Evaluation of Egyptian Banana Peel (Musa sp.) as a Green Sorbent for Groundwater Treatment

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ABSTRACT

Present study was conducted to investigate the removal of manganese from aqueous solution by using eco-friendly biosorbent of Banana peels activated carbon (BPAC). Batch experiments have been carried out to determine the influence of parameters such as pH, biosorbent dose, initial metal ion concentrations and contact time on the biosorption process. From these investigations, a significant increase in percentage removal of manganese 97.4 % is observed at pH value 5.0, biosorbent dose 0.8 g, initial concentration 20 ppm, temperature 25 ± 2 °C, stirring rate 200 rpm and contact time 2h. The equilibrium concentration and the adsorption capacity at equilibrium of the experimental results were fitted to the Langmuir, Freundlich and Dubinin-Radushkevich (D–R) isotherm models; the Langmuir isotherm was found to well represent the measured adsorption data implying BPAC had heterogeneous surface. The predicted maximum monolayer adsorption capacity of manganese for BPAC are found to be 11.806 mg/g. Pseudo-first-order, pseudo-second-order kinetic and intraparticle diffusion model were used to analyze the biosorption data; it was observed that the pseudo-second-order model best represented the relationship. The calculated thermodynamic parameters showed that the biosorption of manganese onto BPAC is spontaneous and endothermic in nature. A raw groundwater samples were collected from Baharmos groundwater treatment plant network at Embaba and Manshiet Elkanater City/District-Giza, Egypt, for treatment at the best conditions that reached at first phase by BPAC. The treatment with BPAC could reduce iron and manganese value of raw groundwater by 91.4% and 97.1 %, respectively and the effect of the treatment process on the microbiological properties of groundwater sample showed decrease of total bacterial count either at 22°C or at 37°C to 85.7 % and 82.4 %, respectively. Also, BPAC was characterized using SEM and FTIR spectroscopy.

Keywords: groundwater treatment; manganese biosorption; banana peels; kinetic; thermodynamics

1. INTRODUCTION

Groundwater is generally considered as the best source for potable water as it is well protected from contamination. The most common problem limiting the use of groundwater in Egypt is its high iron and/or manganese content (Karakash 2005, Dahiya et al. 2008, Chen et al. 2008). The world health organization stipulates that the maximum acceptable level of iron in drinking water is less than 0.3 ppm and manganese less than 0.1 ppm (WHO 2004). The Egyptian authorities limit the iron in drinking water to 0.3 ppm and manganese to 0.4 ppm according to Egyptian Ministry of Health degree No. 458/2007. Manganese and iron are quite abundant metals in the earth crust and their presence in groundwater are due to leaching processes and vary widely depending on the rock types. They affect the appearance, taste, odor and color of the water. It is known that manganese exposure damages the nervous system functions (Bouchard et al. 2007) and several reports are available on the effects of exposure to manganese in water (Wasserman et al. 2006). Manganese and iron have variety of applications such as in metallurgical processes, mining, ceramics, dry cell batteries, pigments and paints which all can be sources of underground pollution (Chang et al. 2009, Rajic et al. 2009). Different techniques to remove iron and manganese are in use now, but the search for better, cheaper and safer technique will never stop (Nassar 2006). There are several methods for the removal of metals from aqueous solution including adsorption on activated carbon, ion exchange, chemical precipitation, and membrane filtration (Yu et al. 1999, Turkler 2012). Adsorption processes are generally known to be one of the most effective techniques for removal of environmentally hazardous metals. In bio-adsorption, removal of metal ions helps in the effective usage of bio-waste as metals stick on to the surface of biological components. Full scale biosorption process requires the biological materials which have high metal binding capabilities and specific heavy metal selectivity. It may involve one process or a blend of processes like adsorption, electrostatic interaction, chelation, micro-precipitation and ion exchange (Monisha et al. 2014). Sorption using plant waste material (if it is available) is impending alternative to chemical methods for ions removal from water system. These methods were reported as low cost (economic), natural (green), renewable and locally available adsorbents methods for water treatment (Zaidan et al. 2013) such as orange peel (Annadurai et al. 2002), rice husk (Saha 2009), rejected tea (Nasuha et al. 2010), pineapple leaves (Weng et al. 2009), garlic peel (Hameed and Ahmad 2009), Luffa cylindrical fibers (Demir et al. 2008).

Banana is one of the largest consumed fruit in the world and useless peels, therefore, creates one of the major agro-waste
problems. Banana (Musa sp.) is considered one of the most important favorable and popular fruits in Egypt and all over the world. In Egypt, the cultivated area reached 45,802 thousand feddans which produce about 760,505 thousand tons of banana fruits (Anonymous 2000). Preliminary investigations showed that several tons of banana peels are produced daily in market places and household garbage that create environmental nuisance. For this reason, BPAC have been tested as a green sorbent for water treatment.

The focus of the present study was to assess the potentiality of Banana peel activated carbon (BPAC), a commonly available waste material as a low-cost, natural and eco-friendly biosorbent for the economical removal of manganese ion from aqueous solution as an ideal alternative to the current expensive methods of removing metals from groundwater. The effects of various parameters such as, pH, biosorbent dose, initial metal ion concentration and contact time on the biosorption capacity were investigated. The equilibrium, kinetics and thermodynamics of biosorption process were also studied.

This study was also extends for the advanced treatment of raw groundwater collected from Baharmos groundwater treatment plant network at Embaba and Manshiet Elkanater City, Giza, Egypt at optimal parameters by BPAC. The efficiency of groundwater treatment depends on removal iron and manganese to certain acceptable limits.

2. MATERIALS AND METHODS

2.1 Adsorbate Solution

Manganese ion solution was prepared from analytical grade manganese sulphate (Merck Ltd). Stock solution of 1000 ppm of manganese was prepared by weighting 3.077 g from MnSO₄·H₂O in 1L double distilled water. The working solutions were prepared from the stock solutions by diluting it to appropriate volumes.

In order to explore the feasibility of BPAC biomass for groundwater treatment, water samples from Baharmos groundwater treatment plant network at Embaba and Manshiet Elkanater City, Giza, Egypt were collected in sterile plastic bottles and stored in a refrigerator at 4 ± 1°C until use and analyzed within 8 h. The physicochemical and microbiological characteristics of collected sample are listed in Table 1. All Physico-chemical and microbiological analyses were analyzed according to Standard Methods for the Examination of Water and Wastewater (APHA 2005).

The treatment with BPAC biomass was carried under optimum conditions similar to the batch adsorption studies.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Water sample</th>
<th>Limits *</th>
<th>Analysis</th>
<th>Water sample</th>
<th>Limits *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>24.37</td>
<td></td>
<td>Chemical Oxygen Demand</td>
<td>0</td>
<td>0 ppm</td>
</tr>
<tr>
<td>pH</td>
<td>7.8</td>
<td>6.5 - 8.5</td>
<td>Biological Oxygen Demand</td>
<td>0</td>
<td>0 ppm</td>
</tr>
<tr>
<td>Turbidity</td>
<td>0.85</td>
<td>1 NTU</td>
<td>Dissolved Oxygen</td>
<td>4.61</td>
<td></td>
</tr>
<tr>
<td>T.D.S.</td>
<td>477</td>
<td>1000 ppm</td>
<td>Total bacterial count (37°C)</td>
<td>17</td>
<td>50 C.F.U/ml</td>
</tr>
<tr>
<td>Total Hardness</td>
<td>321</td>
<td>500 ppm</td>
<td>Total bacterial count (22°C)</td>
<td>35</td>
<td>50 C.F.U/ml</td>
</tr>
<tr>
<td>Calcium Hardness</td>
<td>180</td>
<td>350 ppm</td>
<td>Total coliform</td>
<td>&lt;1</td>
<td>&lt;2 C.F.U/100 ml</td>
</tr>
<tr>
<td>Magnesium Hardness</td>
<td>141</td>
<td>150 ppm</td>
<td>Fecal coliform</td>
<td>&lt;1</td>
<td>&lt;1 C.F.U/100 ml</td>
</tr>
<tr>
<td>Iron</td>
<td>1.4</td>
<td>0.3 ppm</td>
<td>Fecal streptococci</td>
<td>&lt;1</td>
<td>&lt;1 C.F.U/100 ml</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.7</td>
<td>0.4 ppm</td>
<td>Parasites (Helminthes - Protozoa - amoeba)</td>
<td>Free</td>
<td>Free</td>
</tr>
</tbody>
</table>

* Limits are according to Egyptian Ministry of Health degree No. 458/2007.

2.2 Preparation of the Biosorbent

Experiments were conducted with peels of bananas, sourced from local Egyptian market. Peels were separated from the fruit gently, washed thoroughly and dried in an oven at 80 °C for 48 h. The dried banana peels were grinded and this material was then thermally activated (carbonized) at 500 ± 5°C in a muffle furnace for 1 h in the presence of air. After activation, the ash content was removed by washing it with distilled water and dried in an oven at 100 ± 5°C for 24 h (Amit et al. 2010).

2.3 Biosorption Experiments

Batch adsorption experiments were carried out at room temperature (25 ± 2°C). Adsorption experiments were conducted at different conditions viz., pH (1–7), Banana Peels activated carbon (BPAC) dose (0.1–1 g / 100 ml), initial manganese ion concentration (5–100 ppm) and contact time (5–120 min). The mixtures were taken in 250 ml conical flask and agitated on a mechanical orbital shaker at 200 rpm. The samples were then filtered through filter paper size 42 and the concentrations of metal ions were determined by using atomic absorption spectrophotometer. Consequently, it was decided to control pH in all equilibrium sorption experiments by adding miniscule amounts of nitric acid (HNO₃) 0.1N or sodium hydroxide (NaOH) 0.1 N. The amount of metal ion adsorbed by the biosorbent at equilibrium (qm, mg/g) was calculated as follows:

Table 1: Physicochemical and microbiological characteristics of collected groundwater sample
$q_e = \frac{C_0 - C_e}{m} \times V$

Where, $V$ is the volume of solution treated (L), $C_e$ is the initial concentration of metal ion in ppm, $C_i$ is the equilibrium metal ion concentration in ppm, $m$ is the biomass in gram.

The percent removal (%) of metal ion was calculated using the following equation:

$$\text{Removal} \% = \frac{C_0 - C_e}{C_0} \times 100$$

### 2.4 Analytical equipment used in the study

- ICE 3000 Series AA Spectrometer– Thermo Scientific atomic absorption spectrophotometer (AAS).
- A Scanning Electron Microscope SEM and elemental analysis of BPAC before and after adsorption of manganese is carried out by the energy dispersive X-ray (EDAX) attached on the Environmental Scanning Electron Microscope ESEM (Inspect S. FEI Company, Holland).
- Functional groups in BPAC before and after biosorption of manganese were obtained by KBr pellets methods operated on FT-IR spectrophotometer (FT-IR-4100 JASCO) in the transmittance % mode in the range 4000 – 400 cm$^{-1}$.
- EUTECH pH-700 instrument Singapore meter was used for measuring pH value, with a range of 0.00 to 14.00 and an accuracy of ± 0.02.
- Millipore (Elix) UV- Milli-Q Advantage A 10 System: - Doubled Distilled Water (DDW) from Millipore Instrument was used throughout the study.

### 3. RESULTS AND DISCUSSION

Biosorption of metal ions was assessed in conjunction with BPAC which are particularly widely used. The BPAC possessed the most pronounced ability to remove metal ions from solution. The decrease of metal ions in the contact solution with time is studied under different environmental conditions at 25 ± 2°C and Stirring rate 200 rpm.

#### 3.1 Effect of pH

Solution pH is an important monitoring parameter influencing the adsorption behavior of adsorbate onto biosorbent surface due to its impact on both the surface binding-sites of the biosorbent and the metal ion solution. In the present study, the effect of pH on biosorption of manganese onto BPAC was studied in a range of 1–7. Batch experiments were occurred at adsorbent dose 0.8 g, initial metal ion concentration 20 ppm for 2h of contacts. The amount of metal ion removed at equilibrium increases with increasing pH, up to pH 5.0. With further increase in pH, there is no significant increase in the amount of metal ion removed. Maximum removal is observed at pH 5.0 as shown in Fig. 1. Hence, all further experiments were carried out at pH 5.0. At low pH values, concentration of H$^+$ ions far exceeds that of the metal ions and hence H$^+$ ions compete with manganese ions for the surface of the adsorbent which would hinder the manganese ions from reaching the binding sites of the adsorbent resulting in low adsorption amount of manganese. As the pH increases, there are fewer protons in the solution and consequently there is lesser competition with manganese for binding sites.

#### 3.2 Effect of Biosorbent Dose

Biosorbent dose is an important parameter influencing the biosorption process since it determines the biosorption capacity of a biosorbent for a given initial concentration of the adsorbate under the operating conditions. Therefore, the effect of biosorbent dose on biosorption of manganese by BPAC was investigated. The amount of biosorbent was varied from 0.1 to 1.0 g in 100 mL metal ion solution, while all the other variables such as pH, agitation speed, contact time, and temperature were kept constant. Batch experiments were occurred at pH 5, initial metal ion concentration 20 ppm for 2h of contacts. Data obtained from the experiments are presented in Fig. 2. With increase in biosorbent dose from 0.1 to 1.0 g, the metal ion removal efficiency increases from 28.0 to 97.70 %, which is probably due to an increase in the number of binding sites available for biosorption (Saeed et al. 2010, Ahmad 2009). Further increase in adsorbent dose did not significantly change the biosorption yield. This is due to the binding of almost all metal ions to the adsorbent surface and establishment of equilibrium between the metal ions on the adsorbent and in the solution (Garg et al. 2003, Pons and Fuste 1993). Similar behavior for the effect of biosorbent dose was observed for biosorption of manganese ion on raw and oxalic acid modified maize husk (Abideen et al. 2013).
3.3 Effect of initial metal ion concentration

In batch biosorption processes, the rate of biosorption is a function of the initial concentration of metal ions, which makes it an important factor for effective biosorption. The percentage metal removal at different initial metal ion concentration (5–100 ppm) of manganese using BPAC was shown in Fig. 3. Batch experiments were occurred at pH 5, adsorbent dose = 0.8 g/100 ml for 2h of contacts. The percentage removal of metal ion decreases with increase in initial metal concentration and shows little decrease at higher concentrations. This can be explained by the fact that the adsorbent has a limited number of active sites that become saturated at a certain concentration (Aksu and Donmez 2003). Although the percentage removal of metal ion decreases the equilibrium biosorption capacity of the adsorbent increases with increasing metal ions concentration. The initial metal ion concentration provides an important driving force to overcome all the mass transfer resistance between the solution and solid phases, hence a higher initial concentration of metal ion may increase the biosorption capacity.

3.4 Effect of contact time

In order to establish the equilibration time for maximum uptake and to know the kinetics of the adsorption process, manganese adsorption on BPAC adsorbent was investigated as a function of contact time. The Effect of contact time on manganese biosorption on BPAC was studied within the range of 5–120 min. The initial concentration of manganese was fixed at 20 ppm, biosorbent dosage of 0.8 g/ 100 ml and solution pH of 5.0. The adsorption profile at different time intervals has been presented in Fig. 4. The adsorption rate was fast initially for about 10 min (increase to 78 %) then later it increased slowly with respect to the contact time increases and finally reaches the equilibrium point at 90 min (increasing up to 96.55 %). Thus equilibrium time was considered to be 90 min, which was considered to be sufficient for the removal of manganese ions by BPAC. The rate of percentage of metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metals.
3.5 Adsorption Isotherms

An adsorption isotherm represents the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbents surface at a given concentration. A number of isotherms have been developed to describe equilibrium relationships. In the present study, Langmuir, Freundlich and Dubinin-Radushkevich (D–R) adsorption isotherm models were used to describe the obtained equilibrium data (Hussain et al. 2009).

3.5.1 Langmuir Isotherm

The Langmuir model suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between the adsorbed molecules (Zainal 2010). The linear form of Langmuir adsorption isotherm is:

\[
\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}
\]

Where \( q_e \) is the amount of ion adsorbed onto adsorbent at equilibrium, \( b \) is the Langmuir constant and \( Q_m \) is the monolayer adsorption capacity. The plot of \( C_e / q_e \) versus \( C_e \) is employed to generate the intercept value of \( 1/bQ_m \) and slope of \( 1/q_m \) as shown in Fig. 5.

One of the essential characteristics of this model can be expressed in terms of the dimensionless separation factor for equilibrium parameter, \( R_L \), defined as (Farooq et al. 2010b).

\[
R_L = \frac{1}{1 + bC_0}
\]

The value of \( R_L \) indicates the type of isotherm to be irreversible (\( R_L=0 \)), favorable (\( 0< R_L<1 \)), linear (\( R_L=1 \)) or unfavorable (\( R_L>1 \)). The value of \( R_L \) in the present investigation was found to be 0.006 indicating that the adsorption of manganese on BPAC is favorable.

It is found that Langmuir isotherm model fit very well according to the correlation coefficient values given in Table 2. Thus, the results of the present study indicate that biosorption of manganese onto BPAC is homogeneous in nature.

3.5.2 Freundlich adsorption

The Freundlich adsorption model on the other hand deals with non-ideal sorption onto heterogeneous surfaces involving multilayer sorption. The linear form of the Freundlich adsorption isotherm is:

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

Where \( K_f \) = adsorption capacity and \( n \) = adsorption intensity, the larger these values, the higher the adsorption capacity and \( n \) gives the favorability of the adsorption is rated as good when \( n \geq 2 \)–10. The value of \( n \) obtained as a result of plotting of \( \log C_e \) versus \( \log q_e \) as shown in Fig. 6. Data given in Table 2 show that adsorption of manganese is favorable for the prepared biomass.
3

.5.3 Dubinin-Radushkevich (D–R) isotherm

The Dubinin–Radushkevich model (Dubinin et al. 1947) was chosen to estimate the heterogeneity of the surface energies and also to determine the nature of biosorption processes as physical or chemical. The D–R sorption isotherm is more general than the Langmuir isotherm. The D–R isotherm doesn't assume a homogeneous surface or constant sorption potential and it has commonly been applied in the following form.

\[ \ln q_e = \ln q_m - \beta \varepsilon^2 \]

Where \( q_m \) is the theoretical saturation capacity (mol g\(^{-1}\)), \( \beta \) is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol\(^2\) J\(^{-2}\)), and \( \varepsilon \) is the Polanyi potential given by the relation \( \varepsilon = RT \ln(1 + 1/ C_e) \). \( C_e \) is the equilibrium concentration of adsorbate in solution mol L\(^{-1}\), \( R \) (J mol\(^{-1}\) K\(^{-1}\)) is the gas constant and \( T \) (K) is the absolute temperature. The D–R constants \( q_m \) and \( \beta \) were calculated from the linear plots of \( \ln q_e \) versus \( \varepsilon^2 \) as shown in Fig. 7 and are given in Table 2.

The constant \( \beta \) gives an idea about the mean free energy \( E \) (kJ mol\(^{-1}\)) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the relationship (Kundu and Gupta 2006).

\[ E = \frac{1}{\sqrt{-2\beta}} \]

If the magnitude of \( E \) is between 8 and 16 kJ mol\(^{-1}\), the adsorption process is supposed to proceed via chemisorption, while for values of \( E < 8 \) kJ mol\(^{-1}\), the sorption process is of physical nature. The value of \( E \) calculated is 7.63 kJ /mol, which indicating that the Physico-sorption process plays the significant role in the adsorption of manganese onto BPAC.

<table>
<thead>
<tr>
<th>Functional parameters for Isothermal Models</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
<th>D-R isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_m ) (mg g(^{-1}))</td>
<td>11.806</td>
<td>2.529</td>
<td>13.52</td>
</tr>
<tr>
<td>( b ) (L mg(^{-1}))</td>
<td>0.539</td>
<td>0.493</td>
<td>8.56 x10(^{-9})</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9963</td>
<td>0.982</td>
<td>0.993</td>
</tr>
</tbody>
</table>

3.6 Kinetic studies

For analyzing the adsorption kinetics of metal ions, the pseudo-first- and pseudo-second-order and intraparticle diffusion model were applied to the experimental data.
3.6.1 Pseudo-first-order

The pseudo first-order rate equation is one of the most widely used equations for the adsorption of a solute from an aqueous solution and is represented as:

\[ \log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \]

Where \(q_e\) and \(q_t\) are the amount of metal ion adsorbed (mg/g) at equilibrium and time t, respectively. \(K_1\) is the first-order reaction rate constant (l/min). Examination of the data shows that the pseudo-first order kinetic model is not applicable to manganese adsorption onto BPAC judged by low correlation coefficient.

3.6.2 Pseudo-second-order

The pseudo-second-order equation based on adsorption equilibrium capacity may be expressed as follows:

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \]

Where \(q_e\) is the equilibrium biosorption capacity and \(K_2\) is the pseudo-second order rate constant (g/mg min). A plot of \((t/q_t)\) versus \(t\) gives a linear relationship for the applicability of the second-order kinetic model as shown in Fig. 8. The initial sorption rate can be calculated using the relation (Koyuncu 2008).

\[ K_0 = K_2 q_e^2 \]

As seen from the Table 3 due to high \(R^2\), the pseudo-second order is predominant kinetic model for the manganese adsorption by Banana peels activated carbon biosorbent.

3.6.3 Intraparticle diffusion model

In order to identify the diffusion mechanism, the intraparticle diffusion model can be represented as:

\[ q_t = K_i t^{1/2} \]

Where \(K_i\) is the intraparticle diffusion rate constant and \(q_t\) is the amount of metal ion adsorbed (mg g\(^{-1}\)) at time t (min). According to this model, the plot of \(q\) versus \(t^{1/2}\) yields a straight line passing through the origin if the adsorption process obeys the sole intraparticle diffusion model. However, it is not the case in Fig. 9 and therefore, the intraparticle diffusion is not the only rate limiting step. It could be stated that this process is complex and may involve more than one mechanism.

The results presented in Table 3 demonstrated that the values of coefficient of determination \((R^2)\) for the intraparticle diffusion was slightly lower than those of a pseudo-second order kinetic model indicating that pseudo-second order model is better obeyed than intraparticle diffusion model for the biosorption of manganese onto BPAC.
Table 3 Kinetic model parameters for the adsorption of manganese onto BPAC

<table>
<thead>
<tr>
<th>Functional Parameters for Kinetic models</th>
<th>Intraparticle diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2$ (g. mg$^{-1}$. min$^{-1}$)</td>
<td>$K_0$ (g mg$^{-1}$. min)</td>
</tr>
<tr>
<td>0.163</td>
<td>0.99</td>
</tr>
<tr>
<td>$R^2$</td>
<td>$q_e$ cal (mg g$^{-1}$)</td>
</tr>
<tr>
<td>0.9999</td>
<td>2.467</td>
</tr>
<tr>
<td>$k_i$ (mg g$^{-1}$ min$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>0.11</td>
<td>0.9025</td>
</tr>
</tbody>
</table>

3.7 Thermodynamic Studies

Thermodynamic consideration of a biosorption process is necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change ($\Delta G^\circ$) is a critical factor for determining the spontaneity of a process and can be computed by the classical Van’t Hoff equation (Chowdhury and Saha 2010a):

$$\Delta G^\circ = -RT \ln K_d$$

Where $K_d$ is the Equilibrium constant ($q_e / C_e$), $\Delta G^\circ$ Gibbs free energy (Joule/mole), $\Delta H^\circ$ Enthalpy (Joule/mole), $\Delta S^\circ$ Entropy (Joule /mol K), $T$ is the absolute temperature (K), $C_0$ is the initial concentration of the adsorbate, $C_{eq}$ is the equilibrium concentration, $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$).

It is also known that $\Delta G^\circ$ is a function of change in enthalpy ($\Delta H^\circ$, kJ mol$^{-1}$) as well as change in standard entropy ($\Delta S^\circ$, J mol$^{-1}$K$^{-1}$) according to the following equation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

A plot of $\ln K_d$ versus $1/T$ for the initial concentration of 20 ppm was linear (Fig. 10). The Values of $\Delta H^\circ$ and $\Delta S^\circ$ were determined from the slope and intercept of the plot as represented in Table 4.

The negative value of $\Delta G^\circ$ at three temperatures confirms the spontaneous nature and feasibility of the biosorption process for manganese onto BPAC. The positive value of $\Delta H^\circ$ confirms that process is endothermic in nature. The positive value of entropy $\Delta S^\circ$ shows increased randomness at the solid–solution interface during the biosorption process (Kelleher et al. 2002).

![Fig. 10 Variation of $\ln K_d$ with temperature (1/T) for adsorption of manganese onto BPAC](image)

Table 4 Thermodynamic parameters for the adsorption of manganese onto BPAC

<table>
<thead>
<tr>
<th>Thermodynamic parameters</th>
<th>$\Delta G^\circ$ (KJ/mol)</th>
<th>$\Delta H^\circ$ (KJ/mol)</th>
<th>$\Delta S^\circ$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298 K</td>
<td>308 K</td>
<td>318 K</td>
<td>323K</td>
</tr>
<tr>
<td>3.55</td>
<td>3.87</td>
<td>4.201</td>
<td>4.36</td>
</tr>
<tr>
<td>0.9895</td>
<td>6.11</td>
<td>32.456</td>
<td></td>
</tr>
</tbody>
</table>

3.9 Application Study

The groundwater is considered to be the most pure water resource regarding biological pollution. Treatment of raw groundwater sample collected from Baharmos groundwater treatment plant network at Embaba and Manshet Elkanater City Giza, Egypt using BPAC biomass was investigated in Table 5 and Figs. 11-12. Batch adsorption study was carried under optimum conditions; pH was firstly adjusted to 5.0 ± 0.02, biosorbent dose 0.8 g/100 ml, stirring rate 200 rpm and at temperature 25± 2°C for 1 h. Results showed iron and manganese removal percentage to 91.4% and 97.1 %, respectively. The effect of the treatment process on the groundwater microbiology was also studied. Microbiological results showed decrease in total bacterial count either at 22°C or at 37°C to 85.7% and 82.4%, respectively. These results indicated that the treatment with BPAC had a positive effect on the microbiological properties of the water. Also the decrease of iron and manganese concentration could reduce some of specific microorganisms such as iron bacteria, which live in the presence of iron and manganese salts.
Table 5: Effect of the treatment method on the groundwater chemistry and microbiology

<table>
<thead>
<tr>
<th>Chemical analysis</th>
<th>Before Treatment</th>
<th>After Treatment</th>
<th>Removal %</th>
<th>Limits *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>1.4</td>
<td>0.12</td>
<td>91.4</td>
<td>0.3 ppm</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.7</td>
<td>0.02</td>
<td>97.1</td>
<td>0.4 ppm</td>
</tr>
<tr>
<td>Total bacterial count (37°C)</td>
<td>17</td>
<td>3</td>
<td>82.4</td>
<td>50 c.f.u/ml</td>
</tr>
<tr>
<td>Total bacterial count (22°C)</td>
<td>35</td>
<td>5</td>
<td>85.7</td>
<td>50 c.f.u/ml</td>
</tr>
<tr>
<td>Total coliform</td>
<td>≤1</td>
<td>≤1</td>
<td>--</td>
<td>≤2 c.f.u/100 ml</td>
</tr>
<tr>
<td>Fecal coliform</td>
<td>≤1</td>
<td>≤1</td>
<td>--</td>
<td>≤1 c.f.u/100 ml</td>
</tr>
<tr>
<td>Fecal streptococci</td>
<td>≤1</td>
<td>≤1</td>
<td>--</td>
<td>≤1 c.f.u/100 ml</td>
</tr>
<tr>
<td>Parasites (Helminthes - Parasitic Protoza - Freshwater living amoeba)</td>
<td>Free</td>
<td>Free</td>
<td>--</td>
<td>Free</td>
</tr>
</tbody>
</table>

* Limits are according to Egyptian Ministry of Health degree No. 458/2007.

3.10 Characterization of biosorbent

3.10.1 Fourier Transform Infrared Spectroscopy analysis (FTIR)

The FTIR is an important technique to qualitatively determine characteristic functional groups, which make the adsorption behavior possible. The FTIR spectra of the prepared adsorbents before and after treatment were presented in Figs. 13(a)-(b), respectively. FTIR spectrum of prepared BPAC coming from banana peel (constituted by carbohydrates, proteins, lipids, and fibers) was recorded to identify functional groups responsible for the metal ion coordination. The FTIR spectra of the biosorbent and metals ions loaded biosorbent were compared to determine which functional groups are responsible for the manganese biosorption. The spectrum of (BPAC) has a broad absorption peaks at around 3200–3500 cm⁻¹, indicates the presence of carboxylic acid and amino groups. The absorption band at 2945 cm⁻¹ could be assigned to asymmetric vibration of –CH. The stretching vibration bands 1700 cm⁻¹ and 1630 cm⁻¹ is due to asymmetric stretching of the carboxylic C=O double bond. A 1404 cm⁻¹ is of phenolic –OH and –C=O stretching of carboxylates. A 1384 cm⁻¹ band could be stretching vibration of
COO. The band at 1072 cm\(^{-1}\) band could be due to the vibration of \(\text{C–O–C}\) and \(\text{–OH}\) of polysaccharides. Peaks in the region of lower wave numbers (under 832 cm\(^{-1}\)) appeared as a broad peak and this could be attributed to N containing bioligands (Salmana et al. 2011). Spectra analysis after manganese biosorption showed that there was a substantial decrease in the wave number of asymmetric stretching of the carboxylic C=O double bond to 1574 cm\(^{-1}\). The band at 1404 cm\(^{-1}\) was also shifted to 1387 cm\(^{-1}\) for manganese-loaded. These results indicates that the carboxylic acid and the hydroxyl groups played a major role in the removal of manganese ions.

3.10.2 Scanning Electron Microscope (SEM)

The surface morphology of fresh BPAC and after manganese loaded BPAC was studied using of SEM as shown in Figs. 14(a)-(b), respectively. From the SEM micrograph, the larger sized fraction of these precipitates showed irregularly shaped crystallized particles. The particles were randomly aggregated, and rough surfaces were observed. Manganese loaded BPAC is brighter than the before one due to manganese particles adsorbed by BPAC indicating the biosorption process.

The EDAX analysis of fresh BPAC and after manganese loaded BPAC was shown in Figs. 15(a)-(b), respectively. The fresh BPAC showed the presence of various elements along with a high amount of potassium, while EDAX spectra of manganese loaded BPAC showed an additional peak confirming the sorption of manganese ion onto the surface of the BPAC.
4. CONCLUSION

The obtained results reveal that the low-cost adsorbent (Banana Peels activated carbon) can be used for the removal of manganese from aqueous solution. The adsorption capacity of BPAC for removal of manganese from aqueous solutions was found to dependent on pH, adsorbent dose, initial metal ion concentration and contact time. The optimum pH for the removal of manganese was 5.0, rate of adsorption increased with increasing adsorbent dose and decreased with increasing metal ion concentration. Equilibrium adsorption data indicated that excellent fit to Langmuir isotherm model than Freundlich isotherm model. So it was indicated a monolayer of manganese ions was adsorbed on homogeneous adsorption sites on the surface of BPAC is 11.806 mg g⁻¹. The result of adsorption kinetic study of manganese on BPAC indicated that the adsorption kinetics followed the pseudo-second-order model. The thermodynamics indicates spontaneous and endothermic nature of the process. The treatment of raw groundwater collected from Baharmos groundwater treatment plant network at Embaba and Manshet Elkanater City/District-Giza, Egypt by BPAC at the best conditions that reached at first phase showed decrease in both of iron and manganese concentrations and these data were confirmed by microbiological analysis, SEM and FTIR spectroscopy.

REFERENCES


