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ORIGINAL ARTICLES

Removal of Mn (II) and Fe (II) ions From Aqueous Solution Using Precipitation and Adsorption Methods

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ABSTRACT

In this study precipitation and adsorption methods were carried out for the removal of Mn and Fe cations from aqueous solution. Adsorption process was applied onto activated carbon prepared from chemical activation of sawdust with 50 % (v/v) H_3PO_4 at 500°C for 2h. One extend precipitation test was examined in a binary system. The effect of pH on the removal efficiency was studied. During precipitation method, the maximum removal observed at pHs 6 and 7 and comprised 98 % and 95 % for Mn (II) and Fe (II) ions, respectively. The X-ray diffraction of the precipitated solid was shown that the iron deposited as Fe_3O_4 with the transfer of CaO to $CaCO_3$ in the presence of Na_2CO_3. Within the change in pH from 2 to 9 in the adsorption process, it was observed also that there is a great effect of the pH medium on the removal efficiency. Consequently, three stages of pH variation were appeared as follows: the first one between 2 to 4, the second between 4 to 6 and the third stage in the basic medium. The obtained data showed that the most suitable medium for removing Mn and Fe (II) ions by activated carbon beings at pH 6. In addition the equilibrium adsorption data were analyzed using Langmuir and Freundlich isotherm models and the results shown that the adsorption behavior of both ions could be described well reasonably by Langmuir model with higher R^2 values (0.9962–0.9975). Overall, the study verified that both methods are significantly effective in the removal of manganese and iron from water at optimum pH 6.

Key words: Mn and Fe removal, Precipitation, Adsorption, Activated carbon

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Introduction

Water is the main component for living organisms, and the increase in water pollution as a result of progress in the industrial technologies, has been reduced using many methods to treat the wastewater (Chapman D., 1992; WHO, 1984). The choice of suitable methods is controlled by different factors such as the efficiency of removing the pollutant materials, the availability of the used chemicals and the chemistry of the contaminated materials beside the process cost (Letterman, 1999). It is well–known that the pollutants in wastewater discharge from industrial effluents, sewage, sludge, pesticides, and fertilizers. The composition of the contaminated water depends on the source of the pollutant, the chemical composition of the original water whether it is surface or underground water and then the chemical reaction with the soil. For example, groundwater contains one or more contaminants like iron, manganese, ammonium, methane and natural organic matter, e.g., humic acid. Hence, before using this water supply for agro-irrigation purposes, these contaminants should be removed or reduced to the acceptable levels. Iron and manganese, which are usually present in the groundwater as divalent cations, considered to be contaminants mainly due to their organoleptic properties. The maximum recommended levels of Mn and Fe in drinking water are 0.1 and 0.3 mg/L, respectively (Letterman, 1999).

There are various methods for removing Mn and Fe cations from the wastewater including ion-exchange method (Vaaramaa and Lehto, 2003), oxidation by oxidizing agents such as chlorine and potassium permanganate (Ellis *et al*., 2000), activated carbon and/or other filtering materials (bin Jusoh *et al*., 2005; Munter *et al*., 2005; Okoniewska *et al*., 2007), supercritical fluid extraction (Andersen and Bruno, 2003), bioremediation (Berbenni *et al*., 2000), and treatment with limestone (Aziz *et al*., 2004). Some of these methods are simple and economic while the others are complicated and expensive (Vaaramaa and Lehto, 2003). In oxidation treatment, oxygen, chlorine or potassium permanganate ($KMnO_4$), is generally used for Fe (II) and Mn (II) oxidation. Adsorption using activated carbon is an effective technique to remove heavy metals from wastewater (Ahmedna *et al*., 2010), that is due to that activated carbon has a pore size distribution which control its adsorption capacity, a chemical structure that influences its interaction with polar and non-polar adsorbates, and active sites which determine the type of chemical reactions with other molecules (Ahmedna *et al*., 2010).

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However, in developing countries such as Egypt, traditional activated carbon remains an expensive material for heavy metal removal. Recently, many researches have been published in the literature including preparation of activated carbons from various cheaper and alternative materials, e.g., agricultural by-products and biomass materials, using chemical activation with H_3PO_4 (El-Sherif and Fathy, 2011; Girgis *et al*., 2007 and 2011; Kazemipour *et al*., 2008). However, there is only limited research on the preparation of activated carbons from woody biomass such as sawdust for uptaking heavy metals such as Hg (II) from wastewaters (Budinova *et al*., 2006).

Balintova and Petrilakova (2010) reported that the removal of Fe, Mn and Cu ions from acid mine drainage (AMD) by precipitation with NaOH depends on the pH value besides the oxidation state of the removed cations. On the other hand, various authors (bin Jusoh *et al*., 2005; Okoniewska *et al*., 2007) found that the removal of iron, manganese and other heavy metals by activated carbon depends on the nature of carbon (porosity, surface area, oxygen functional groups, etc.). Within the frame of this policy, the present paper narrates the investigation of Mn and Fe (II) ions removal from aqueous solution using precipitation and adsorption methods in order to determine the optimum pH for the effective removal. The adsorption was carried out using an activated carbon obtained from the chemical activation of sawdust biomass with 50% H_3PO_4. The adsorption data was analyzed by using Langmuir and Freundlich isotherm models. Overall, this study was also intended to determine the efficiency and the optimum conditions in precipitation and adsorption processes for removal of both cations.

Materials and Methods

Preparation of metal ion solution and activated carbon adsorbent:

Iron solution was prepared from $FeSO_4.7\ H_2O$ (2.489 g in 500 ml distilled water equivalent to one gram/liter). Manganese solution was prepared from $MnSO_4.H_2O$ (1.538 g in 500 ml distilled water equivalent to one gram/liter).

The activated carbon was prepared-in-laboratory by activation of ground sawdust with 50 % (v/v) H_3PO_4 in an electric furnace at 500^{o}C for 2 h under its own atmosphere. After cooling, the pyrolyzed sample was washed for several times with distilled water until pH of filtrate becomes ~ 6 and then dried overnight at 100^{o}C. This sample is labelled as *SAC*. Surface texture (total surface area, total pore volume and pore diameter) and morphology for SAC were characterized using Quantachrome Nova Automated N_2 gas adsorption at 77K and scanning electron microscopy (SEM-JEOL, JXA–840A Electron Probe Micro-Analyzer, Japan), respectively.

Metal ion precipitation by jar test:

The jar test procedure was adopted to evaluate the removal of iron and manganese by precipitation using a calcium oxide dose (300 mg/l) under different pH values (from 6 to 9). 0.1 M of Na_2CO_3 or HNO_3 solution was used to adjust the pH followed by flash mixing for one minute at 300 rpm, and then reducing the speed to 50 rpm for 15 minutes. This was followed by plain settling of flocks for 30 minutes at 25^{o}C. Two initial concentrations of 1 and 2 mg/L from Mn and Fe (II) aqueous solutions, respectively, were prepared. Under the above experimental conditions, a binary solution of both metal ions with 2 mg/L was also prepared in order to examine the removal efficiency. Samples from the supernatant were collected to determine the residual iron and manganese concentrations. The pH measurement was performed by a Knick Digital pH meter model 646. A sample from the filtrate of Fe and Mn cations was analyzed using X-ray diffraction to determine the two metal ions content after precipitation.

Adsorption of Mn (II) and Fe (II) ions by SAC adsorbent:

A stock solution of 1000 mg/L was prepared by dissolving appropriate amount of each metal ion in a 1 L distilled water. Single bottle test was carried out using SAC adsorbent in a 250 ml stoppered conical flask containing 100 ml of test solution at 25^{o}C. The effect of pH on the equilibrium adsorption of Mn and Fe (II) ions removal was followed in the range of 2–9. The required pH values were adjusted by adding 0.1M Na_2CO_3 or 0.1 M HNO_3 solution.

Batch experiments were carried out by shaking 100 mg of the dried finely powdered carbon with 100 ml of the solution of metal ions to attain an adsorption equilibrium state. By maintaining pH, contact time and temperature, batch adsorption experiments were carried out at various initial metal concentrations (1 – 6 mg/L). Then the residual concentrations of Mn and Fe (II) ions were determined using an atomic absorption spectrophotometer (*AAS, Varian model 210*). The amount of adsorbed metal ions was calculated from the mass balance expression given by:

$$q_e = \frac{(C_o - C_e)}{M} V \qquad (1)$$

where q_e is the amount of metal ions adsorbed by the SAC (mg/g), C_o initial ion concentration of Mn or Fe (mg/L), C_e equilibrium concentration of metal ions (mg/L) after the adsorption procedure, M the mass of adsorbent in (mg) and V the volume of metal solution in contact with the adsorbent (ml).

The adsorption percentage of metal ions was calculated as follows:

$$\%\ \text{Removal}\quad \text{Effeciency} = \left(C_o - C_e \big/ C_o\right) \times 100 \qquad (2)$$

Results and Discussion

Effect of pH on precipitation of manganese and iron by the jar method:

pH is an important parameter that controls the metal ion adsorption process. In this research the precipitation and adsorption behavior of metal ions were studied at pH ranges of 6-9 and 2-9 to determine the optimum pH, respectively.

Precipitation experiments were carried out in the pH range of 6 to 9 using two different initial concentrations of 1 and 2 mg/L for Mn and Fe cations, respectively. The results are plotted as shown in Fig. 1 (a and b). In the case of Mn (II) ions, the results indicated that the efficiency of removal reaches 75 % and 98 % at pH 6 for 1 and 2 mg/L concentrations, respectively, and then these values decrease slightly as pH increases to 7. By increasing the pH to 9, the percentage of the efficiency increases slightly. At the acidic medium the manganese may be precipitated as oxide or hydroxide, while at pH 7 this oxide may be stabilized in the medium or solution. The slight increase in the efficiency in the basic medium may due to the formation of some aggregates in the produced precipitate which form a surface coating on both metal ions. For removing of Fe (II) ions, it is found that in the acidic medium at pH equals 6, the removal efficiency equals 15.5 and 60 % for the initial concentrations equal to 1 and 2 mg/L, respectively. As the pH increases from 6 to 7, the efficiency of removal increases rapidly recording 60 and 95 % at the neutral medium and then decreases slightly as the pH transfers from pH 7 to 9.

As shown in Fig.2, the X-ray diffraction of the precipitate indicates the formation of both oxides Fe_3O_4 and $CaCO_3$. The appearance of the $CaCO_3$ may be due to the reaction of the buffered solution Na_2CO_3 with the excess CaO which was added to precipitate the metal ions as described in the experimental section. From theses results, it can be concluded that the preferred medium for removing iron is the neutral or slightly basic medium, while for manganese it is the acidic medium.

For a mixture solution consists of Mn (II) and Fe (II) ions with initial concentration of 2 mg/L, the results indicated that the maximum removal efficiency was reached to 98.6 and 97.9 % for manganese and iron at pHs 8 and 7, respectively, during the precipitation process. In comparison to precipitation data for two metal ions separately, it can be detected that the removal of Mn (II) and Fe (II) ions by precipitation in a binary solution is a successful process. So that, it is recommended that the precipitation process for two metal ions is carried out in a slightly basic medium.

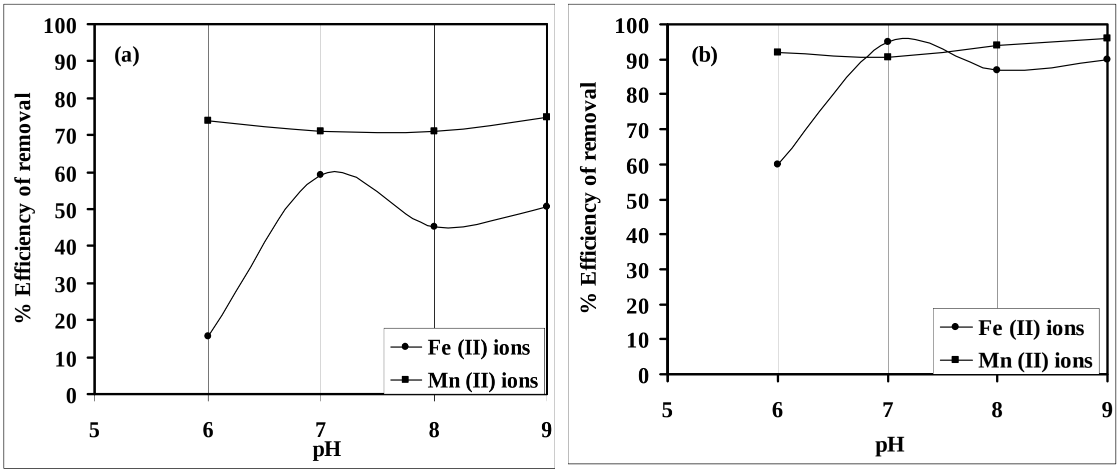

Fig. 1: Effect of pH on the precipitation efficiency of Fe (II) and Mn (II) ions with initial concentrations (a) 1 mg/L and (b) 2 mg/L.

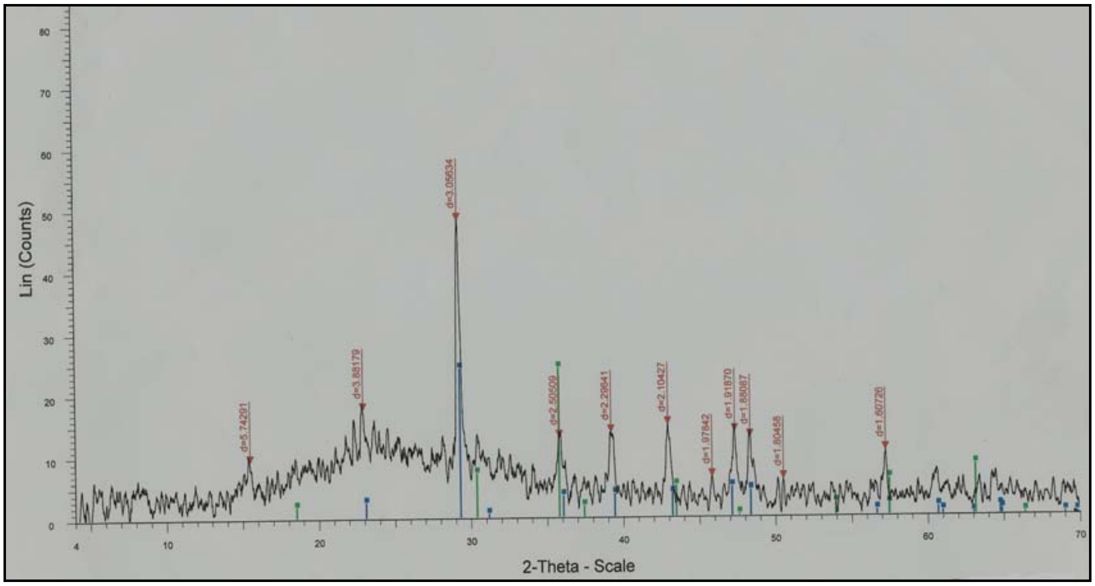

Fig. 2: X-ray diffraction patterns of iron and manganese precipitates in solution at pH 6.

Characterization of the prepared adsorbent SAC:

In this study an active carbon adsorbent was used that is prepared by the activation of sawdust with phosphoric acid (50 % v/v). The characteristics of this adsorbent are summarized as follows: carbon yield (44.8 %), slurry pH (3.5), total acidity (2.45 mequiv H^+/g) and iodine number (350 mg/g). According to these data, the SAC adsorbent surface has acidic character and contains predominantly acidic oxygen functional groups. Hence, this property enhances the attraction of the metal ions on the surface of the used active carbon. Also, the porous texture of prepared activated carbon showed a moderate internal porosity (the total surface area and total pore volume equal 400 m^2/g and 0.120 cm^3/g, respectively), and pore diameter equals 12 Å. Figure 3 shows the Surface morphology of sawdust and activated sawdust, respectively, at magnification 1000x. the activated sawdust shows highly rough surface with defined pores and cavities.

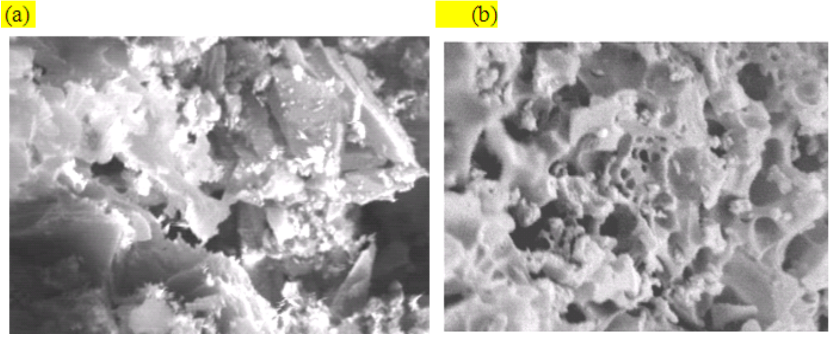

Fig. 3: SEM photographs at magnification 1000x for (a) sawdust and (b) SAC samples.

Effect of pH values on the efficiency of removing Mn and Fe by adsorption on SAC adsorbent:

The hydrogen ions on the adsorbent surface can be competing with metal ions, which determine the valence state of the ions and their precipitation process, and hence pH acts as an important factor in the adsorption process.

Figure 4 depicts the variation of the efficiency of removal with the pH values of the medium containing the desired metal ion. It shows that as the pH values increase from 2 to 9, the efficiency the removal of Mn (II) ions increases rapidly in the acidic medium (from 2 to 4), and then decrease in the basic medium (from 6 to 9) passing by the neutral state at pH 7. On the other hand, the efficiency of removal of Fe (II) ions goes through three stages. The first one is between pH 2 to 4 and shows an abrupt increase. The second stage is between the pH 4 to 6 and shows a plateau shaped curve, while the third stage represents the decrease in the efficiency reaching to the minimum value at pH 9. The last stage may due to the electrostatic repulsion between the positively charged metal ion and the active sites on the surface of the activated carbon in the basic medium. The change in the behavior between Mn and Fe ions may due to the ability of the active carbon to attract the Mn ions more than Fe ions. Okoniewska *et al.* (2007) found that the maximum removal of Fe and Mn ions from underground water by impregnated activated carbon was attained at pH 9, respectively. Also, they reported that $KMnO_4$ enhanced the removal of Mn (II) ions. Finally, it can be concluded that the maximum removal of both cations obtained at pH 6 as a result of both adsorption as well as precipitation. Hence, pH 6 was chosen as the optimum pH for Mn and Fe adsorption onto the hereby SAC adsorbent.

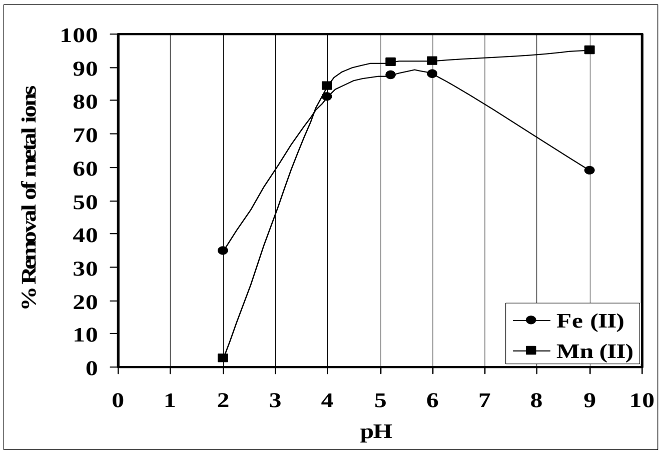

Fig. 4: Effect of pH on the removing efficiency of Mn (II) and Fe (II) by adsorption onto the prepared adsorbent (SAC).

Adsorption isotherms of Mn (II) and Fe (II) ions onto SAC adsorbent:

Adsorption isotherms were constructed and adsorption capacities were calculated using the Langmuir model for monolayer saturation of metal ions on carbon binding sites. The non-linear form of the Langmuir equation is given as follows:

$$q_e = K_L\, Q_0\, C_e \big/ (1 + K_L\, C_e) \tag{3}$$

where q_e is the amount of metal ion adsorbed per unit mass, C_e is the equilibrium metal ion concentration in solution, Q_o is the adsorption maximum or adsorption capacity and K_L is the affinity or association constant of the cation for the adsorbent. This adsorption model is valid when: (i) the adsorbent surface is homogeneous; (ii) both surface and bulk phases exhibit ideal behavior; and (iii) the adsorption film is monomolecular.

The Freundlich model is an empirical equation and can be applied for non-ideal adsorption on heterogeneous surfaces and multilayer adsorption. The equation is commonly given by:

$$q_e = K_F\, C_e^{1/n} \tag{4}$$

where K_F (mg/g (L/mg)$^{1/n}$) is a constant related to the adsorption capacity and *1/n* is an empirical parameter related to the adsorption intensity, which depends on the heterogeneity of the material. The slope of 1/n ranging between 0 and 1 is a measure of the surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Sari and Tuzen, 2009). A value for 1/n below one indicates a normal Langmuir isotherm while 1/n above one is indicative for cooperative adsorption (Sari and Tuzen, 2009).

Table 1 summarizes all the constants and correlation coefficients (R^2) of the two adsorption isotherm models in order to determine the adsorption isotherm which fitted with adsorption of both metals onto studied adsorbent. Fig. 5 shows the adsorption isotherms of Mn and Fe ions by an adsorbent (SAC) at different initial concentrations of 1 – 6 mg/L of manganese and iron cations. From Table 1, it was found that the Langmuir isotherm model yielded the best fit with R^2 which was higher than 0.99 as compared to Freundlich isotherm. Conformation of the experimental data into the Langmuir isotherm equation indicated the homogenous nature of SAC adsorbent, i.e., each heavy metal ion/SAC adsorption had equal adsorption activation energy. The results also demonstrated the formation of monolayer coverage of heavy metal ions at the outer surface of this adsorbent. In addition the values of 1/n are less than 1, which indicates the Langmuir adsorption of two metal ions onto the SAC adsorbent.

The shape of the isotherm can also be considered when predicting whether an adsorption system is "favorable" or "unfavorable". The essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter $R_L = 1/(1+K_LC_o)$. According to the value of R_L, the isotherm shape may be interpreted as given in Table 2.

Table 1: Langmuir and Freundlich constants for adsorption of Mn (II) and Fe (II) onto activated carbon

	Langmuir model				*Freundlich model*		
Heavy metals	Q_o (mg/g)	K_L (L/g)	R_L	R^2	K_F (mg/g (L/mg)$^{1/n}$)	*1/n*	R^2
Mn (II)	4.72	4.78	0.0337	0.9962	4.67	0.502	0.909
Fe (II)	6.54	4.32	0.0371	0.9975	5.83	0.435	0.976

Table 2: Separation factor for shape of isotherm

Value of R_L	Type of adsorption isotherm
$R_L > 1$	*Unfavorable*
$R_L = 1$	*Linear*
$0 < R_L > 1$	*Favorable*
$R_L = 0$	*Irreversible*

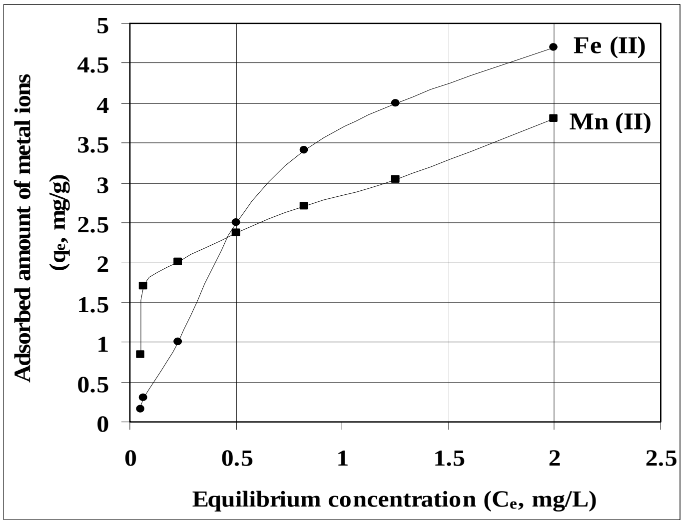

Fig. 5: Adsorption isotherms of Mn and Fe onto an SAC adsorbent at pH 6.

As it is observed from Table 1, the values of R_L were found to be between 0 and 1 (0.033–0.037), which points to a favorable adsorption of Fe (II) or Mn (II) ions on the prepared adsorbent. This again confirmed that the Langmuir isotherm was favorable for adsorption of Mn and Fe cations onto SAC adsorbent under the conditions used in this study. The Q_o values calculated using the Langmuir isotherm are 6.54 and 4.72 mg/g for Fe (II) and Mn (II) ions, respectively. Thus the adsorption capacity demonstrates that Fe (II) ions are more adsorbed than Mn (II) ions by SAC adsorbent because of the ionic radius and electronegativity of Fe ions are smaller than those of Mn. The adsorption capacity of SAC adsorbent for Fe (II) and Mn (II) ions is larger than that obtained either by impregnated activated carbon with $KMnO_4$ (Okoniewska *et al.*, 2007) or commercial granular activated carbon (bin Jusoh *et al.*, 2005). The values of K_F calculated using the Freundlich model indicate that the activated carbon used as adsorbent has a high affinity towards the two heavy metal ions. The constant value of K_F is higher for adsorption of Fe (II) ions onto the present adsorbent which is consistent with the experimental observations. Also, not much difference between the adsorption intensities (1/n) of Fe (II) and Mn (II) ions is observed.

Conclusions:

The following conclusions can be drawn from the present study:

1) The removal efficiency of Mn (II) and Fe (II) cations from aqueous medium was pH dependent in both precipitation and adsorption methods as well as the initial concentration.

2) For the precipitation method, it is preferred to remove iron from water in neutral medium and manganese removal in acidic medium when pH varied from 6 to 9. In a binary solution of two cations, the maximum

removal for two cations occurred in slightly basic medium at pH 8. The X-ray patterns for the precipitate indicated that iron precipitated as Fe_3O_4.

3) By the adsorption technique, the preferred medium for removing both cations by the studied SAC adsorbent attained at pH 5–6, i.e., in acidic medium.

4) The adsorption of both iron and manganese follows Langmuir isotherm. The adsorption capacity of the prepared carbon is 6.54 and 4.72 mg/g for Fe and Mn ions, respectively. Finally, the study revealed that both methods are significantly effective in the removal of manganese and iron from water at optimum pH 6.

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