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ORIGINAL ARTICLE

Rice husk and activated carbon for waste water treatment of El-Mex Bay, Alexandria Coast, Egypt

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Abstract Activated carbon and rice husk were successfully applied for the removal of Fe(III) and Mn(II) ions from El-Umum drain water, Alexandria coast, Egypt. Langmuir and Freundlich adsorption isotherms are applied to give fruitful results. The rice husk was the best, as controlled from Xm and K_F values.

1. Introduction

The presence of heavy metals in the environment is a major problem due to their toxicity to many life forms. The treatment of metals using precipitation is not always able to meet the metal discharge standards. Technologies such as reverse osmosis, while able to meet the standards, are expensive. What needed are the innovative technologies that are cost-effective and are able to reduce heavy metal concentration to low levels (Abdo, 2002). Rice husk, an undesirable agriculture mass residue in Egypt, is a by product of the rice milling industry. It is one of the most important agricultural residues in quantity. It represents about 20% of the whole rice produced, on weight basis of the whole rice (Daifullah et al., 2003). The estimated annual rice production of 500 million tones in developing countries, approximately 100 million tones of rice husk are available annually for utilization in these countries alone. Traditionally, rice husks have been used in manufacturing block employed in civil construction as panels and was used by the rice industry itself as a source of energy for boilers (El-Nemr et al., 2005). However, the amounts of rice husk available are so far in excess of any local uses and have posed disposal problems. The main purpose for chosen rice husk is due to its granular structure, chemical stability and its local availability at very low cost (El-Nemr et al., 2005). The rice husk compositions (Daifullah et al., 2003; Rhman et al., 1997) are: 32.24% cellulose, 21.34% hemicellulose, 21.44% lignin, 1.82% extractives, 8.11% water and 15.05% mineral ash. The mineral ash is 94.5–96.34% SiO_2.

In this study, some applications were done for the removal of some heavy metals of the effluents discharged from El-Umum

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drain to the Alexandria coast, Egypt, especially at El-Mex region using modified rice husk and activated carbon as adsorbents.

2. Material and methods

(i) Adsorbates: The wastewater samples of the El-Umum drain.
(ii) Adsorbent: One precursor (rice husk) is obtained from rice mills of Egypt. This is used in the preparation of two adsorbents (1 and 2) by using two different types. The first adsorbent (1) is basic surface, while the latter (2) has acidic surface as follows (Abdo, 2002).

2.1. Preparation of activated rice husk (1)

Rice husk was obtained from local rice mills and was washed several times with bi-distilled water followed by filtration. In the first step, (carbonization), a 25 g of rice husk was heated gradually at the temperature rate (50 °C/15 min), in a stainless steel pipe (furnace tube) up to 500 °C. In the second step (activation), the temperature of the furnace tube was raised suddenly to 900 °C for 1 h. At this temperature the carbon dioxide was supplied from a gas cylinder at a constant flow rate. The product was cooled giving the desired pure adsorbent.

2.2. Preparation of activated rice husk (2)

Natural rice husk was stirred with 4% KOH and heated to boiling for 30 min, then the mixture was left overnight, and filtered. To the filtrate, 10% HCl was added until the pH reacted (5–7), where a white precipitate was formed, then filtered, dried at 105 °C. This precipitate was used as sorbent (2).

2.2.1. Sorption experiments

0.4 g of each adsorbent was placed with 200 ml of the wastewater in plastic bottles provided with screw caps. The bottles were shaken for 3 h at room temperature. The mixture was filtered and the residual concentration of heavy metal was measured using atomic absorption spectrophotometry (Abdo, 2002). The adsorption behaviours of the samples were studied by evaluating the percentage removal efficiency (%R) of some metals of El-Umum drain from the relation (Abdo, 2002).

$$\%R = \frac{C_\circ - C}{C_\circ} \times 100$$

Where:

%R = Percent removal.
C_o = Initial concentration of the metal of wastewater.
C = Residual concentration of the metal of water sample.

3. Results and discussion

3.1. Treatment of water using rice husk

It seems that, the (%R) of the heavy metals in wastewater of El-Umum drain after treatment using activated rice husk (1) is better than that of the absorbent (2), due to the higher percent of ash content (Abdo, 2002). The (%R) of rice husk (1) for Fe (III) and Mn (II) is 99% and 98% respectively. Also, it is deduced that the activated rice husk (2) is successful for the removal of Mn (II) but it is useless in Fe (III) treatment. It appears that, the type (1) has a basic surface and type (2) has an acidic one. This imports the predominant effect on the removal of the heavy metal ions under investigations. The ash content of the adsorbents imports some surface chemical characteristics where as the ash% increases, the uptake increases too (Abdo, 2002), Table 1.

Since the main constituent of ash content is silica, the ion-exchange reaction on the silica surface is accomplished through the substitution of protons of the surface silanol groups by the metal ions from solution as:

$$M^{n+} + \chi(\equiv \mathrm{SiOH}) \leftrightarrow M(\equiv \mathrm{SiOH})_x^{(n-x)} + \chi H^+$$

Where:

M^{n+} = metal ion with n^+ charge.
SiOH = group Silanol on the SiO_2 surface.
χH^+ = number of protons released.

Since electrostatic attraction was not possible between positively charged adsorbent and positively charged metal ion species, it seems that some non-electrostatic force called “specific adsorption” was involved in the process of adsorption (Abdo, 2002). However the possible adsorption mechanism includes the following:

$$SO^- + M^{2+} \rightarrow SOM^+$$

$$SO^- + MOH^+ \rightarrow SOMOH$$

$$SOH + M^{2+} \rightarrow SOM^+ + H^+$$

$$SOH + MOH^+ \rightarrow SOMOH + H^+$$

Where SO^- denotes negatively charged surface, SOH denotes neutral surface and M denotes metal ions.

Besides, two major types of chemical bindings can be responsible for the adsorption of various metal ions onto carbon surface: covalent and hydrogen bonding (Khalil and Girgis, 1994). The covalent bonding results from the sharing of free electron pairs between the surface oxygen atom and the metal atom or the formation of an O—M bonding. The hydrogen bonding results from the surface oxygen atom and the hydrogen atom of the hydrated metal ions (Abdo, 2002).

3.2. Adsorption isotherms

Adsorption data were analysed according to Langmuir (Langmuir, 1915) and Freundlich (Freundlich, 1926) models. Fe(III) and Mn(II) were selected for the studies, as representative examples, where both gave interesting results.

The Langmuir equation has been successfully applied to many adsorption systems given by the equation:

Table 1 Characterization of rice husk adsorbent is given in the following.

Parameters	Activated rice husk (1)	Activated rice husk (2)
pH	9.9	3.2
Ash content (%)	90.4	68.1

$$X = 1/X_m bCe + bCe \quad (1)$$

Where

X = x/m, the amount of solute adsorbed x per unit weight of adsorbent m
Ce = equilibrium concentration of the solute
Xm = retention capacity of the adsorbent
b = constant related to the energy of adsorption

For linearization plotting of the data, equation (1) can be written in the form:

$$\mathrm{Ce/X = 1/bXm + Ce/Xm} \quad (2)$$

Dividing equation (2) by Ce, the following is given as follows:

$$\mathrm{1/X = 1/Xm + (1/Ce)(1/bXm)} \quad (3)$$

The effect of different weights of rice husk 1 (100–600 mg) on the adsorption of Fe(III) and Mn(II) was monitored. Again, rice husk 1 is the best for adsorption. The data are calculated and given in Table 2(a,b,c,d,e,f).

A linear plot of 1/X versus 1/Ce was obtained using activated rice husk 1, Figs. 1 and 2.

Regression data and adsorption parameters obtained are indicated in Table 3. An advantage of the Langmuir equation in its linear form points to the high successful application of rice husk for the removal of metals. The data for the sorption of metals onto activated rice husk were fitted to the Langmuir model. r^2 = 0.94 and 0.91 for Fe and Mn, respectively, indicate the monolayer coverage of metals on the outer surface of sorbent, in which the mechanism of adsorption occurs uniformly on the reactive part of the surface. The fits are quite well for the sorbent, to suggest the applicability of the Langmuir model for the investigated system. Xm and *b*, Langmuir constants, are the measures of maximum adsorption capacity. The values of Langmuir parameters with correlation coefficients were computed from the intercept and the slope of the fitted Langmuir equation.

It seems that **Xm**Fe > **Xm**Mn and $\mathbf{r^2}$ Fe > $\mathbf{r^2}$ Mn, to assign the successful application to adsorbent Fe more than Mn. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor RL as follows.(El-Nemr et al., 2005)

$$\mathrm{RL = 1/[1 + (bC_o)]}$$

Where C_o is the initial concentration and RL indicates the trend of the isotherm. The types of equilibrium isotherms are related with the RL values, for RL > 1 unfavourable process is the dominant and for values 0 < RL < 1 favourable mechanism could be reached. In the present work, Table 4, the values of RL were found to be less than (1) and slightly higher than (0) indicating the favourable adsorption of Fe(III) and Mn(II) metals on rice husk.

Table 2 Effect of the weight of activated rice husk 1 (mg) on the adsorption of Fe(III) and Mn(II) ions.

Ion	Concentration (mg/l)		*x* (mg)	*X*
	Initial Co	Final Ce		
(a) *m* = 100 (mg)				
Fe(III)	2.0	1.3	0.7	0.0070
Mn(II)	1.0	0.2	0.8	0.0080
(b) *m* = 200 (mg)				
Fe(III)	2.0	0.8	1.2	0.0060
Mn(II)	1.0	0.09	0.91	0.0045
(c) *m* = 300 (mg)				
Fe(III)	2.0	0.44	1.56	0.0052
Mn(II)	1.0	0.06	0.94	0.0031
(d) *m* = 400 mg				
Fe(III)	2.0	0.07	1.93	0.0048
Mn(II)	1.0	0.02	0.98	0.0024
(e) *m* = 500 mg				
Fe(III)	2.0	0.03	1.97	0.0039
Mn(II)	1.0	0.01	0.99	0.0019
(f) m = 600 mg				
Fe(III)	2.0	0.01	1.99	0.0033
Mn(II)	1.0	0.0057	0.993	0.0016

Where x = Ce – Co, X = x/m.

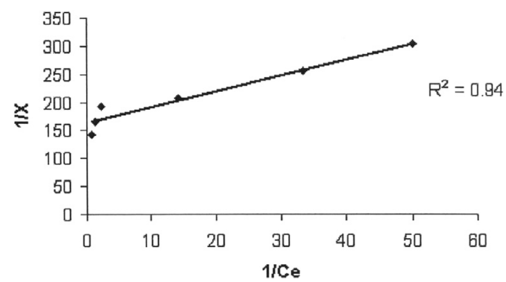

Figure 1 Langmiur adsorption isotherm for iron using activated rice husk.

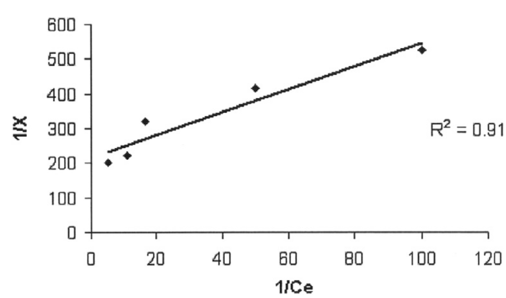

Figure 2 Langmiur adsorption isotherm for manganese using activated rice husk.

Table 3 Langmuir parameters for the adsorption of Fe(III) and Mn(II) using rice husk 1.

Ion	Xm	*b*	r^2
Fe(III)	0.0061	58.37	0.94
Mn(II)	0.0046	65.84	0.91

Table 4 The RL values of adsorption Fe(III) and manganese using rice husk (1).

Ion	RL
Fe(III)	0.008
Mn(II)	0.01

The 'RL' values are in good relation to the 'b' constant.

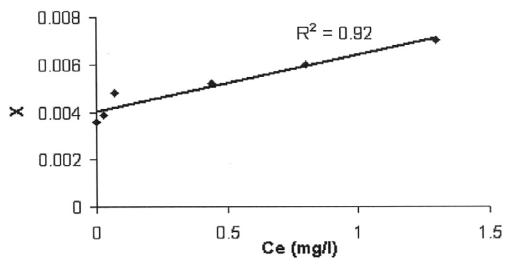

Figure 3 Relation between X and Ce of iron using activated rice husk.

3.2.1. Freundlich adsorption isotherm

Freundlich adsorption isotherm was used, based on the following equation (Freundlich, 1926):

$$X/m = K_F Ce^{1/n} \quad (1)$$

Where:

X/m is amount of metal adsorbed per unit weight of adsorbent (mg/g).
Ce is the metal concentration at equilibrium (mg/1).
K_F, *1/n* are Freundlich constants, which are the empirical constants and indicative of sorption capacity and sorption intensity, respectively.

The calculated K_F and *1/n* values were fitted by logarithmic transfer of Eq. (1) to:

$$\log X/m = \log K_F + 1/n \log Ce \quad (2)$$

The Freundlich adsorption isotherms with the correlation coefficient are presented in Figs. 3–6 and Table 5. The observed linear relationships as evidenced by the r^2 and *1/n* values indicating the applicability of adsorption isotherms and the monolayer coverage on adsorbent surface. The monolayer adsorption capacities of the adsorbents possess high adsorption capacity and hence it could be employed as low-cost adsorbent for the removal of metals. The KF values are in harmony with the Xm values i.e. as Xm increases, KF increases in turn.

3.2.2. Kinetics of adsorption

Effect of time on adsorption of both Fe(III) and Mn(II) using activated rice husk (1) was studied. Figs. 7 and 8, and Tables 6 and 7 showed that the concentrations of the metals ions are decreased with increasing time (min).

The rates of adsorption are measured by determining the change of concentration of the metal as a function of time. Linearization of the data is obtained by plotting the log C_t, (C_t is the concentration of metal at different times) versus time (min), Figs. 9 and 10. The adsorption rates were calculated from the slopes (slope = −K/2.303), Table 8. The process followed first order reaction.

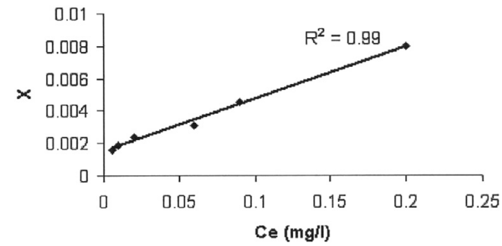

Figure 4 Relation between X and Ce of manganese using activated rice husk.

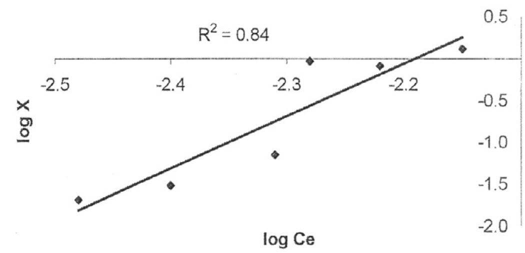

Figure 5 Freundlich plot for iron adsorption onto activated rice husk.

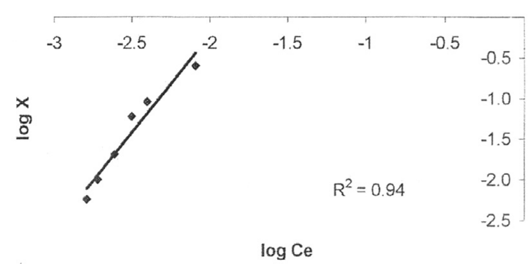

Figure 6 Freundlich plot for manganese adsorption onto activated rice husk.

Table 5 Freundlich isotherms for the adsorption of Fe(III) and Mn(II) using rice husk 1.

Ion	K_F	*1/n*	r^2
Fe(III)	4.7×10^{13}	6.25	0.84
Mn(II)	3.3×10^{5}	2.38	0.94

4. 2-Treatment of water using activated carbon

The properties of activated carbon are attributed mainly to its highly porous structure and relatively large surface area. A particle of activated carbon is composed of a complex network of pores that can be divided into two distinct classes with

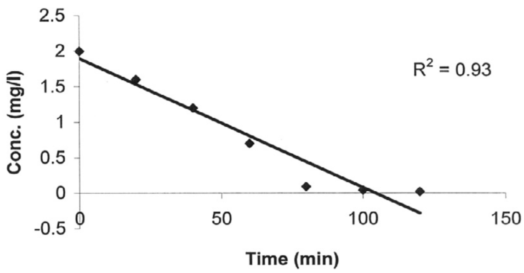

Figure 7 Effect of time on the adsorption of iron using activated rice husk.

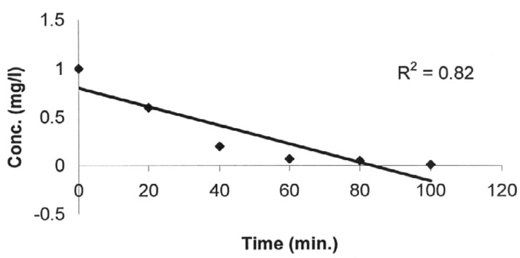

Figure 8 Effect of time on the adsorption of manganese using activated rice husk.

Table 6 Effect of time on the adsorption of Fe(III) using activated rice husk 1.

Fe(III) (mg/l)	2.0	1.6	1.2	0.7	0.09	0.04	0.02
Time (min)	0	20	40	60	80	100	120

Table 7 Effect of time on the adsorption of Mn(II) using activated rice husk 1.

Fe(III) (mg/l)	1.0	0.6	0.2	0.07	0.05	0.01
Time(min)	0	20	40	60	80	100

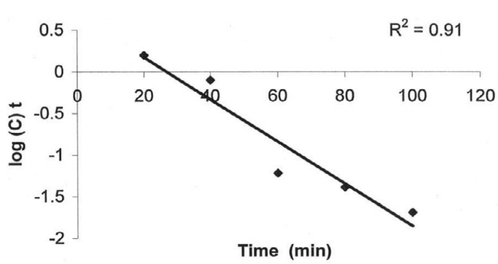

Figure 9 Relation between time (min) versus concentration of iron using activated rice.

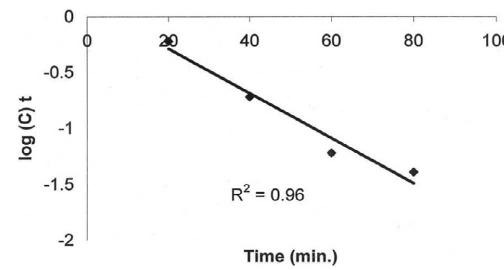

Figure 10 Relation between time (min) versus concentration of manganese using activated rice husk.

Table 8 Adsorption rates of Fe(III) and Mn(II) ions on activated rice husk.

Ion	Rate of reaction (*K*)
Fe(III)	0.058
Mn(II)	0.048

respect to size: macropores and micropores (El-Hadad, 2006). Activated carbons have been produced from carbonaceous substances (Hasster, 1974). The most common materials are wood, coal, peat, lignin, nut shells, sawdust, bone, and petroleum coke. The nature of the starting materials does not have a significant effect on the properties of the resulting activated carbon, since different characteristics can be imparted by the selective introduction of additives, and by controlling the production processes. The quality of the active carbon obtained of porous structure by physical activation depends upon the degree of burn-off of the carbon. A lower degree of burn-off generally produces active carbon with a more microporous structure with a very narrow distribution of pores (Faust and Aly, 1986). Considerable research has been conducted on the activated carbon removal of various inorganic species from water (Pignon et al., 2000). Due to its high surface area, it can efficiently adsorb gases and compounds dispersed or dissolved in liquids (Lua and Guo, 2001). The adsorption of several organic contaminants in water, such as pesticides, phenols and chlorophenols, has been reported (Baup et al., 2000). Moreover, activated carbon can easily be functionalized and used as an efficient adsorbent for heavy metal cationic contaminants. In this concern, the treatment of some metals in water samples using activated carbon was given. Different weights of active carbon (3000–3800 mg) were used. 500 ml of water sample was flowed though a column that contains activated carbon. The effect of time was studied. The results are collected in Tables 9–12, and represented graphically in Figs. 11 and 12.

4.1. The data give the following

- Decreasing of Fe(III) and Mn(II) concentrations after passing the samples through active carbon filters occurred, due to adsorption.
- The adsorption of the metals is increased with the increase of the weight of activated carbon.

4.1.1. Adsorption isotherms

Adsorption data were analysed according to Langmuir (Langmuir, 1915) and Freundlich (Freundlich, 1926) models. The effect of different weights of activated carbon (3000–3800 mg) on the adsorption of Fe(III) and Mn(II) ions was monitored. The data are calculated and given in Table 9(a,b,c,d,e,f). The

Table 9 Effect of the weight of activated carbon on the adsorption of Fe(III) and Mn(II) ions.

Ion	Concentration (mg/l)		x (mg)	X
	Initial Co	Final Ce		
(a) m = 3000 mg				
Fe(III)	1.2	0.3	0.90	0.00030
Mn(II)	0.95	0.1	0.85	0.00028
(b) m = 3200 mg				
Fe(III)	1.2	0.1	1.10	0.00034
Mn(II)	0.95	0.08	0.87	0.00028
(c) m = 3400 mg				
Fe(III)	1.2	0.09	1.11	0.00032
Mn(II)	0.95	0.05	0.90	0.00026
(d) m = 3600 mg				
Fe(III)	1.2	0.05	1.15	0.000319
Mn(II)	0.95	0.02	0.93	0.00025
(e) m = 3800 mg				
Fe(III)	1.2	0.02	1.18	0.000310
Mn(II)	0.95	0.01	0.94	0.00024

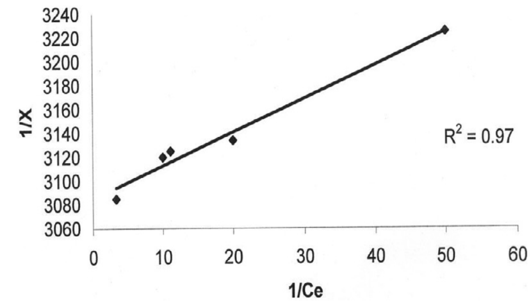

Figure 11 Langmiur adsorption isotherm for iron (using activated carbon).

Table 10 Langmuir parameters of Fe(III) and Mn(II) removal using activated carbon.

Ion	Xm	b	r^2
Fe(III)	0.00032	1116	0.97
Mn(II)	0.00027	644	0.85

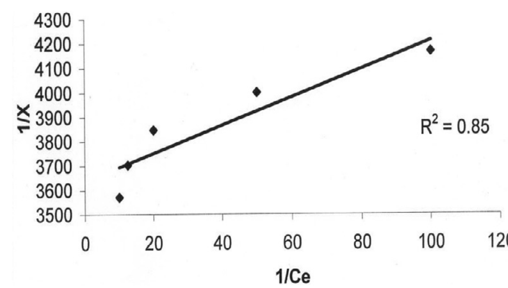

Figure 12 Langmiur adsorption isotherm for manganese (using activated carbon).

Table 11 Freundlich isotherms for the adsorption of Fe(III) and Mn(II) using activated carbon.

Ion	K_F	$1/n$	r^2
Fe(III)	0.0006	0.25	0.89
Mn(II)	0.0003	0.04	0.79

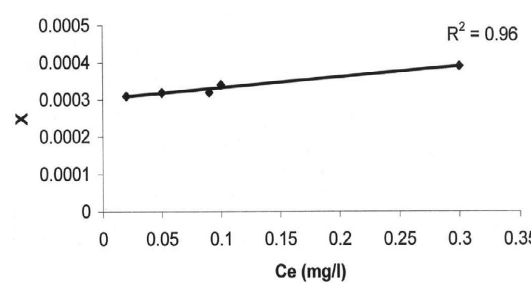

Figure 13 Relation between X and Ce of iron using activated carbon.

Table 12 Comparative studies between rice husk and activated carbon for the removal of Fe and Mn.

	Rice husk/(activated carbon)						
	Langmuir				Freundlich		
	Xm	b	r^2	R_L	K_F	$1/n$	r^2
Fe	0.0061	58.37	0.94	0.008	4.7×10^{13}	6.25	0.84
	(0.00032)	(1116)	(0.97)	(0.0008)	(0.0006)	(0.25)	(0.89)
Mn	0.0046	65.84	0.91	0.01	3.3×10^5	2.38	0.94
	(0.00027)	(644)	(0.85)	(0.0017)	(0.0003)	(0.04)	(0.79)

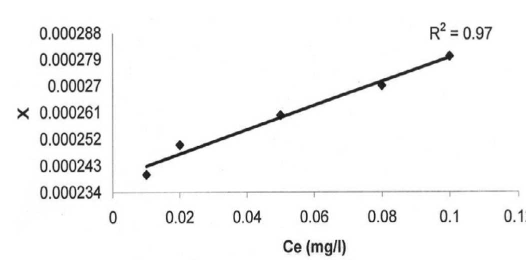

Figure 14 Relation between X and Ce of manganese using activated carbon.

metals adsorption data were plotted according to linear Langmuir isotherms. Linearized plots of 1/X versus 1/Ce were obtained, Figs. 11 and 12. Simply, we can say that: x = Co–Ce and X = x/m.

Regression data and adsorption parameters are given in Table 10. Langmuir equation in its linear form points to the high successful application of activated carbon for the removal of metals. (Figs. 13–15)

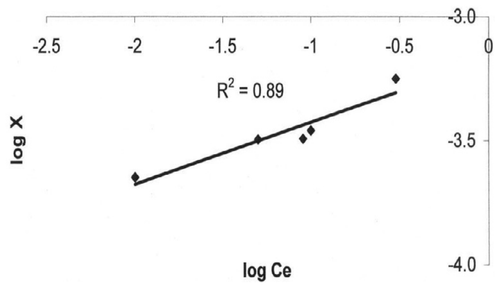

Figure 15 Freundlich plot for iron adsorption onto activated carbon.

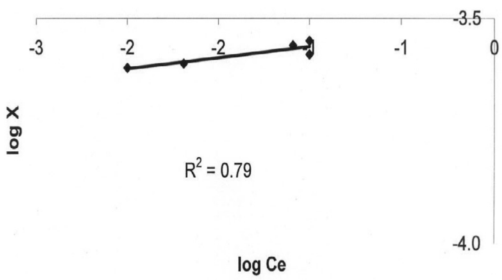

Figure 16 Freundlich plot for manganese adsorption onto activated carbon.

4.1.2. Freundlich adsorption isotherms

A straight line with a slope *1/n* and an intercept log KF is obtained. This reflects the satisfaction of the Freundlich isotherm model for the adsorption of Fe(III) Mn(II) ions. The log KF, is an indication of adsorption capacity and the slope, *1/n*, is a criterion for adsorption intensity. The Freundlich parameters for the adsorption of the metal ions are given in Table 11 and Figs. 10–16.

It is apparent that Fe(III) and Mn(II) could be treated by activated carbon in sequence depending on the K_F, Xm, b, r^2 values. All these parameters are high for Fe with respect to Mn.

In spite of that both rice husk and activated carbon could be successfully used for the removal of Fe and Mn. But, it seems that rice husk is the best (as controlled from Xm and K_F values). In Egypt due to the problems that arise from the storage of rice and the firing clouds obtained from the husk, its use for the treatment is excellent for the costs and environmental aspects.

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