

Banana Peels as an Eco-Sorbent for Manganese Ions

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Abstract—This study was conducted to evaluate the manganese removal from aqueous solution using 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 times 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 $25 \pm 2^\circ\text{C}$, 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 and Freundlich isotherm models; the Langmuir isotherm was found to well represent the measured adsorption data implying BPAC had heterogeneous surface. 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—Biosorption, banana peels, isothermal models, manganese.

I. 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 [1]-[3]. 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 [4]. 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 [5] and several reports are available on the effects of exposure to manganese in water [6]. Manganese and iron have variety of applications such as in metallurgical processes, mining, ceramics, dry cell batteries, pigments and paints which all can be the sources of underground pollution [7], [8]. Different techniques to remove iron and manganese are in use now, but

the search for better, cheaper and safer technique will never stop [9]. There are several methods for the removal of metals from aqueous solution including, adsorption on activated carbon, ion exchange, chemical precipitation, and membrane filtration [10], [11].

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 [12]. Sorption using plant waste material 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 [13] such as orange peel [14], rice husk [15], rejected tea [16], pineapple leaves [17], garlic peel [18], Luffa cylindrical fibers [19].

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 [20]. 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.

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/District-Giza, Egypt at optimal parameters by BPAC. The efficiency of groundwater treatment depends on removal of iron and manganese to certain acceptable limits.

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II. MATERIALS AND METHODS

A. 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 $MnSO_4 \cdot H_2O$ 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 $4 \pm 1^\circ C$ until use and analyzed within 8 h. The physicochemical and microbiological characteristics of collected sample are listed in Table I. All Physico-chemical analyses were analyzed according to Standard Methods for the Examination of Water and Wastewater [21].

Also, analysis for the total bacterial count at $22^\circ C$ and $37^\circ C$ were done for water samples before and after treatment according to Standard Methods for the Examination of Water and Wastewater [21].

TABLE I
 PHYSICO-CHEMICAL AND MICROBIOLOGICAL CHARACTERISTICS OF
 COLLECTED GROUNDWATER SAMPLE

Analysis	Water sample	Limits *
Temperature	24.37	—
pH	7.8	6.5 - 8.5
Turbidity (NTU)	0.85	1
T.D.S. (ppm)	477	1000
Iron (ppm)	1.4	0.3
Manganese (ppm)	0.7	0.4
Total bacterial count ($37^\circ C$) C.F.U/ml	17	50
Total bacterial count ($22^\circ C$) C.F.U/ml	35	50

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

B. 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 $80^\circ C$ for 48 h. The dried banana peels were grinded and this material was then thermally activated (carbonized) at $500 \pm 5^\circ C$ 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 $100 \pm 5^\circ C$ for 24 h [22].

C. Biosorption Experiments

Batch adsorption experiments were carried out at room temperature ($25 \pm 2^\circ C$). 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 (HNO_3) 0.1N or sodium hydroxide (NaOH) 0.1 N. The amount of metal ion adsorbed by the biosorbent at equilibrium (q_e , mg/g) was calculated as follows:

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (1)$$

where, V is the volume of solution treated (L), C_0 is the initial concentration of metal ion in ppm, C_e 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:

$$\text{Removal \%} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

D. 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 $4000 - 400 \text{ cm}^{-1}$.
- 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.

III. 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 $25 \pm 2^\circ C$ and Stirring rate 200 rpm.

A. 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. These explanations were in agreed with [23], [24].

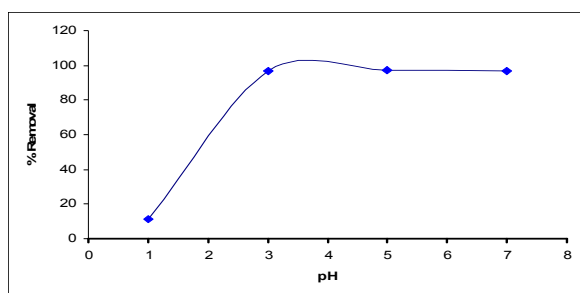


Fig. 1 Effect of pH on manganese biosorption by BPAC

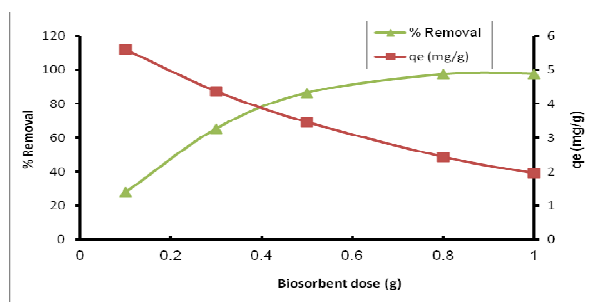


Fig. 2 Effect of BPAC dose on manganese biosorption

B. 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 [25], [26]. 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 [27], [28]. Similar behavior for the effect of biosorbent dose was observed for biosorption of manganese ion on raw and oxalic acid modified maize husk [29].

C. 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 [30]. 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.

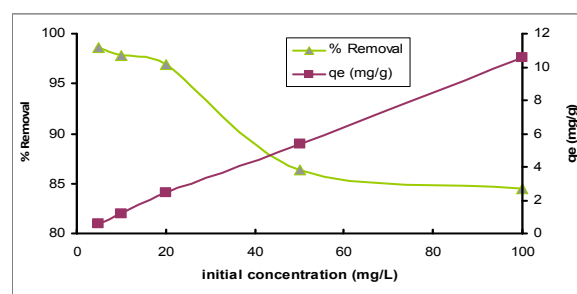


Fig. 3 Effect of initial metal ion concentration on manganese biosorption by BPAC

D. 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.

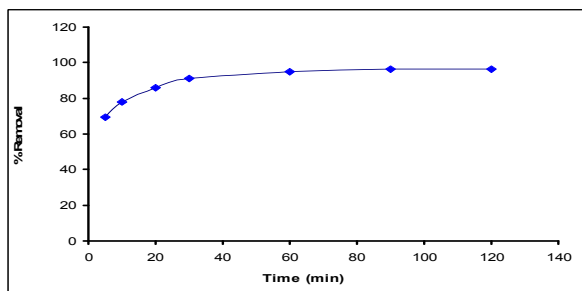


Fig. 4 Effect of contact time on manganese biosorption by BPAC

E. 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 and Freundlich adsorption isotherm models were used to describe the obtained equilibrium data [31].

1. Langmuir Isotherm

The Langmuir model suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between the adsorbed molecules [32]. The linear form of Langmuir adsorption isotherm is;

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad (3)$$

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 [33].

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

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 II. Thus, the results of the present study indicate that biosorption of manganese onto BPAC is homogeneous in nature.

TABLE II
FUNCTIONAL PARAMETERS FOR ISOTHERMAL MODELS

Langmuir isotherm			Freundlich isotherm		
q_m ($\text{mg} \cdot \text{g}^{-1}$)	b ($\text{L} \cdot \text{mg}^{-1}$)	R^2	K_F ($\text{mg} \cdot \text{g}^{-1}$) (1mg^{-1}) ^{1/n}	1/n	R^2
11.806	0.539	0.9963	2.529	0.493	0.982

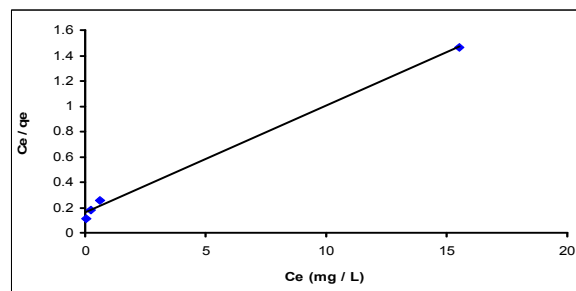


Fig. 5 Langmuir isotherm plot for adsorption of manganese onto BPAC

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;

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

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 $n = 2-10$. 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 II show that adsorption of manganese is favorable for the prepared biomass.

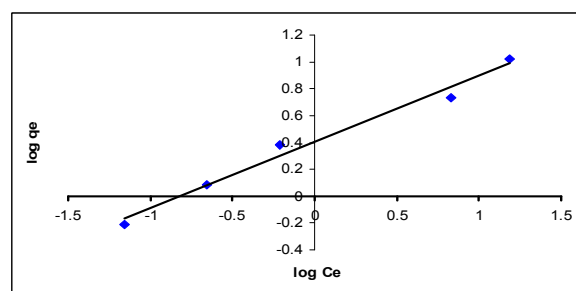


Fig. 6 Freundlich isotherm plot adsorption of manganese onto BPAC

F. 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 Manshiet Elkanater City Giza, Egypt using BPAC biomass was investigated in Table III and Figs. 7, 8. 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 $25 \pm 2^\circ\text{C}$ 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 III
EFFECT OF THE TREATMENT METHOD ON THE GROUNDWATER CHEMISTRY AND MICROBIOLOGY

Analysis	Removal %
Iron	91.4
Manganese	97.1
Total bacterial count (37°C)	82.4
Total bacterial count (22°C)	85.7

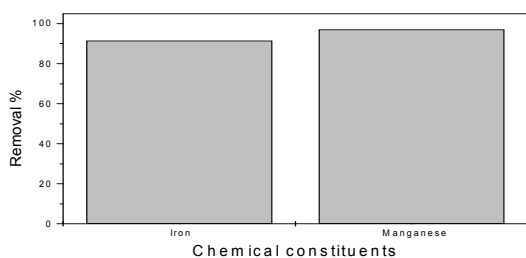


Fig. 7 Removal percentage of chemical constituents of collected groundwater sample after treatment by BPAC

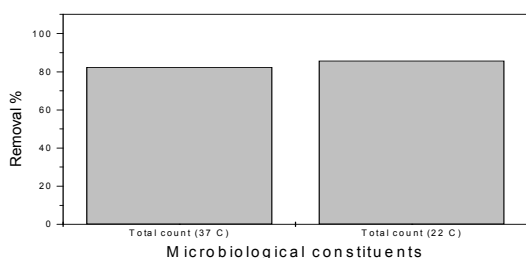


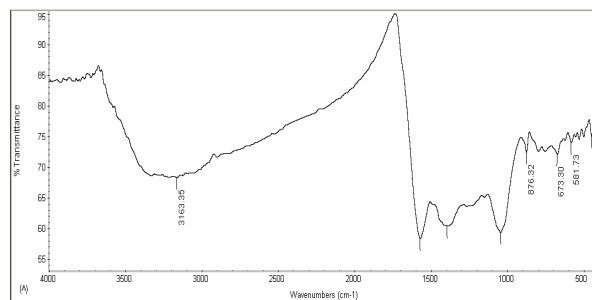
Fig. 8 Removal percentage of microbiological constituents of collected groundwater sample after treatment by BPAC

G. Characterization of Biosorbent

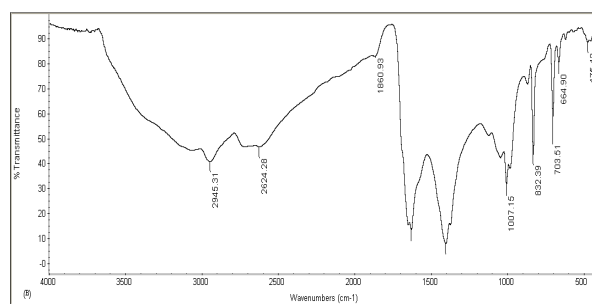
1. Fourier Transform Infrared Spectroscopy Analysis (FTIR)

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. 9 (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 $-\text{CH}$. The stretching vibration bands 1700 cm^{-1} and 1630 cm^{-1} is due to asymmetric stretching of the carboxylic $\text{C}=\text{O}$ double bond. A 1404 cm^{-1} is of phenolic $-\text{OH}$ and $-\text{C}=\text{O}$ stretching of carboxylates. A 1384 cm^{-1} band could be stretching vibration

of $-\text{COO}$. The band at 1072 cm^{-1} band could be due to the vibration of $-\text{C}-\text{O}-\text{C}$ 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. Spectra analysis after manganese biosorption showed that there was a substantial decrease in the wave number of asymmetric stretching of the carboxylic $\text{C}=\text{O}$ double bond to 1574 cm^{-1} . The band at 1404 cm^{-1} was also shifted to 1387 cm^{-1} for manganese-loaded. These results indicate that the carboxylic acid and the hydroxyl groups played a major role in the removal of manganese ions.



(a) Fresh BPAC



(b) Manganese loaded BPAC

Fig. 9 FTIR spectral analysis for (A) fresh BPAC and (B) manganese loaded BPAC

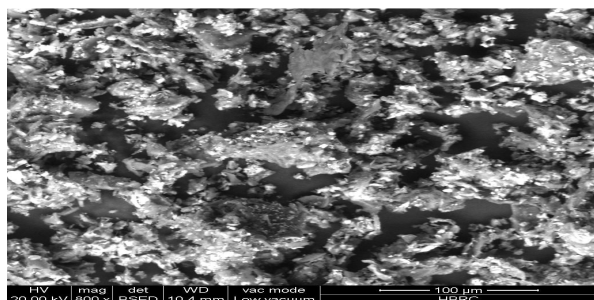
2. Scanning Electron Microscope (SEM)

The surface morphology of fresh BPAC and after manganese loaded BPAC was studied using of SEM as shown in Figs. 10 (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. 11 (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.

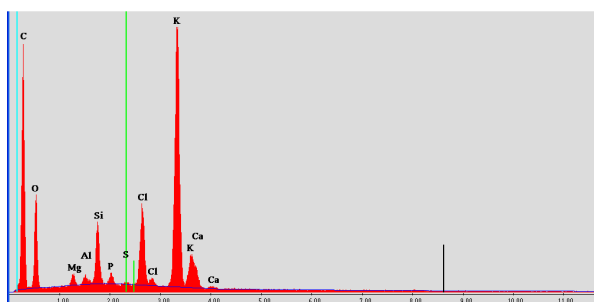


(a) Fresh BPAC

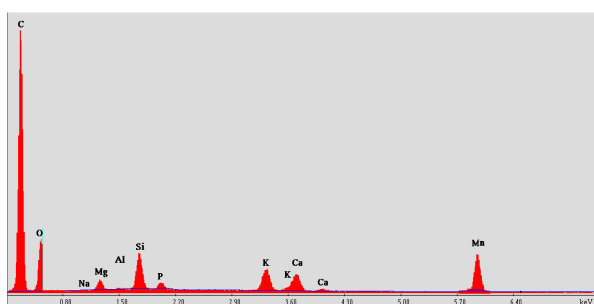


(b) Manganese loaded BPAC

Fig. 10 SEM micrographs of (a) fresh BPAC (b) Mn(II) loaded BPAC



(a) Fresh BPAC



(b) Manganese loaded BPAC

Fig. 11 EDAX spectra of (a) fresh BPAC (b) manganese loaded BPAC

IV. 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 treatment of raw groundwater collected from Baharmos groundwater treatment plant network at Embaba and Manshiet 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.

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