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FULL LENGTH ARTICLE

# Removal of aluminum, iron and manganese ions from industrial wastes using granular activated carbon and Amberlite IR-120H



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## KEYWORDS

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 Langmuir;  
 Sorption capacity

**Abstract** The removal of aluminum, iron and manganese from some pollution sources that drain into Ismailia Canal has been investigated using two different sorbents; granular activated carbon (GAC) and Amberlite IR-120H (AIR-120H). Batch equilibrium experiments showed that the two sorbents have maximum removal efficiency for aluminum and iron pH 5 and 10 min contact time in ambient room temperature, while pH 7 and 30 min were the most appropriate for manganese removal. Dosage of 2 g/l for both GAC and AIR-120H was established to give the maximum removal capacity. At optimum conditions, the removal trend was in order of  $Al^{+3} > Fe^{+2} > Mn^{+2}$  with 99.2, 99.02 and 79.05 and 99.55, 99.42 and 96.65% of metal removal with GAC and AIR-120H, respectively. For the three metals, Langmuir and Freundlich isotherms showed higher  $R^2$  values, with a slightly better fitting for the Langmuir model. In addition, separation factors ( $R_L$ ) and exponent ( $n$ ) values indicated favorable Langmuir ( $0 < R_L < 1$ ) and Freundlich ( $1 < n < 10$ ) approach. GAC and AIR-120H can be used as excellent alternative, effective and inexpensive materials to remove high amounts of heavy metals from waste water.

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## Introduction

In Egypt, the pollution by trace metal ions is one of the most serious environmental problems. Effluents, resulting from daily domestic and industrial activities may induce considerable changes in the physical and chemical properties of Nile

water. These changes may greatly alter the environmental characteristics of river reaches (El-Sayed, 2011).

Unlike many organic wastes, heavy metals cannot be degraded biologically into harmless products. As a result, heavy metals tend to accumulate in the food chain and environment (Huang et al., 1991). Most of the heavy metals are bound to particles in sediment, but only a small quantity becomes dissolved in the water and it can spread widely in the food chains (Khadr, 2005). Heavy metal contamination exists in the aqueous waste streams of many industries like,

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metal plating, mining operations, metal smelters, microelectronics, radiator, alloy, storage battery, plastics and textiles manufacturers, wood preservatives producing industries, as well as agricultural sources where fertilizers, pesticides and fungicidal spray are intensively used (Bhatti et al., 2007; El-Ashtouky et al., 2008; Hegazi, 2013).

Wastes that contain metals are considered to be hazardous to both human life and the environment due to their acute toxicity and non-biodegradability, even when the heavy metals are present at trace concentrations (Zhang et al., 2005). Heavy metal ions can be accumulated by aquatic organisms that would then endanger human health through the food chain (Singanan, 2011). They accumulate in living tissues throughout the food chain where humans are at its top. Their accumulation over time causes damage to the kidney, liver, nervous system, reproductive system in addition to cancer nervous system (Malik et al., 2010) and brain damage if found above the tolerance levels (Brown et al., 2000).

Removal of toxic heavy metals from the environment is an important challenge. Several methods for removal of metal ions from waste waters have been developed. A removal process must be simple, effective and inexpensive (Ahn et al., 2008). Several processes have been suggested to remove heavy metals from wastewaters, such as chemical precipitation, ion exchange, cementation, coagulation and flocculation, complexation, biosorption, adsorption, and membrane processes (Ahn et al., 2009; Xiong et al., 2009). However, most removal processes have disadvantages, such as continuous input of chemicals, high costs and even incomplete metal removal (Minceva et al., 2007).

Adsorption is a very effective process for a variety of applications, and is considered economical and widely applicable. It creates relatively little sludge and is an efficient method for metal ions removal from wastewaters (McKay, 1996; Kannan and Rengasamy, 2005). The most generally used solid adsorbent is activated carbon, which is used as a very efficient solid adsorbent in many different applications (Cooney, 1998). Activated carbon is the carbon produced by activation of any carbonaceous material such as coconut shells, bamboo, wood chips, sawdust, coal, lignite, paddy husk, etc. Activated carbon is a black, solid, powdered, granular, microcrystalline or a pelletized substance non-graphitic form of carbon with an excessively porous material and a large internal surface area, which is known for its high capacity to bind contaminants by adsorption (El-haddad, 2012). Activated carbon can be characterized by a large specific surface area of 500–2500 m<sup>2</sup>/g, this is its most important physical property, which allows the physical adsorption of gases or vapors and dissolved or dispersed substances from liquids (Kadirvelu et al., 2001; Bansode et al., 2003). Activated carbon removes heavy metals by complexation or by electrostatic attraction of metal ions to various surface oxygen-containing functional groups (Yin et al., 2007).

Another effective method used for the removal of heavy metals is ion exchange. Ion exchange may be defined as the exchange of ions between the substrate and surrounding medium. Ion exchange is one of the most frequently studied and widely applied techniques for the treatment of metal-contaminated wastewater and the renewal of solutions for reusing, in addition to recovery of metallic substances (Lee et al., 2007). Ion exchange resins are usable at different pH values and suitable at high temperatures. Ion exchange is

insoluble in most organic and aqueous solutions. They contain a covalent bonding between the charged functional groups and the cross linked polymer matrix (Sherrington, 1998). The ion exchangers are classified into anion and cation exchangers, which contain anions or cations as oppose-ions, respectively. The cation and anion exchangers are categorized into strongly acidic, weakly acidic, strongly basic, weakly basic ion exchanger based on nature of functional groups (Hubicki and Kolodynska, 2012).

In the present study two sorbent substances, granular activated carbon (GAC) and Amberlite-IR-120H (AIR-120H), were used to remove some metal ions from industrial waste, which discharged into Ismailia Canal. Ismailia Canal is one of the most important branches of Nile River in Egypt with about 128 km length from Cairo to Ismailia governorate. It is the main source of drinking and irrigation water for many governorates, cities and villages (Goher et al., 2014).

The main objective of this study was to remove metals from aqueous solutions, as well as to remediate high metal content wastes, which were discharged into Ismailia Canal using granular activated carbon and strongly cationic exchanger Amberlite-IR-120H. A detailed investigation on the effect of pH, contact time and dosage on metal removal from a mixed solution of three metals was carried out. Isotherm studies were used to quantify the adsorption process. Comparing equilibrium studies was performed using GAC and AIR-120H.

## Materials and methods

### Preparation of metal solutions

Industrial waste water samples from some source of pollution that is effluent to Ismailia Canal, Egypt, were collected in February-2014. They were preserved and analyzed for metals contents following standard method procedures (APHA, 1998). 1000 mg/l of metal solutions of aluminum, iron and manganese from Sigma–Aldrich analytical grade were used to prepare the mixed synthetic solutions. The initial total metal ion concentration, used in the adsorption equilibrium experiments, was prepared in the laboratory based on metal concentration in the industrial effluent.

### Adsorbent

The granular activated carbon (GAC) and Amberlite-IR-120H (AIR-120H), which were used as sorbents in this study were bought from Dohrmann Company and Rohm and Hass company respectively. The characteristics of GAC and AIR-120H are shown in Tables 1 and 2 respectively.

The specific surface area and pore volume of the GAC were measured by Quantachrome instrument model NOVA 3200

**Table 1** Physico-chemical properties of GAC.

Physical properties	Elemental analysis		%
Ash content	10 (%) max	C	82.23
Bulk density	0.813 g/m <sup>3</sup>	Mo	6.16
Density	49 g/cm <sup>3</sup>	Ag	4.46
Surface area	688.6 m <sup>2</sup> /g	Cl	3.68
Total pore volume	0.3445 cc/g	S	0.19

**Table 2** Physico-chemical properties of Amberlite IR-120H.

Matrix	Styrene divinylbenzene copolymer
Functional groups	Sulfonates
Physical form	Amber beads
Ionic form as shipped	H <sup>+</sup>
Total exchange capacity	≥ 1.8 eq/L (H <sup>+</sup> form)
Moisture holding capacity	53–58% (H <sup>+</sup> form)
Shipping weight	800 g/L
Specific gravity	1.185–1.215 (H <sup>+</sup> form)
Uniformity coefficient	≤ 1.8
Harmonic mean size	620–830 μm
Fine contents	< 0.300 mm: 2% max
Maximum reversible swelling	Na <sup>+</sup> → H <sup>+</sup> : 11
Chemical resistance	Insoluble in dilute solutions of acids or bases

surface area analyzers, using N<sub>2</sub> as adsorbate at –196 °C (the liquid nitrogen temperature). The environmental scanning electron microscope (ESEM) FEI Quanta model FEG 250, was used to study the surface morphology of the GAC and the energy dispersive X-ray (EDX) spectra analysis to indicate the elemental composition of the GAC. Samples of 5% GAC in KBr and cast in disks were examined with a JASCO FT/IR-6300 FTIR spectrometer within the wave number (400–4000 cm<sup>-1</sup>) at ambient conditions to elucidate the chemical characteristics relevant to metallic ion sorption (Raize et al., 2004).

#### Batch equilibrium studies

A batch equilibrium experiment was conducted. The batch experiment was performed in a wide variety of conditions including variation in the pH, sorbent dosages and agitation periods. For each experiment, a 50 ml of synthetic water sample containing mixed metals of 100 mg/l Al, 10 mg/l Fe and 2 mg/l Mn was prepared based on industrial wastewater

metal concentration. The prepared solutions were added into shaker flasks with different amounts of adsorbents, pH adjustments were done using 1.0 M NaOH and 1.0 M HCl. Solutions were oscillated at a speed of 150 rpm in a mechanical shaker at 25 °C (± 2). After filtration of the solution using a GF/C glass microfiber filter, the residual metals in solution were analyzed by using GBC atomic absorption reader (Model SavantAA AAS with GF 5000 Graphite Furnace).

For the isotherm study, Equilibrium concentration of metals at various sorbent doses (0.2, 0.4, 0.8, 1.2 and 2 g/l) at ambient temperature was used. The removal efficiency (sorption capacity) of each sorbent was calculated as follows:

$$q_t = \frac{(C_o - C_t)V}{m} \quad (1)$$

where,  $q_t$  (the amount of adsorbed metal per gram of sorbent) is the sorption capacity of the sorbent at time  $t$ ;  $C_o$  is the initial concentration of metal in the solution (mg/l);  $C_t$  is the equilibrium concentration of metal in the solution (mg/l) after a period of time  $t$ ;  $V$  is the volume tested solution (in liter) and  $m$  is mass of the sorbent in the tested solution (in gram) (Shama and Gad, 2010).

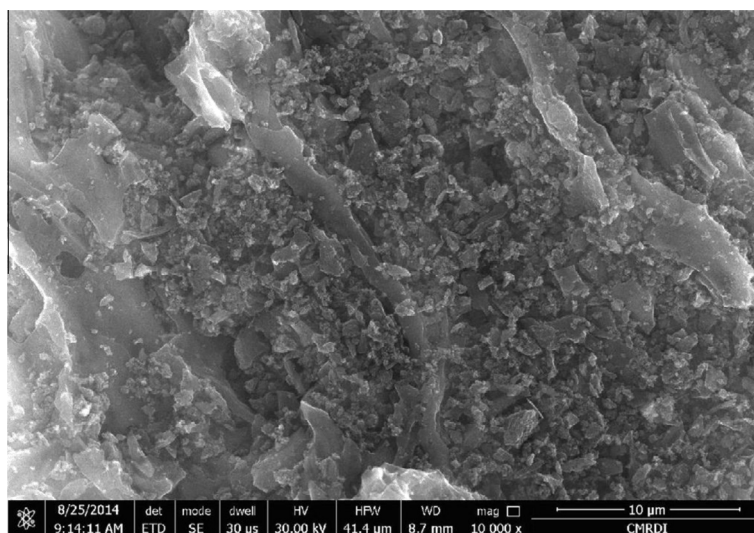
The removal percentage of metal ( $R$  %) can be calculated using the following formula.

$$R(\%) = \frac{(C_o - C_t)}{C_o} \times 100 \quad (2)$$

## Results and discussion

### Physical and chemical characterization of GAC

The surface morphology of GAC was examined using Quanta, FEI Quanta model FEG 250 environmental scanning electron microscopy. The SEM image detected the structure of the GAC surface porous, which indicates the amorphous nature of the GAC (Fig. 1). FTIR analysis was achieved to identify the different functional groups present in GAC. Fig. 2 shows the peaks of FTIR spectrum of different functional groups according to their corresponding wave numbers (Chen and



**Figure 1** SEM image of GAC surface.

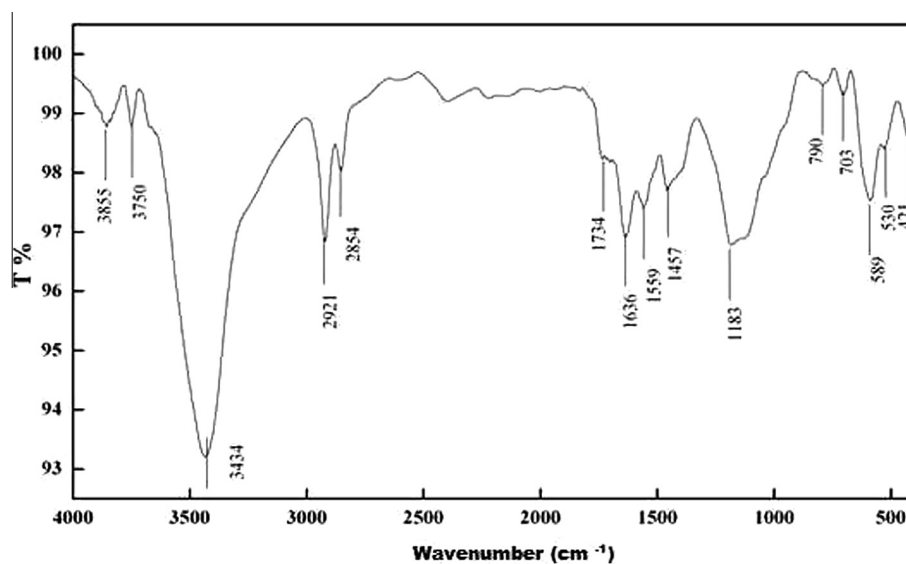


Figure 2 FTIR spectrum of GAC.

Table 3 Possible assignment of GAC spectra.

Functional class	Band position/cm	Intensity	Assignment
Disulfide	530	Weak	S-S
Alkyl halide	589	Strong	C-Cl
Esters	703	Strong	S-OR
Thiocarbonyl	1183	Strong	C=S
Aromatics	1457	Strong	C-C (in-ring)
Alkenes	1636	Variable	C=C (symmetry reduces intensity)
Aliphatic aldehydes	1734	Strong	C=O (saturated aldehyde)
Alkanes	2854	Strong	C-H
Carboxylic	2921	Strong	-COO-H (very broad)
Alcohols	3434	Strong	O-H (H-bonded), usually broad

Wu, 2004) and their assignments are presented in Table 3. The obtained data of FTIR analysis indicated that GAC surface contains acidic functional groups, which increase metal adsorption; such as alkyl halides, alcohols, carboxyl, carbonyl and sulfur groups (Edwin, 2008).

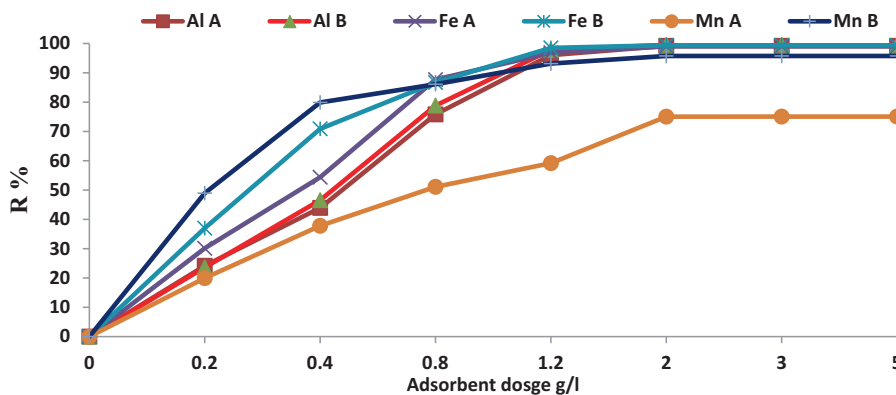
#### Effect of adsorbent dosage

To design the optimum treatment systems a series of batch experiments were conducted with the adsorbent dosage of 0.2, 0.4, 0.8, 1.2, 2, 3 and 5 g/l of test solution at pH 5. A maximum removal of 99.2% and 99.55% of Al, 99.02% and 99.42% of Fe and 79.05% and 95.75% of Mn was obtained at 2 g/l of GAC and AIR-120H, respectively. Fig. 3a shows that a 2 g/l of sorbent dose was sufficient for optimal removal of the three metals in aqueous solutions of 100, 10 and 2 mg/l of Al, Fe and Mn, respectively. A further increase of GAC or AIR-120H doses would not have any significant effect on the removal of metals from the solution. This observation was confirmed by Potgieter et al. (2006) and Singanan (2011) for

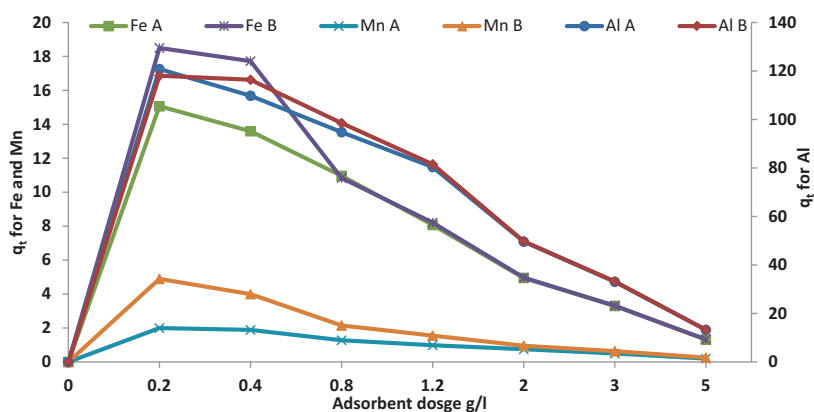
heavy metal removal from aqueous solutions by using activated biocarbon and palygorskite clay as an adsorbent, respectively. Furthermore, adsorbent recorded a maximum sorption capacity of 120.8 and 118.05 mg/g for Al, 15.07 and 18.5 mg/g for Fe and 2.0 and 4.9 mg/g for Mn at 0.2 g/l dosage of GAC and AIR-120H, respectively (Fig. 3b). The results showed that the adsorption capacity decreased with the increase of the sorbent dosages, which coincided with those obtained by Onundi et al. (2010) and Ghoniem et al. (2014). The high sorbent dosage could cause the agglomeration of particles and a consequent reduction in inter-particle distance. Therefore, the intersecting of the adsorption sites due to the overcapacity of adsorbent particles above a dose of 0.2 g/l may have explained the reduction of sorption capacity. Moreover, the high sorbent dosage could cause the agglomeration of particles and a consequent reduction in inter-particle distance. They may have also produced a screening effect on the dense outer layer of the particles, which cover the binding sites from metals (Pons and Fuste, 1993).

#### Effect of pH

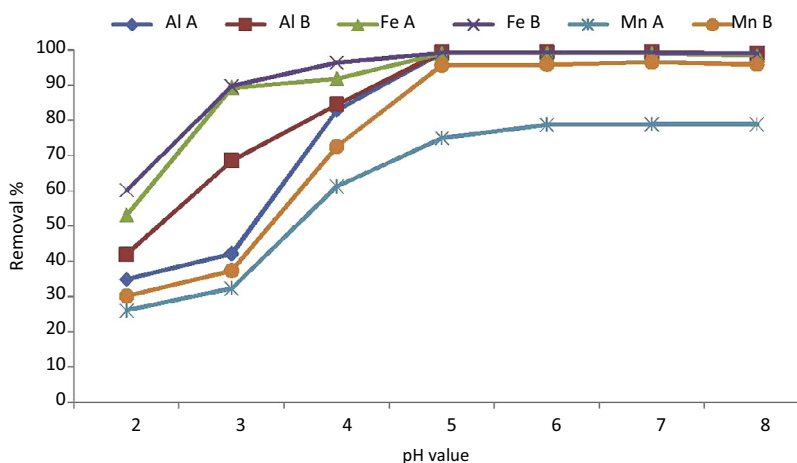
The effect of pH variation on the sorption of metal ions with GAC and AIR-120H is represented in Fig. 4. During the pH effect, the parameters of temperature, solution volume, sorbent dosage, shaking time and initial metals ion concentration were fixed at 25 °C, 50 ml, 0.1 g, 60 min and 100, 10 and 2 mg/l for Al, Fe and Mn, respectively. Effects of pH were tested at pH 2, 3, 4, 5, 6, 7 and 8. The pH of the aqueous solution is an important operational parameter in the adsorption process because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction (Amuda et al., 2007). It can be seen from Fig. 4, the removal percentage of metal ions was increased as the pH values increased too. It is notable that at the lower pH value (pH = 2); the uptake of Fe with AIR-120H recorded the highest removal among the metals with a percentage of 60.33%, while adsorption of Mn with GAC recorded the



**Figure 3a** Effect of adsorbent dosage on the percentage removal of heavy metals with GAC and AIR-120H at pH 5 and 60 min retention time. \*A = removal of the metal with GAC and B = removal of the metal with AIR-120H.



**Figure 3b** Effect of sorbent dosage on the adsorption capacity of GAC and AIR-120H at pH 5 and 60 min retention time. \*A = removal of the metal with GAC and B = removal of the metal with AIR-120H.



**Figure 4** Effect of pH on removal of heavy metals from waste water by using GAC (A) and AIR-120H (B) at 60 min retention time and 2 g/l sorbent dosage.

lowest one of 26.14. The removal rate of Mn increased slowly to reach the maximum removal percentage of 96.65% and 79.05% with AIR-120H and GAC, respectively at pH 7. On the other hand, the adsorption capacity of Al and Fe ions

was close to saturation at pH 5 where they increased from 35% and 42.08% for Al, 53.25% and 60.33% for Fe at pH 2 to 99.2% and 99.55% for Al, 99.02% and 99.42% for Fe at pH 5 with GAC and AIR-120H, respectively.



Generally, at low pH values the metal removal decreased. This might be related to the competition between  $H^+$  and  $M^{2+}$  ion species for the adsorption sites, due to the high  $H^+$  concentration (Fernando et al., 2009). In addition, reduction of the attraction between metal cations and adsorbents due to the positive charge of the sorbents' surface. In contrast, at higher pH, the negative charge on the surface of adsorbent increases, which provides electrostatic interactions that are favorable for adsorbing cationic species (Stafiej and Pyszynska, 2007; Zhou et al., 2011). It could be deduced that the sorption of metal cations increased with increasing pH, where the metal ionic species become less stable in the solution due to the surface complexation or by ion exchange with other ions bound to acidic functional group or by both mechanisms (Chen and Wu, 2004; Yin et al., 2007). For example, carboxylic groups ( $-COOH$ ) are important groups for metal uptake by biological materials (Ajmal et al., 2000). At pH higher than 3–4, carboxylic groups are deprotonated and negatively charged. Consequently, the attraction of positively charged metal ions would be enhanced (Norton and Baskaran, 2004). Increasing of pH value after saturation, does not increase the metal sorption, but a partial metal desorption may occur due to the reaction of metal ions with  $OH^-$  ions and precipitate as a metal hydroxide (Farooq et al., 2010).

#### Effect of retention time

The variations of metal removal percentage at different retention oscillation times with GAC and AIR-120H are represented in Fig. 5. 0.1 g of GAC was added to 6 flasks of 50 ml waste water at pH 5; other similar flasks were prepared using AIR-120H. The flasks were oscillated from 2, 5, 10, 20, 30 to 60 min, respectively. The sorbents showed a sharp metal reduction for the first 5 min of contact time, with a further increase in time the sorption kinetics decreased progressively (Gueu et al., 2007). The equilibrium of metal removal was achieved at 10 min for Fe, Al and 30 min for Mn. At the beginning, the adsorption is very fast due to the high number of available adsorptive sites (Zhou et al., 2011). The sorption capacity, for the two sorbents at equilibrium, was in trend of  $Al > Fe > Mn$ , That indicates the affinity of acidic groups on the GAC and the sulfonic groups on AIR-120H for the

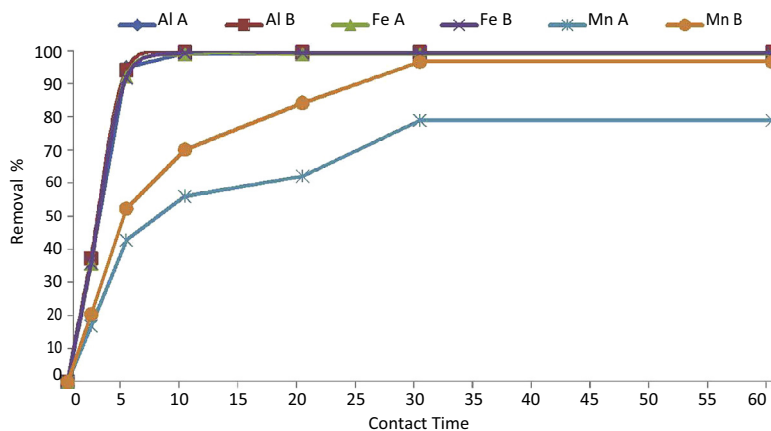
three metals. The observed trend was probably due to the adsorption phenomena depending on the charge density of cations ( $Al^{+3} > Fe^{+2} = Mn^+$ ) and the diameter of hydrated cations where the biggest diameter ( $Mn^{+2}$  ionic radius = 80 pm) has minimum adsorption than ( $Fe^{+2}$  ionic radius = 76 pm). That caused faster equilibrium for Al and Fe than Mn ions (Erdem et al., 2004). In addition, sulfonic acid resins have affinity toward higher charged cations and the cations with higher atomic number in the case of different cations with the same charge (Fritz, 2005). Further increasing of oscillation time did not show significant change in removal of metals, which is in agreement with (Zhou et al., 2011).

#### Application study on the wastes discharged into Ismailia Canal

Ismailia Canal is one of the most important irrigation and drinking water resources in Egypt. It is the principle source of drinking water supply for a great number of Egyptian citizens, as well as agricultural and industrial purposes (Geriesh et al., 2008). Many sources of pollution, which are rich in aluminum, iron and manganese, are discharged into the canal. The most serious of these sources include the effluent wastes of Water Treatment Plant at El-Amiria region, Water Treatment Plant at Musturod city, Abu Zaabal Fertilizers Company and Alum (Aluminum Sulfate) Company. The obtained results of metal removal from the selected industrial wastewater that runoff into Ismailia Canal are presented in Table 4. The treatment of the selected industrial wastewater was carried out with GAC and AIR-120H for 2 gm/l dosage, 20 min retention time and pH of 7.26, 7.33, 7.58 and 7.18 for Water Treatment Plant (WTP) at El-Amiria region, Water Treatment Plant (WTP) at Musturod city, Abu Zaabal Fertilizers Company and Alum (Aluminum Sulfate) Company, respectively. It is noted that the three analyzed metals, aluminum, iron and manganese, were -nearly- completely removed from all tested industrial wastes.

#### Sorption isotherms

The adsorption isotherms are very important in describing the adsorption behavior of solutes on specific sorbents (Singanan, 2011). They are used to describe the equilibrium between the



**Figure 5** Effect of retention time on removal of heavy metals from wastewater by using GAC and AIR-120H at 2 g/l sorbent dosage and pH 5.

**Table 4** Metal removal ratio of different wastes water discharged into Ismailia Canal using 2 gm/l GAC and AIR-120H for 20 min retention time.

Adsorbent	Source of pollution	Al			Fe			Mn		
		$C_o$	$C_f$	R %	$C_o$	$C_f$	R %	$C_o$	$C_f$	R %
GAC	WTP at El-Amiria	25.90	N	100	2.5	ND	100	0.5	0.03	99.9
	WTP at Musturod	37.55	N	100	2.2	ND	100	0.4	0.02	99.9
	Abu Zaabal Fertilizers Co.	6.530	N	100	2.0	ND	100	0.3	0.01	99.9
	Alum Company	121.9	1.7	99.9	2.2	0.07	99.9	0.3	0.03	99.9
AIR-120H	WTP at El-Amiria	25.90	N	100	2.5	0.12	99.9	0.5	0.01	99.9
	WTP at Musturod	37.55	N	100	2.2	ND	100	0.4	0.01	99.9
	Abu Zaabal Fertilizers Co.	6.530	N	100	2.0	ND	100	0.3	0.00	99.9
	Alum Company	121.9	N	100	2.2	ND	100	0.3	0.01	99.9

concentration of the dissolved adsorbate and the amount of adsorbate that accumulated on the sorbent. Adsorption data for adsorbate concentrations are most commonly described by sorption isotherm, such as the Langmuir and Freundlich isotherm models (Freundlich, 1906; Langmuir, 1916). The sorption isotherm is the mathematical model, which gives an explication for the adsorbate species behavior between liquid and solid phases (Ghoniem et al., 2014).

The theoretical principle of Langmuir isotherm cited that there is only an adsorption monolayer on an adsorbent. This single layer represents the distribution of equilibrium for the metal ions between the liquid and solid phases. After formation of the adsorbate monolayer on the adsorbent outer surface, no additional adsorption occurs (Badmus et al., 2007). It is valid for monolayer adsorption onto a surface containing a finite number of identical sites with regular energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface (Shama and Gad, 2010).

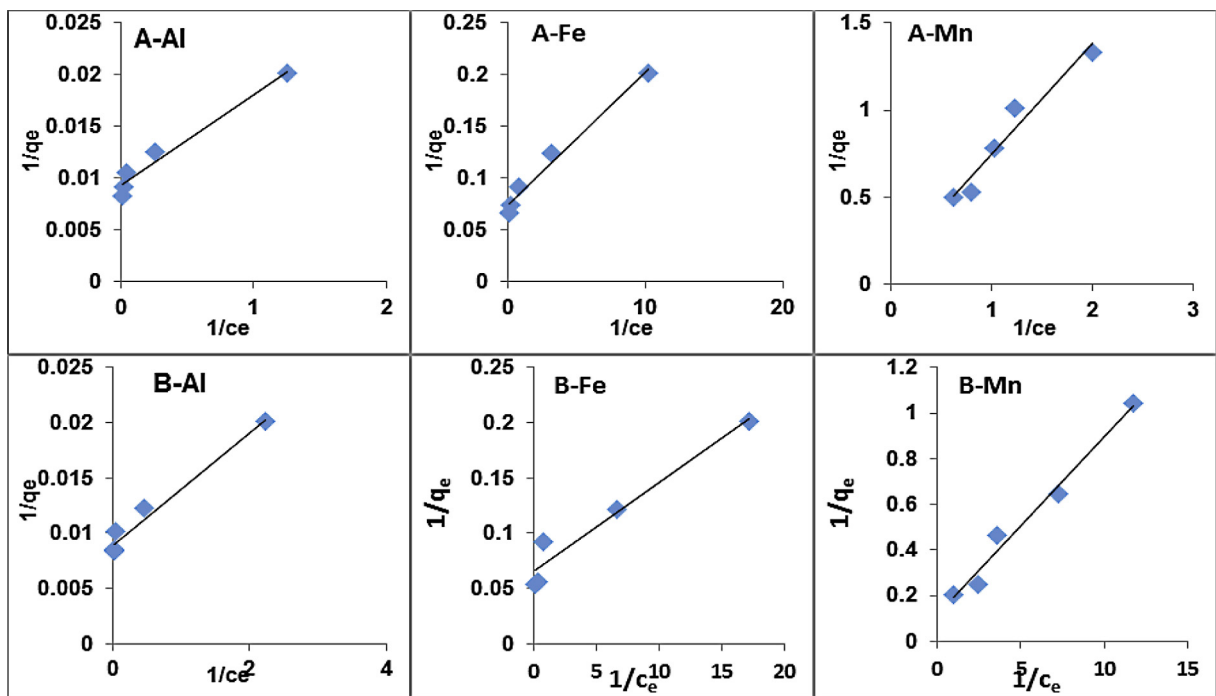
This indicates that the sorption of metal ions take place on a homogeneous surface by monolayer sorption without any interaction with the adsorbed ionic species (Meshram et al., 2012). A general form of the Langmuir equation is:

$$q_e = x/m = q_{max} b C_e / (1 + b C_e) \tag{3A}$$

while, the linear form of isotherm equation is:

$$1/q_e = 1/q_{max} + (1/b q_{max})(1/C_e) \tag{3B}$$

where  $q_e$  is the amount of solute adsorbed per weight unit of solid adsorbent at equilibrium (mg/g);  $C_e$  (mg/L) is the equilibrium concentration (concentration of solute remaining in solution at equilibrium);  $q_{max}$  and  $b$  are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The constants  $b$  and  $q_{max}$  are obtained from slope and intercept of the linear relationship of plotting  $(1/q_e)$  vs.  $(1/C_e)$  (Fig. 6). The restrictive  $q_{max}$  values of the different sorbents can be used to compare their adsorption capacity.



**Figure 6** Langmuir isotherm plot of metals sorption with (A) GAC and (B) AIR-120H.

Freundlich isotherm is based on the theoretical principle, which assumes that the uptake or sorption of metal ions occurs on a heterogeneous surface by monolayer adsorption (Badmus et al., 2007). The Freundlich isotherm theory states that the ratio of the adsorbed amount of solute onto a known sorbent mass to the solute concentration in the solution – at different concentrations – is not constant (Prasad et al., 2000; Rao et al., 2006). Freundlich equation is derived to model the multilayer sorption and the sorption on heterogeneous surfaces.

The model is described by the following equation

$$q_e = K_f C_e^{1/n} \quad (4A)$$

The logarithmic form of Freundlich model gives the linear relation by plotting of  $\text{Log } q_e$  vs.  $\text{Log } C_e$  (Fig. 7).

$$\log q_e = \log K_f + 1/n \log C \quad (4B)$$

$K_f$  is the Freundlich constant that indicates the relative adsorption capacity of the adsorbent (mg/g). The constant  $1/n$  is the intensity of sorption and indicates the tendency of

the adsorbate to be adsorbed. (Bishop, 2004; Goel et al., 2005). Values of  $k$  and  $n$  were calculated from the intercept and slope of the plot  $\log q_e$  and  $\log C_e$  (Fig. 7).

Langmuir and Freundlich constants and correlation coefficients are illustrated in Table 5. The results showed that the Langmuir and Freundlich isotherm models were well fitted for the studied metal ions for the two sorbent material with high correlation regression coefficient ( $R^2$ ) values (Table 5). It was observed that Langmuir adsorption isotherm provides a better fit to the experimental data of the studied metals than the Freundlich model in terms of  $R^2$  value. Values of ( $b$ ) which related the affinity of the metals to the sorbent surface, indicated that the metals have higher affinity with the AIR-120H surface than GAC. This observation was confirmed with the constant  $1/n$  values, which indicates the tendency of the adsorbate to be adsorbed (Bishop, 2004; Goel et al., 2005). In the same manner,  $q_{\max}$  and  $K_f$  values clarified, that AIR-120H has a relative advantage to the removal of metals than GAC, which is in agreement with the obtained experimental data of the metal removal ratio (Fig. 3a).

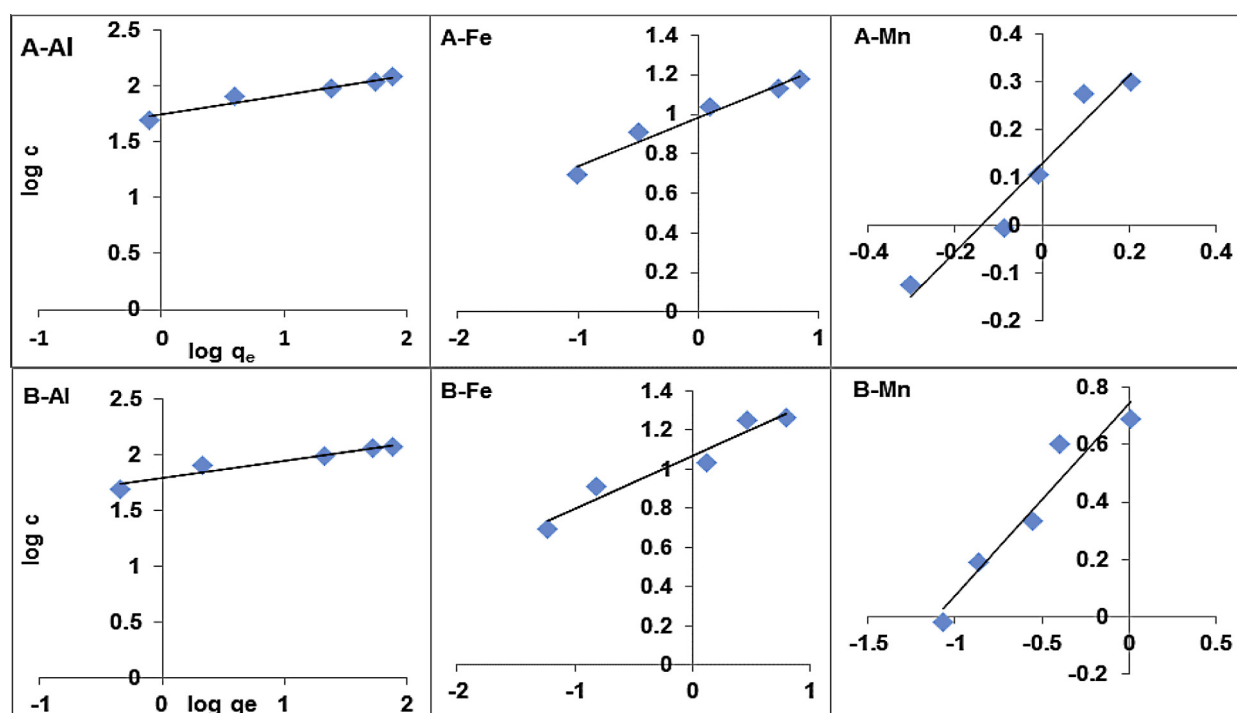


Figure 7 Freundlich isotherm plot of metals sorption with (A) GAC and (B) AIR-120H.

Table 5 Langmuir and Freundlich isotherm parameters.

Adsorbent	Metals	Langmuir isotherm				Freundlich isotherm		
		$b$	$q_{\max}$	$R^2$	$R_L$	$n$	$K_f$	$R^2$
GAC	Al	1.034	106.50	0.975	0.010	5.587	55.463	0.955
	Fe	4.912	14.86	0.984	0.020	4.057	9.716	0.965
	Mn	0.176	7.63	0.945	0.740	1.086	1.357	0.943
DVB	Al	1.840	108.70	0.983	0.005	6.406	62.259	0.934
	Fe	8.013	15.60	0.993	0.012	4.717	11.763	0.939
	Mn	1.453	8.71	0.992	0.256	1.489	5.569	0.943



For Langmuir isotherm model, the separation factor ( $R_L$ ) can be used to predict affinity between the adsorbate and sorbent in the sorption system (Hall et al., 1996),  $R_L$  parameter can be calculated from the equation of  $R_L = 1/(1 + bC_0)$  (Kagaya et al., 2006), where  $b$  is Langmuir constant and  $C_0$  is the initial concentration of metal ions. The separation factor ( $R_L$ ) value represents the behavior of Langmuir isotherm to be irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavorable ( $R_L > 1$ ) (Mckay et al., 1982). It is well noted for the all selected metals that ( $0 < R_L < 1$ ), which illustrates the favorable sorption conditions.

As for the Freundlich sorption isotherm model, the  $n$  value was found to be  $1 < n < 10$ , that indicated the beneficial sorption behaviors. Kadirvelu and Namasivayam, 2000 reported that  $n$  value could give sorption favorability, where  $n$  value between 1 and 10 represents beneficial sorption. According to Hasany et al. (2002), Freundlich isotherm does not predict any saturation of the sorbent by the adsorbate; thus infinite surface coverage is predicted mathematically, indicating multi-layer adsorption on the surface.

## Conclusion

The batch equilibrium experiment was carried out to assess the sorption capacity of Al, Fe and Mn with GAC and AIR-120H. At ambient room temperature, maximum removal of Al and Fe was achieved at pH 5 and 10 min retention time, while pH 7 and 30 min were the most appropriate for manganese removal. 2 g/L of GAC and AIR-120H was established to give the maximum removal percentage. Both of GAC and AIR-120H showed a higher efficiency to remove the metals from the aqueous solution, with a relative advantage of metals removal by AIR-120H. The Langmuir and Freundlich adsorption models were used for the mathematical description of the sorption equilibrium of metal ions to GAC and AIR-120H. The obtained data obeyed Langmuir and Freundlich sorption models in terms of correlation regression coefficient ( $R^2$ ) with a slightly better performance for Langmuir model. The results of separation factors ( $0 < R_L < 1$ ) and exponent ( $n$ ) values ( $1 < n < 10$ ) indicate favorable Langmuir and Freundlich approach. Finally, GAC and AIR-120H can be used as an excellent alternative, effective and inexpensive materials to remove high amounts of heavy metals from some aqueous wastes, such as the wastes discharged into Ismailia Canal.

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