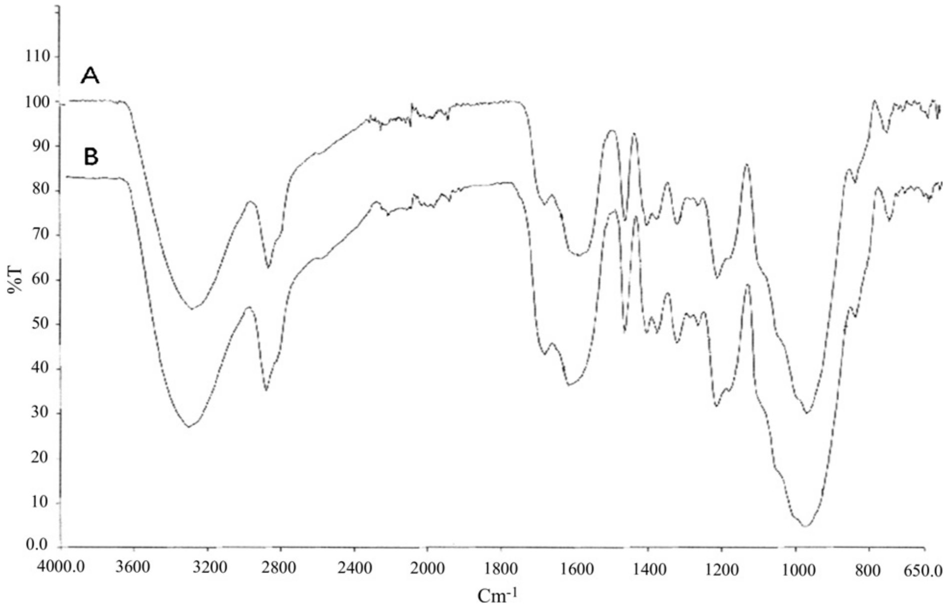

Fig. 1. FTIR spectras for the (a) raw and (b) Fenton's reagent treated pine.

the oxidation and extraction of plant components for the pine cone matrix, this oxidation process increases 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.

3.2.2. *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.

3.2.3. *FTIR analysis 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. 1 is 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-Martini, Meseguer-Zapata, Ortuno, Aguilar, & Llorens, 2010) and the peak observed at 2927.95 cm^{-1} represents the aliphatic C—H group while the peak at 1607.67 cm^{-1} corresponds to the C=O stretch. The peaks between 1023.26 and 559.32 cm^{-1} may be assigned to the —C—C— and —CN stretching, respectively (Malkov, 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.

An increase in the intensities of the above peaks is due to oxidation of the functional groups on the pine cone surface. Argun et al. (2008) also reported that pine cone surface was oxidized during Fenton's reagent treatment. Oxidation of primary or secondary alcohols of the pine cone surface may occur leading to increased number of carbonyl groups. This will lead to a reduction in —OH and a corresponding increase in the acidity of the surface. The other functional groups present on the surface did not show any significant difference indicating that Fenton's oxidation did not produce any other modification to the structure of the pine cone.

3.2.4. *Acid number analysis*

The conversion of free —OH groups on wood products has been measured by acid number (AN mg KOH/g) determination (Doczekalska, Bartkowiak, & Zakrweski, 2007; Papadopoulos, Militz, & Pfeffer, 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. 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 28.05 mg KOH/g as the concentration of Fe^{2+} increased from 50 to 2000 mg/dm^3 (see Fig. 2). 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.

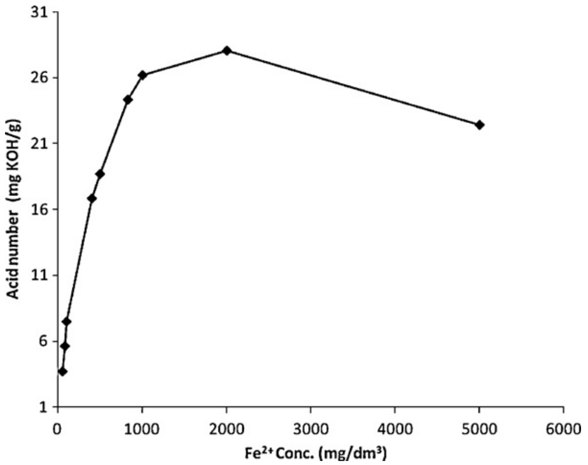

Fig. 2. Acid number of Fenton's reagent treated pine cone versus the concentration of of Fe^{2+} added.

3.3. Initiation of grafting reaction

Grafting of functional polymers onto a substrate involves three basic steps; (i) formation of free radicals using a radical initiator, (ii) formation of free radical sites on substrate, and (iii) grafting of monomer units onto the substrate. 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:

$$MnO_4^- + 3e^- + 4H^+ \rightarrow MnO_2 + 2H_2O, E^0 = 1.68\,V \qquad (10)$$

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:

$$Mn^{4+} + HNO_3 \rightarrow Mn^{3+} + H^+ + NO_3^{\bullet} \qquad (11)$$

The nitrate radical produced abstracts hydrogen ion from the substrate to transfer the radical site to the substrate molecules as shown in Eq. (12):

$$\text{PineCone} - OH + NO_3^{\bullet} \rightarrow \text{PineCone} - O^{\bullet} + HNO_3 \qquad (12)$$

Therefore, varying the initial concentration of $KMnO_4$ in Eq. (10) 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 $NO_3^{\bullet}$ in solution and also due to NO_3 radical interacting with the pine cone powder surface. It will also be observed that Eq. (11) 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.

Fig. 3a shows 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. At this stage (Eq. (10)), 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. 3a). 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 the initiator system with pine cone, it was also observed that the final ORP values were lower for higher concentrations than for lower concentrations of $KMnO_4$ (Fig. 3a). 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 for higher initial concentration of $KMnO_4$ than with 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. (11)) 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 result, 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 mequiv./100 g of pine cone. The results as observed from Fig. 3b, reveals that the amount of MnO_2 deposited was higher for the solutions with higher production of

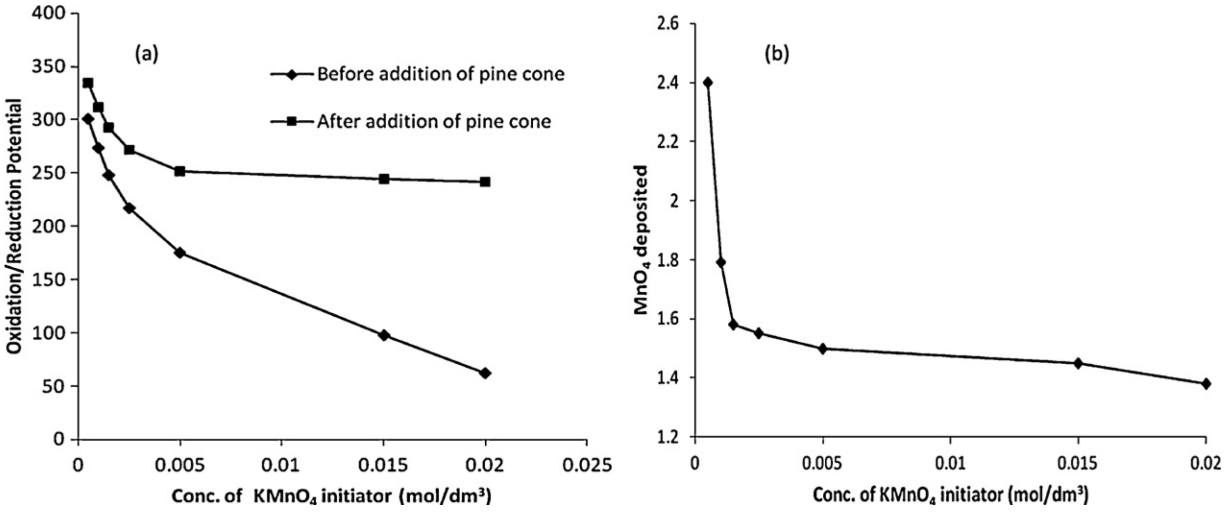

Fig. 3. Relationship between initial $KMnO_4$ concentration and (a) oxidation/reduction potential and (b) amount of MnO_2 deposited on the pine cone surface of acrylic acid grafted Fenton's reagent treated pine cone.

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). 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 (Fig. 4), 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). According to Eq. (11), 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 favored by higher initial $KMnO_4$ concentrations than lower concentrations. This result therefore confirms that 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.

3.4. Effect of plant materials on grafting

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

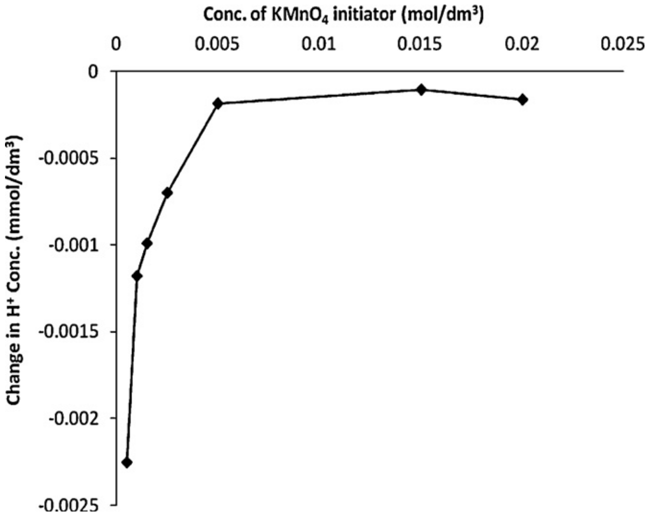

Fig. 4. Relationship between change in hydrogen ion concentration with initial $KMnO_4$ concentyration for Fenton's reagent treated pine cone.

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

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 are measured using the expressions below:

Homopolymer conversion (HPC)

$$HPC = \frac{\text{wt. of homopolymer}}{\text{wt. of monomer}} \times 100 \tag{13}$$

Monomer conversion (MC)

$$MC = \frac{\text{wt. of crude product} - \text{wt. of original material}}{\text{wt. of monomer}} \times 100 \tag{14}$$

Grafting efficiency (GF)

$$GF = \frac{\text{wt. of grafted material after extracting homoplymer} - \text{wt. of original material}}{\text{wt. of grafted crude product} - \text{wt. of original material}} \times 100 \tag{15}$$

These parameters were monitored against the increasing concentration of the radical initiator ($KMnO_4$). The results of this analysis are shown in Table 2. From the results, it was observed that as the concentration of the radical initiator increased, the weight of the crude product increased while the weight 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 radicals 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 mequiv./100 g) had higher MnO_2 deposited values than the Fenton's treated grafted pine (1.38 mequiv./100 g). The change in hydrogen ion concentration, ΔH^+, was found to be lower for the raw grated pine than for the Fenton's treated sample, meaning that less Mn^{4+} to Mn^{3+} conversion took place. This result may be

Table 2
Grafting parameters for the grafting of acrylic acid onto Fenton's modified and raw pine cone at different concentrations.

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

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.

3.5. Changes in surface properties of grafted pine and grafted Fenton's treated pine cone

3.5.1. Surface 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 functions increased, they 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 0.00557 to 0.00225 mol/g as the concentration of $KMnO_4$ increased from 0.0005 to 0.0200 mol/dm^3. This result indicates that the samples treated with lower concentrations of $KMnO_4$ would likely have grafted more of the acrylic acid onto its surface than those treated with a higher concentration of $KMnO_4$.

3.5.2. 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. 5 shows the functional groups on the acrylic acid monomer while Fig. 6 shows the raw pine (not grafted) and Fenton's treated pine (grafted) and Fig. 7 shows the raw (grafted) and Fenton's treated pine (grafted).

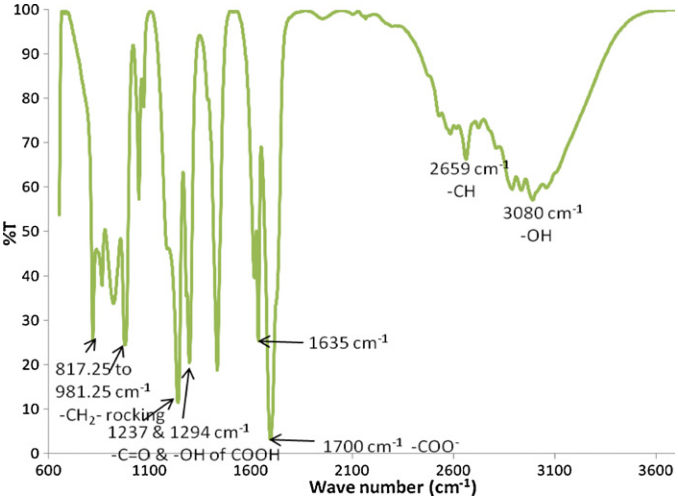

Fig. 5. FTIR spectra for acrylic acid monomer.

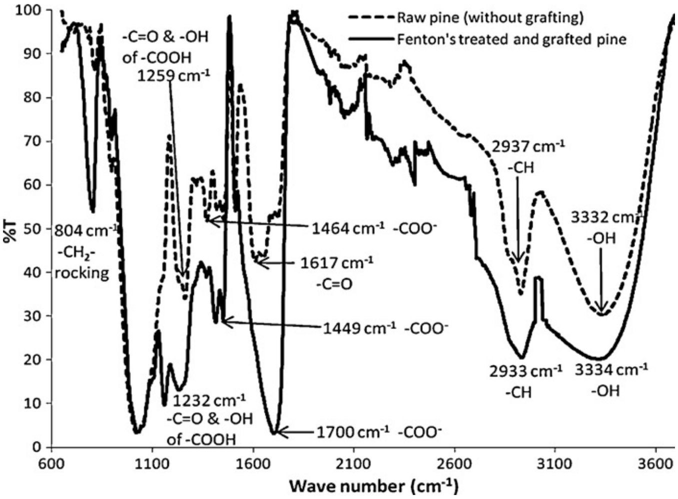

Fig. 6. Comparison of FTIR spectra's for the raw and Fenton's reagent treated grafted pine cone.

Fig. 5 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, Chuai, Aljaz, Iqbal, & Hiu, 2009). Peaks 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

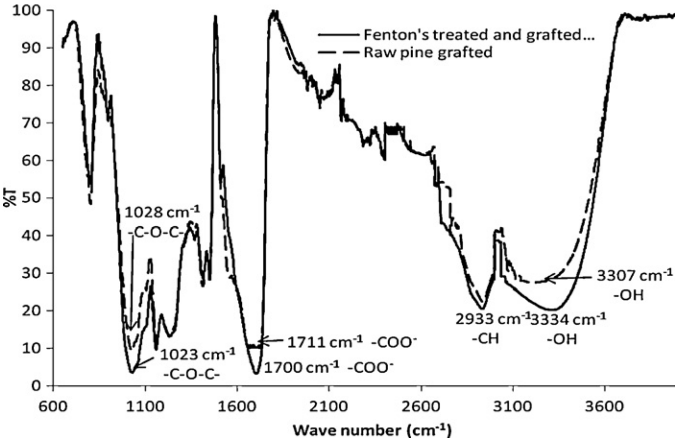

Fig. 7. Comparison of FTIR spectra's for the raw grafted and Fenton's reagent treated grafted pine cone.

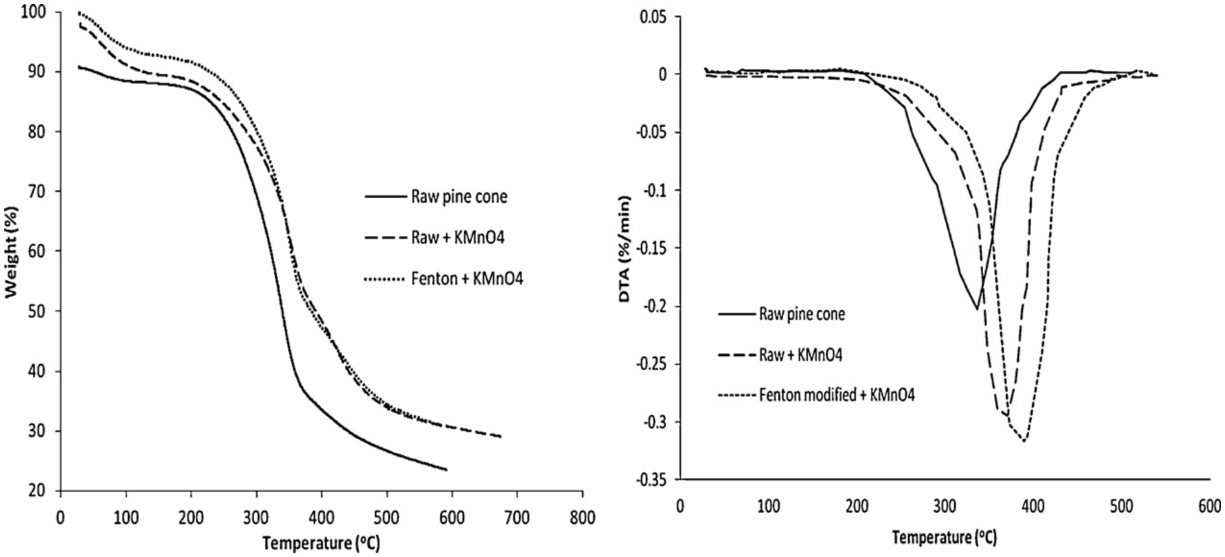

Fig. 8. (a) TGA and (b) DTA for raw pine, raw grafted and Fenton's reagent grafted pine.

(Neira, Tarraga, & Catalan, 2008). The peak at 2659 cm^{-1} is indicative of CCH stretching (C sp^3), while —OH band is since at 3080 cm^{-1} (Neira et al., 2008).

Fig. 6 shows the comparison between the spectra's of the raw pine cone (with no grafting) and the grafted Fenton's treated pine cone. It will be observed that the major peaks of both samples are 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} indicting 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 concludes 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. 7). For examples, higher peak intensities with slight shifts of —OH and —COO$^-$ were observed for the Fenten'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.

3.5.3. 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. 8a and b shows the thermogravimetric curve (Fig. 8a) and the derivative thermogravimetric (DTA) curves (Fig. 8b) for the raw pine cone, raw pine cone grafted with acrylic acid and Fenton's modified pine grafted with acrylic acid.

Fig. 8a shows an initial loss of weight loss at low temperature (below 140 °C) which can be attributed to desorption of water molecules from the materials. Several authors have shown this water loss below 140 °C for various cellulosic materials, while the stability of the cellulosic matrix reduces at higher temperatures causing instability and decomposition at higher temperatures (Dahou, Ghemati, Oudia, & Aliouche, 2010; Fares, Salem, & Khanfar, 2011). The raw pine cone began to show signs of decomposition at 169 °C, whereas the grafted raw pine and Fenton's modified grafted pine cone started decomposing at 260 and 281 °C, respectively. Final decomposition temperatures were observed at 495, 521 and 532 °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. Brebu, Ucar, Vasile, and Yanik (2010) reported similar trends of pine cone having lower decomposition temperature than synthetic polymers. These results indicates that grafting of acrylic acid onto pine cone to 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. 8b 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 °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 °C respectively. Similar shifts in endothermic peaks after grafting of polymer onto bamboo cellulose has also been reported by Wan et al. (2011). This 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.

3.6. Percentage methylene blue removal

The values of percentage methylene blue 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 3.

Table 3
Grafting parameters for the grafting of acrylic acid onto Fenton's modified and raw pine cone at different concentrations.

$KMnO_4$ conc. (mol/dm^3)	Surface charge (mol/g)	Percentage methylene blue removal	BET (m^2/g)
0.0005	0.00557	83.52	4.09
0.0010	0.00452	88.36	4.18
0.0015	0.00268	92.84	4.26
0.0025	0.00243	94.20	4.67
0.0050	0.00236	95.11	7.39
0.0150	0.00227	96.95	8.22
0.0200	0.00225	97.90	10.51
Raw grafted + 0.0200	0.00178	74.77	1.24
Raw	0.00122	57.75	4.90

The results revealed that the percentage 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. The results also show that there is an inverse relationship between the methylene blue adsorbed and the surface charge. Therefore the surface charge which is determined by the concentration of carboxylic acid grafted on the surface does not control methylene blue adsorption. 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 smaller than the Fenton's treated material and this affected the percentage methylene blue removal of the sample. Therefore we can conclude the surface areas of the samples are more significant for the dye adsorption than the percentage grafting.

4. Conclusion

The effect of plant organic component on the grafting of acrylic acid onto pine cone has been determined and the effect of concentration of radical initiator, $KMnO_4$ measured. Plant components were extracted using Fe^{2+}/H_2O_2 ratio of 1:50. ORP and ΔH^+ were employed in monitoring the Mn^{3+} generated and MnO_2 deposited during initiation process. Increasing $KMnO_4$ concentrations increased the MnO_2 deposited but reduced the Mn^{3+} generated. Presences of plant components reduce the OPR and pH, thereby reducing the grafting efficiency.

Surface charge and FTIR analysis of the raw and grafted pine cone confirms that acrylic acid monomers were actually incorporated onto the pine cone as was observed from the increased surface charge of the final product and the increased intensity of the carbonyl peaks in the grafted sample. Comparison of the raw grafted and Fenton's treated grafted pine also showed that Fenton's reagent treatment improved the ability of the pine cone to be grafted with acrylic acid. The methylene removal from aqueous solution was correlated with the BET surface area of the samples rather than the grafting efficiency.

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