

## Adsorption of barium and iron ions from aqueous solutions by the activated carbon produced from masot ash

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**Abstract:** Activated carbon produced from mazot ash, was tested for the adsorption of barium and iron metal ions using batch experiments in single metal solution under controlled experimental conditions. The adsorption processes were affected by various parameters such as equilibrium time, pH, concentration of metals, adsorbent dose and particle size. The adsorbent exhibited good sorption potential for barium and iron metal ions at pH  $7.5 \pm 0.5$ . C = O and S= O functional groups present on the carbon surface were the adsorption sites to remove metal ions from solution. The results shown that the Freundlich isotherm model achieved best fit with the equilibrium adsorption data for adsorption of barium and iron metal ions. The maximum adsorption capacities of barium and iron metal ions were 10.62 and 83.96 mg/g, respectively. The values of separation factor were between zero and one indicating favorable sorption for two tested metals ions. The surface coverage values were approaching unity with increasing solution concentration indicating effectiveness of adsorbent under investigation.

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**Key words:** Activated carbon, Barium and iron, Sorption isotherm, zero point charge.

### 1. Introduction

Heavy metals pollution is an important environment problem because of their toxicity and threat to human life and to environment. Therefore the elimination of heavy metals from water and wastewater is important to protect public health. Toxic metal compounds not only contaminate surface water sources (seas, lakes, ponds and reservoirs), but also contaminate underground water in trace amounts by leaching from the soil after rain and snow (Sun *et al.*,2006).The main sources of toxic metals are industrial wastes from processes such as electroplating, metal finishing, mining and chemical manufacturing (Abdel-Halim *et al.*,2003). Removal of metal ions from wastewaters has been performed by chemical precipitation, membrane filtration, ion exchange, reverse osmosis, evaporation, electrolysis and adsorption processes (Kandah,2002; Yan *et al.*, 2003; Kandah *et al.*,2004; and Cao *et al.*, 2004). Among them adsorption process is found to be the most effective method for removing dissolved metal ions from wastes (Aslam *et al.*,2004).

Activated carbon has been widely used as an adsorbent with great success (Mckay, 1982; Chand *et al.*, 1994; Jusoh *et al.*, 2007 and Aluyor *et al.*, 2009).The activated carbon is a microcrystalline, non-graphitic form of carbon with a porous structure that has been processed to develop its internal porosity. Also this material can be characterized by a large specific surface area of 500-2500 m<sup>2</sup>/g, the most important physical property of activated carbon which allows the physical adsorption of gases or vapors and dissolved or dispersed substances from liquids (Hassler, 1974).

The major use of activated carbon is in solution purification and for the removal of taste, color, odors and other objectionable impurities from liquids, water supplies and vegetable and animal oils. In recent years it has been increasingly used for the prevention of environmental pollution and antipollution laws have increased the sales of activated carbon for control of air and water pollution. Activated carbon is a broad-spectrum agent that effectively removes toxic and biorefractive substances such as insecticides, herbicides, chlorinated hydrocarbons, and phenols, typically present in many water supplies. The use of activated carbons is perhaps the best broad-spectrum control technology available at present. Commercial grades of activated carbon are assigned as either gas-phase or liquid phase adsorbents. Liquid-phase carbons, generally in the form of powdered or granular, are characterized as having larger pores (3 nm in diameter and larger) because of the need for rapid diffusion in the liquid decolorizing activated carbon are usually employed as powdered. Powdered activated carbon has an extremely high ratio of area to volume, and since adsorption is a surface phenomenon, this increases its effectiveness but also makes it slow to settle and difficult to remove once added (Ansari *et al.*,2005).

Adsorption using activated carbon is well suited to remove heavy metals and organic compounds due to its high surface area and the combination of a well developed pore structure and surface chemistry properties. Activated carbon surface is predominantly hydrophobic but may also contain functional groups formed during the activation process. These groups contain heteroatom such as

oxygen and hydrogen and may also contain chlorine, nitrogen, and sulfur. The nature of these functional groups depends on activation conditions and contributes to the acid/base character of the surface and to specific interactions with adsorbed compounds (Kilduff *et al.*, 1996).

In this study, Ba(II) and Fe(II) removal from aqueous solutions was investigated by using activated carbon. The effects of pH, adsorbent amount, contact time and initial metal concentrations on adsorption capacity were experimentally studied. Langmuir and Freundlich isotherm models were used for the evaluation of findings. Also, the primary objectives of this study were to find point zero charge and to determine the range of optimum pH and to find surface acidity/basicity which will assist in investigating the possibilities of utilizing activates.

## 2. Material and Methods

### 2.1. Preparation of adsorbent

The activated carbon was prepared by mixing a mazot ash (MA) and 5% sulfuric acid (S) solution (S/MA ratio 1/3). The obtained slurry was agitated for 4 hrs at 100°C and the insoluble residue was separated by filtration. The insoluble residue was treated with 10% hydrochloric acid using stirring for 2 hrs, at room temperature. The insoluble activated carbon was obtained by filtration and drying. Dried activated carbon was stored in desiccators until used (Abu Rihab, 2011).

Proximate and ultimate analysis of the activated carbon was conducted as described in Table 1. The surface morphology of the activated carbon was analyzed by scanning electron microscope (SEM). Perkin Elmer FTIR spectrometer was used to analyze functional groups presence in activated carbon. The apparent density of activated carbon was determined by a tapping procedure using a 5 ml graduated glass cylinder (Malik *et al.*, 2007). Surface area of the adsorbent was determined by the methods described by Rao *et al.*, 2007). Carbon, hydrogen and nitrogen content was determined by CHN Analyzer.

### 2.2. Determination of Point Zero Charge

The point zero charge ( $pH_{pzc}$ ) of activated carbon produced from mazot ash (MA) was determined by the solid addition method. The net charge of surface is zero on the adsorbent surface at  $pH_{pzc}$ , therefore, no activation of acidic or basic functional groups are detected on the solution pH. Batch equilibrium method was used for the

determination of point of zero charge. To each of the flask 0.1 g of respective adsorbents was added including 100 ml solution  $KNO_3$  (0.01 N) in the pH range between 2 to 10. The initial pH of solutions were adjusted by adding drops of 0.5 N NaOH and 0.5 N HCl solutions and each flask was sealed and shaken thoroughly for 48 hrs at room temperature and the final pH of the solution was measured and recorded. The total charge adsorbed on activated carbon surface was determined by  $\Delta pH$  (the difference in the value of pH of the solution before and after 48 hrs). The intersection of obtained curve with  $pH_0$  axis indicated the  $pH_{pzc}$  value.

### 2.3. Determination the chemical property of the adsorbent surface

The Boehm titration procedure was used to calculate the amount of surface acidic and basic functional. All experimental was carried out in a batch mode. The surface chemistry was determined with the use of four independent solutions of 0.1 N HCl, 0.1N  $NaHCO_3$ , 0.1N  $Na_2CO_3$  and 0.1 N NaOH. In each adsorption experiment, 0.1 g adsorbent was added to 50 ml of the solutions with known concentration in a 250 ml round bottom flask under room temperature and the mixture was subjected to continuous stirring for 96 h using a shaker with a speed of 150 rpm. The suspension was then centrifuged at 5000 rpm for 5 min., 10 ml from each solution was taken and the excess of base and acid was titrated against 0.1 N HCl first and then later against 0.1 N NaOH. The amount of HCl that reacted with the adsorbent was then used to calculate the number of surface basic sites while the amount of NaOH,  $Na_2CO_3$  and  $NaHCO_3$  reacted with the adsorbent was used to calculate the number of surface acidic sites.

The calculation of surface chemistry is based on the consumed volumes of HCl and NaOH for titration. Groups of carboxyl, lactones and phenolics are acidic groups. Carboxyl groups were calculated by the consumed volume of 0.1N HCl for titration of  $NaHCO_3$  solution. Lactone groups were estimated by difference between the consumed volume of 0.1 N HCl. Phenolic groups were determined by difference between the consumed volume of HCl (0.1 N) for titration of NaOH and  $NaCO_3$  solutions. The basicity groups were obtained by calculation of the consumed volume NaOH (0.1 N) for titration of HCl (0.1N). The amount of functional group is calculated as following:

$$\text{Functional group (mmol/g)} = \frac{(\text{Normality} \times \text{Volume}_{\text{consumed}})}{\text{Molecular weight}} \times \frac{\text{Initial volume}}{\text{Selected volume for titration}} \quad (1)$$

### 2.4. Preparation of adsorbate

All the chemicals used were of analytical reagent grade and were obtained from Merck

(Germany). The stock solution containing 1g/L of standard barium and iron metal ions were prepared by dissolving 1gm of A.R.  $Ba(NO_3)_2$  and  $Fe(NO_3)_3$  in

double distilled water (DDW). All experimental solutions were prepared by diluting the stock solution to the required concentration. The pH of each experimental solution was adjusted to the required initial pH value using 0.5 N NaOH and 0.5 N HCl before mixing the adsorbent. The pH values of all prepared solutions were measured using pH-meter model OP-02/2 (Germany) with a combined electrode reading to  $\pm 0.05$  pH values. The concentration of residual barium and iron metal ions was determined using the conductance measurements were carried out by conductivity/TDS/temperature Meter model 4510. Its features include; Automatic range selection, calibration on standard solution or direct cell constant entry, automatic temperature compensation.

### 2.5. Batch adsorption studies

The effect of various parameters on the removal of barium and iron metal ions onto activated carbon was studied. For each experimental run, 50 ml of metal ions solutions of known initial concentration and pH were taken in a 100 ml plugged conical flask. A suitable adsorbent dose of activated carbon was added to conical flasks containing 50 mL metal ions solutions, adsorption of metal ions was carried out at  $30 \pm 1$  °C for 24 h in batch system and the mixture was shaken at a constant agitation speed (200rpm) for 30 min. Adsorption equilibrium isotherms were studied using activated carbon dosages from (0.002-0.2 g/L) per 50 ml of Ba(II) and Fe(II) solutions. Initial concentrations were ranged from ( 5-150 mg/L) using initial pH  $7.5 \pm 0.5$  the solution was separated from the mixture and analyzed for Ba(II) and Fe(II) concentration. The amount of metal adsorbed per unit mass of the adsorbent was calculated as follows:

$$q_e \text{ (mg/g)} = (C_o - C_e) V/M \quad (2)$$

and the percent removal may be calculated as:

$$\text{Removal \%} = [(C_o - C_e) / C_o] \times 100 \quad (3)$$

Where  $C_o$  is the initial concentration (mg/L) and  $C_e$  is the metal concentration (mg/L) at any time, V is the volume of the solution (L) and m is the weight of the sorbent used (g).

The effect of pH on the rate of adsorption was investigated using metal ions concentration of 100 mg/L for constant activated carbon dosages. The pH values were adjusted with 0.5N HCl and 0.5N NaOH solutions.

The suitability of the Langmuir and Freundlich adsorption models to the equilibrium data were investigated for Ba(II) and Fe(II) sorbent system.

## 3. Results and Discussion

The adsorption of barium and iron metal ions in aqueous solution on activated carbon (MA) were examined by optimizing various physicochemical parameters such as pH, amount of adsorbent, adsorbent size and adsorbate initial concentration. Analysis of adsorption data is important for

developing equilibrium isotherm equations that can be used for design purposes.

### 3.1 Characteristics of the adsorbent

#### 3.1.1 FT-IR spectrum and Scanning electron microscopic photographs

The physical characteristics along with the percentage of carbon, hydrogen and nitrogen in the activated carbon produced from mazot ash (MA) are presented in Table 1. The FTIR spectrum of the activated carbon is shown in Figure 1. The absorption at  $3420 \text{ cm}^{-1}$  indicates the presence of OH group, which was probably attributed to adsorbed water on the carbon (Vinke *et al.*, 1994 and Chen *et al.*, 2002). The bands appearing at  $1376$  and  $1653 \text{ cm}^{-1}$  are ascribed to the formation of oxygen functional groups like a highly conjugated C=O stretching in carboxylic groups, and carboxylate moieties, respectively (Jia *et al.*, 2000). The additional peaks at  $1456$  and  $1154 \text{ cm}^{-1}$  indicate the presence of C-H and S=O groups, respectively (Krishnam *et al.*, 2003). The C=O and S=O functional groups show very high coordination with heavy metals. Hence, the good sorption properties of the adsorbent towards barium and iron can be attributed to the presence of these functional groups on the adsorbent.

Scanning electron microscopic photographs of activated carbon shown in Figure 2 reveal the surface texture and porosity of the sample. The availability of pores and internal surface is requisite for an effective adsorbent.

#### 3.1.2. Determination of Point Zero Charge

The point zero charge of activated carbon produced from mazot ash (MA) was determined and the results shown in Figure 3. Since  $\text{KNO}_3$  solution was used, it is desirable to have a fixed background electrolyte concentration that is high enough to minimize the total salt concentration changes during the titration and no clear effect of  $\text{KNO}_3$  was found on mobility. The values were known by determining the position where the resulting curve cut through the  $\text{pH}_o$  axis as shown in Figure 3. The  $\text{pH}_{\text{pzc}}$  was found to be 6.9 for activated carbon produced from mazot ash sample. Cation adsorption becomes enhanced at higher than the  $\text{pH}_{\text{pzc}}$ , while adsorption of anions is equally enhanced at pH less than  $\text{pH}_{\text{pzc}}$  (Hamadaoui, 2006; Almeida *et al.*, 2009 and Farahani *et al.*, 2011).

#### 3.1.3. The chemical property of the adsorbent surface

The Boehm's technique was used to characterize the surface chemical property of the adsorbent. Several assumptions were made before the surface acidity and basicity could however be calculated. It was assumed that acidic group generally, could only be neutralized by NaOH,  $\text{NaCO}_3$  and  $\text{NaHCO}_3$  while all basic groups would be neutralized by HCl. Table 2 shows the summary of the properties of the surface functional groups through the Boehm titration. The concentration of acidic sites for the activated carbon

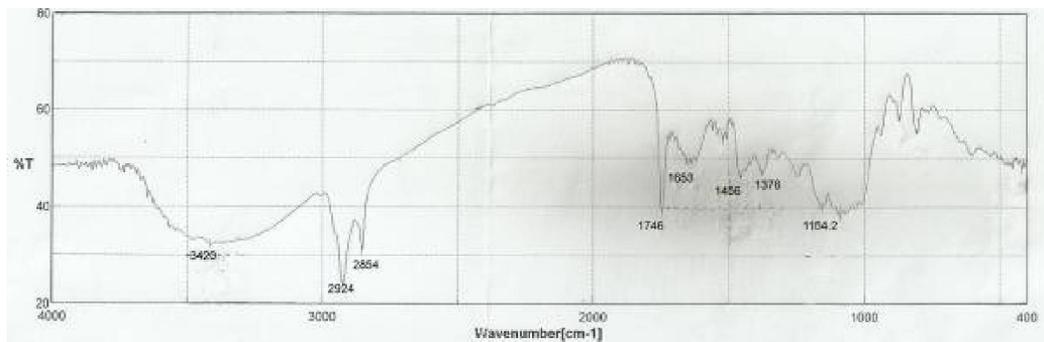
produced from mazot ash is 0.2137 mmol/g, while the basicity groups are very low. The basicity groups value is correspond to 0.0103 mmol/g. The significant increase of acidity groups in compared to the basicity groups, suggesting that the majority of functional groups on the adsorbent surface are acidic. The more acidity groups, indicating more oxygenated functional groups, gave rise to higher adsorption of heavy metals (Farahani *et al.*, 2011).

**Table 1:** Characteristics Properties of the Activated Carbon (MA).

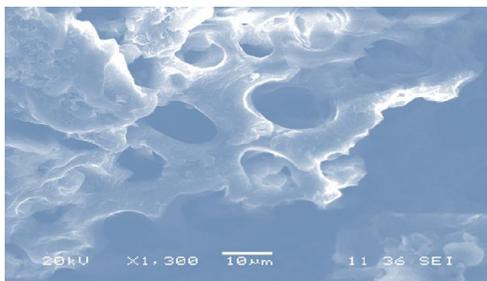
Parameter	Value
pH <sub>pzc</sub>	6.9
Conductivity(μS/cm)	32
Moisture content (%)	5.1
Volatile matter content (%)	7.8
Ash content (%)	4.3
Fixed carbon (%)	82.8
C content (%)	85.3
H content (%)	0.4
N content (%)	0.6
Apparent density(g/cm <sup>3</sup> )	0.2

**Table 2. The Boehm's Titration Data for Activated Carbon (MA).**

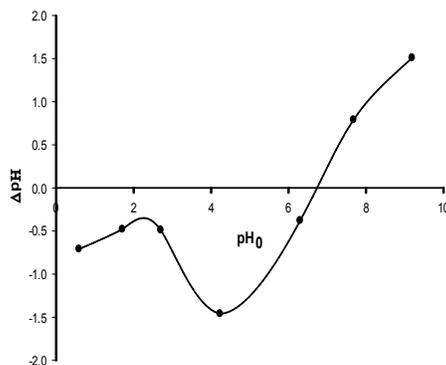
Adsorbent	Boehm's titration method				
	Carboxyl groups	Phenolic	Lactone	Basicity	Acidity
Activated carbon made from mazot ash	0.1220	0.0991	0.0027	0.0103	0.2137



**Figure 1.** FT-IR Spectrum of activated carbon (MA).



**Figure 2.** SEM photographs of the activated carbon (MA).



**Figure 3.** Point zero charge of activated carbon (MA).

### 3.2. Effect of initial pH on Ba(II) and Fe(II) adsorption

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The results for the adsorption of Ba(II) and Fe(II) are shown in Figure 4 using 100 mg/L initial metal concentration and 0.02 g/L adsorbent concentration, the removal percentage of heavy metal is pH dependent. From the Figure 4, it was clear that the degree of metal ions adsorption onto activated carbon (MA) increased from 32.23 to a maximum 48.00 of Ba(II), while increased from 49.23 to a maximum 55.90 of Fe(II) when the solution pH was increased from 2 to 10. Hence the optimum pH of Ba(II) adsorption was taken as 7.95 while 7.43 of Fe(II) adsorption. The reason that activated carbon behaved differently in adsorbing of metal ions at different solution pH can be explained by considering the pH<sub>pzc</sub> of the adsorbent as well as molecular nature of metal ions. The pH<sub>pzc</sub> of activated carbon surface is 6.9, meaning that the surface of the adsorbent was positively charged at a solution pH below 6.9. This causes competition between protons and the metal ions formed cations for adsorption locations (Hamadaoui, 2006 and Almeida *et al.*, 2009) as well as the repulsion of cationic metal ions molecules, resulting in the reduction of metal ions adsorption. The lower the

pH goes below  $pH_{pzc}$  the greater the density of positive ions on the surface of activated carbon will be which in turn for less adsorption. When solution pH increases above  $pH_{pzc}$  a negative charge is present on the surface of activated carbon causing better metal ions adsorption through the electrostatic attraction phenomenon (Gholamreza *et al.*, 2010).

### 3.3. Effect of adsorbent dose

The effect of varying doses of activated carbon (MA) was investigated using 100 mg/L of initial Ba(II) and Fe(II) concentration at initial pH  $7.5 \pm 0.5$ . The removal of metal ion was found to increase with an increase in adsorbent dosage from 0.002-0.2g/L. Figure 5 shows an increase in percentage removal of Ba(II) and Fe(II) ions with the increase in dose of adsorbent up to a certain limit and then it remains almost constant. Increase in the adsorption with increasing dose of adsorbent is expected due to the increase in adsorbent surface area and the availability of more adsorption sites (Mall *et al.*, 2006).

### 3.4. Effect of mesh sizes

Adsorption rate of Ba(II) and Fe(II) for different particle sizes of activated carbon (MA) (0.09, 0.18, 0.36 and 0.85 mm) was studied keeping the other parameters as constant. The results of variation of these particle sizes on heavy metals adsorption rate are shown in Figure 6. The adsorption efficiency of activated carbon decreased from 58.09 to 52.23 % for Fe(II) while decreased from 49.01 to 35.51 % for Ba(II) as the particle size increased from 0.09 to 0.85 mm. It can be attributed to the fact that the smaller adsorbent particles have shortened diffusion path and increased total surface area and therefore the ability to penetrate all internal pore structure of the adsorbent is very high (Gupta *et al.*, 2009). It can be seen from Figure 6, that the equilibrium time is almost constant for all the selected sizes of the adsorbent. From this, it can be concluded that the equilibrium time is dependent on surface characteristics of adsorbent and adsorbate and independent on adsorbent size. As shown in Figure 6 the maximum removal percentage of ions was obtained when the pellet diameter was 0.09 mm for activated carbon, therefore, 0.09 mm pellet diameter consider the optimum diameter.

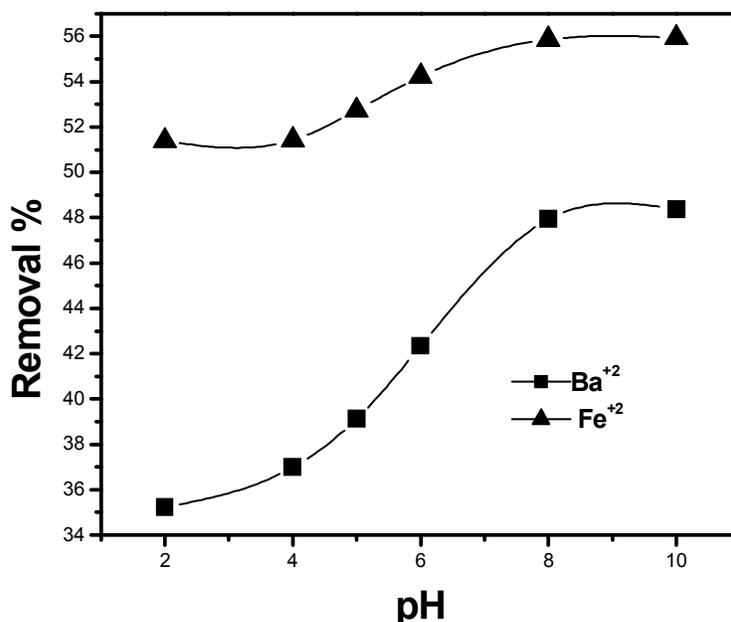


Figure 4: Effect of pH on adsorption of Ba(II) and Fe(II) by activated carbon(MA), initial concentration = 100 mg/L, 0.02 g/L adsorbent dose, contact time 30 min.

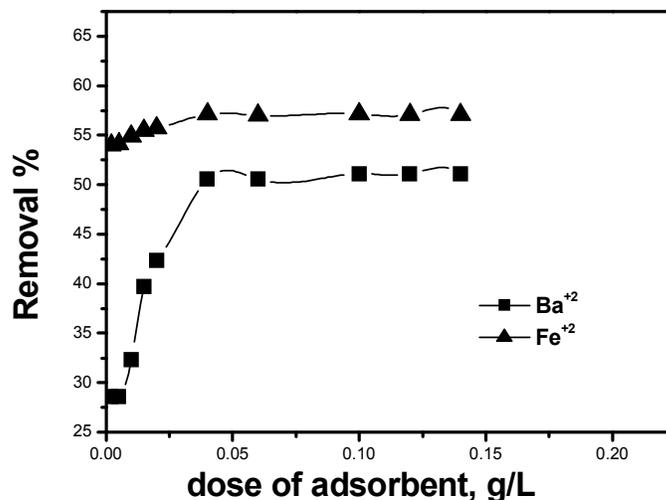


Figure 5: Effect of adsorbent dosage on adsorption of Ba(II) and Fe(II) by activated carbon(MA), initial concentration = 100 mg/L, contact time 30 min.

### 3.5. Effect of initial metal ions concentration

Adsorption characteristics indicated that percentage of metal ions removal was fairly dependent on the initial concentration of metal ions. Horsfall and Spiff (Horsfall *et al.*, 2005) reported that adsorption sites take up available metal more quickly at low concentrations. However, at high concentrations metals need to diffuse to the adsorbent surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a slower rate. The adsorption experiments were carried out with metal ions concentrations of 5, 10, 15, 20, 25, 50, 75, 100, 125 and 150 mg/L with a constant amount of adsorbent, 0.02 g/L, time 30 min and pH  $7.5 \pm 0.5$  for Ba(II) and Fe(II) ions. The experimental results of the effect of initial metal ion concentration on

removal efficiency were presented in Figure 7. As in Figure 7 is shown, Ba(II) and Fe(II) ions removal efficiency decreased with the increase in initial metal ion concentration. In case of low metal ion concentrations, the ratio of the initial number of moles of metal ions to the available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of metal ions which depends upon the initial concentration, decreases (Yu *et al.*, 2003).

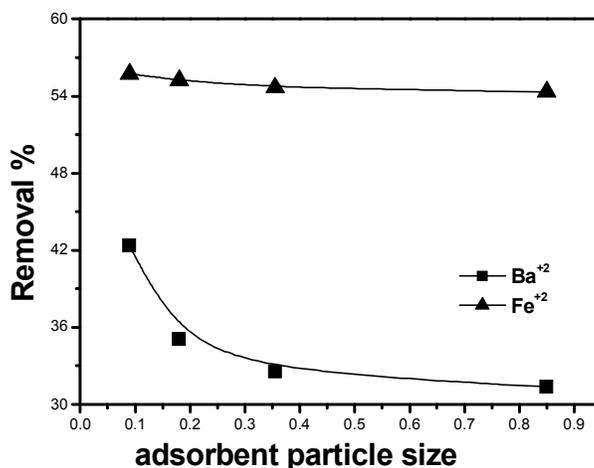


Figure 6: Effect of adsorbent particle size of adsorbent in the removal of Ba(II) and Fe(II) ions, initial concentration = 100 mg/L, 0.02 g/L adsorbent dose, contact time 30 min.

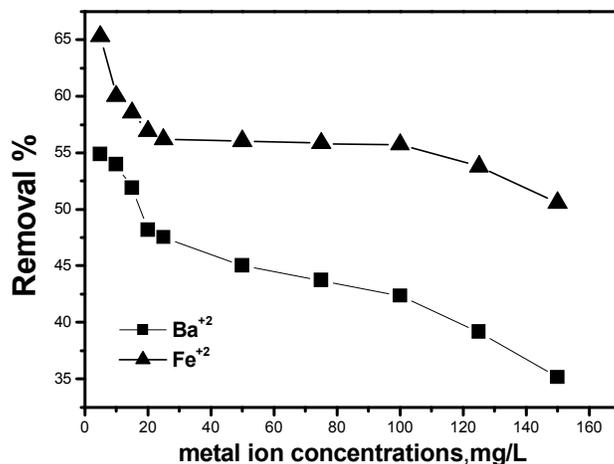


Figure 7: Effect of metal ion concentration on adsorption of Ba(II) and Fe(II) by activated carbon(MA), pH  $7.5 \pm 0.5$ , adsorbent dosage 0.02 g/L, contact time 30 min.

### 3.6. Adsorption Isotherms

Adsorption equilibrium is the set of conditions at which the number of molecules arriving on the surface of the adsorbent equals the number of molecules that are leaving. The relation between the amount of substance adsorbed by an adsorbent (solid) and the equilibrium concentration of the substance at constant temperature is called the adsorption isotherm (Thajeel, 2013). In order to show the design of a sorption system to remove barium and iron metal ions from effluents, it is important to establish the most appropriate correlation for the equilibrium curve. Two isotherm equations have been tested; Langmuir and Freundlich.

#### 3.6.1 Freundlich and Langmuir Model

Langmuir and Freundlich isotherms are commonly used to describe the equilibrium characteristic of adsorption. This experimental data were fitted to both isotherm models. Linear regressions were used to determine the best fit model and least squares has been widely used for obtaining the isotherm constant.

The Langmuir isotherm is based on assuming a monolayer sorption onto a surface with a fixed number of well defined sites; the equation is given below (Norton et al., 2004 and Langmuir, 1916):

$$C_e/q_e = 1/K_L q_m + C_e/q_m \quad (3)$$

where  $C_e$  is the equilibrium liquid-phase concentration (mg/L),  $q_e$  the equilibrium amount adsorbed (mg/g),  $q_m$  the maximum amount of sorbate per unit sorbent (adsorption capacity) to form a complete monolayer, and  $K_L$  is the Langmuir constant related to the affinity between sorbent and sorbate. The Freundlich model attempts to account for surface heterogeneity (Shahwan *et al.*, 2002) and is presented as follows:

$$\log q_e = \log k_f + 1/n \log C_e \quad (4)$$

where  $k_f$  and  $n$  are Freundlich constants that are related to the adsorption capacity and intensity, respectively.

The Langmuir and Freundlich adsorption constants evaluated from the isotherms with correlation coefficients are presented in (Table 3) which illustrates the relationship between adsorbed and aqueous concentration at equilibrium. The Langmuir and Freundlich adsorption constants are evaluated from the isotherms with correlation coefficients. The results indicate that the Freundlich isotherm model achieved best fit of barium and iron metal ions, it indicates to multilayer adsorption nature of these metal ions. The higher  $K_L$  (the energy of absorption), related to the higher affinity of the adsorbent for the metal ions.  $q_m$  can also be interpreted as the total number of binding sites that are available for adsorption and  $q_e$  as the number of binding sites that are in fact occupied by the metal ions at the concentration  $C_e$ . To get the equilibrium data, initial metal concentrations were varied while the adsorbent weight in each sample was kept constant, 30 min. of equilibrium periods for sorption experiments were used to ensure equilibrium conditions. The Freundlich model better represented the sorption process for Ba(II) and Fe(II) in comparison to the model of Langmuir due to very close experimental values of  $q_m$  with the theoretical values calculated from these models. Although correlation coefficient ( $R^2$ ) values show best fitting of both models but Freundlich is best. The linear regression of Langmuir and Freundlich are shown in Figures 8,9. The values of isotherm parameters calculated from the slope and intercept are given in Table 3. The values of  $n$  are greater than one indicating the favorable adsorption.

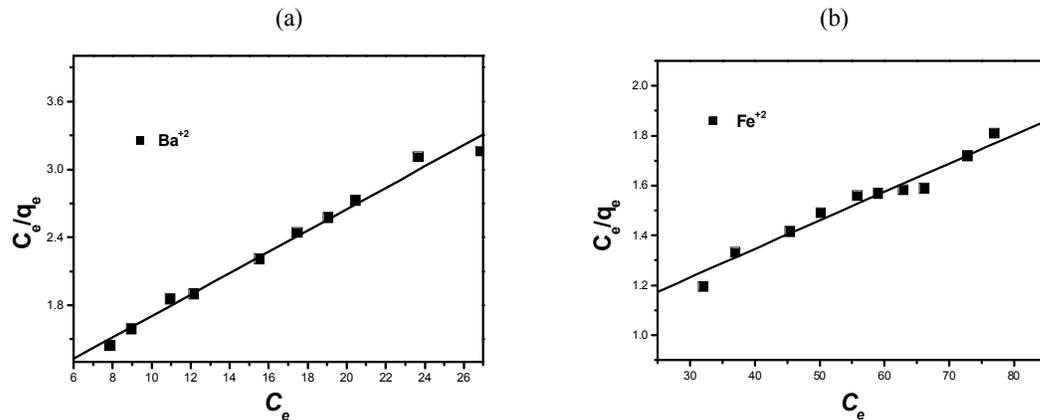


Figure 8: Langmuir Isotherm Plot for Adsorption of (a) Ba(II) and (b) Fe(II) by activated carbon (MA).

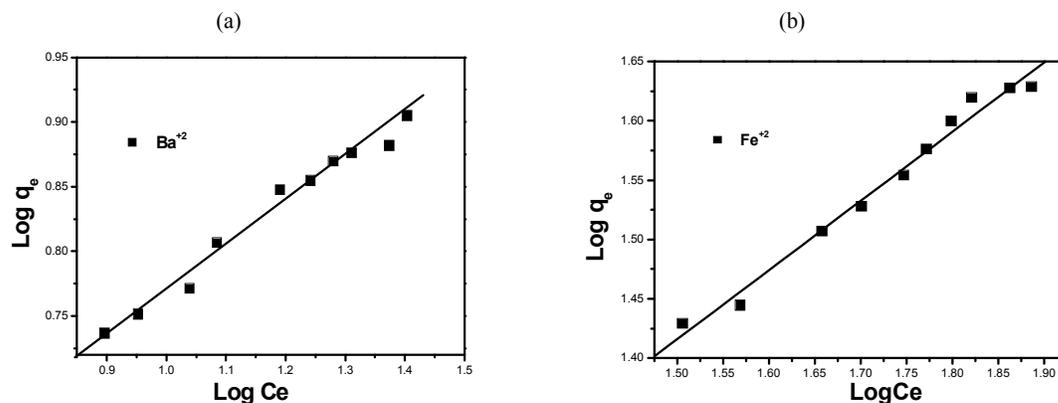


Figure 9: Freundlich Isotherm Plot for Adsorption of (a) Ba(II) and (b) Fe(II) by activated carbon (MA).

Table 3: Isotherm Parameters for Adsorption of Ba(II) and Fe(II) by Activated Carbon (MA).

Adsorbate	Langmuir constants			Freundlich constants		
	$q_m$	$K_L$	$R^2$	$n$	$\text{Log } K_f$	$R^2$
Ba(II)	10.62	0.123	0.988	3.0	0.437	0.990
Fe(II)	83.96	0.014	0.981	1.71	0.539	0.991

### 3.6.2 Separation Factor

The shape of the isotherm can be used to predict whether adsorption system is favorable or unfavorable in a batch adsorption system. Accordingly, the essential feature of Langmuir isotherm was expressed in term of dimensionless constant called the separation factor. It is defined by the following relationship.

$$SF = 1/(1+K_L C_0)$$

where  $SF$  is the a dimensionless equilibrium parameter or separation factor,  $K_L$ , the constant from Langmuir equation (adsorption coefficient ) and  $C_0$  the initial metal ion concentration. The parameter,  $SF$ , indicates the shape of the isotherm and nature of the sorption process. If  $SF > 1$  then unfavorable isotherm  $SF = 1$  then linear isotherm  $SF = 0$  then irreversible isotherm  $0 < SF < 1$  then favorable isotherm (Horsefall *et al.*,2005). The  $SF$  values of Ba(II) and Fe(II) for activated carbon adsorbent is calculated from above equation and plotted against initial metal ion concentration (Figure 10a). The

results indicates the values of  $SF$  between 0 and 1, this represents favorable isotherm.

### 3.6.3 Surface Coverage ( $\theta$ )

To account for adsorption behavior of the metal ions on the activated carbon adsorbent the Langmuir type equation related to surface coverage is used (Ashraf *et al.*, 2010). The equation is expressed as follow:

$$K_L C_0 = \theta/(1-\theta) \text{ and } \theta = K_L C_0/(1+bC_0)$$

where  $K_L$  is the adsorption coefficient,  $C_0$  the initial concentration and  $\theta$  the surface coverage.

The fraction of adsorbent surface covered by metal ion was studied by plotting the surface coverage values ( $\theta$ ) against metal ions concentration. The data is presented in Figure10b. The figure shows that, increase in initial metal ion concentration for activated carbon adsorbent increases the surface coverage on the adsorbent until the surface is nearly fully covered with a monomolecular layer. Further examination of Figure 10b reveals that the surface coverage ceases to vary significantly with

concentration of metal ions at higher levels. The results showed the order of removal of two metals under investigation is, iron ion > barium ion. This

attributed to the highest of molecular weight and ionic radius of barium compared to iron.

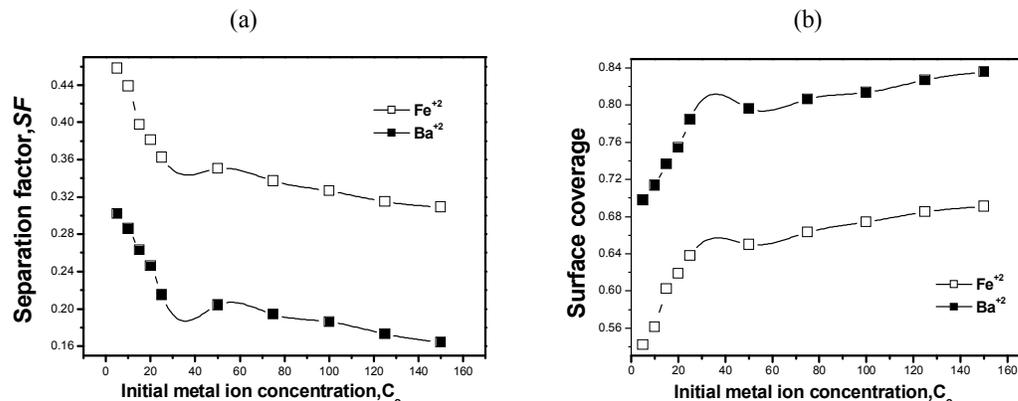


Figure 10: A plot of separation factor,  $SF$  and surface coverage,  $\theta$  against initial metal ion concentration of Ba(II) and Fe(II) for activated carbon adsorbent (MA).

#### 4. Conclusion

To find surface acidity/basicity we used Boehm's titration method and we found 0.1220 for carboxyl groups, 0.0027 for lacton, 0.0991 for phenolic, 0.0103 for basicity and 0.2137 for acidity. For metal ions we need acidity to be high and this acidity is acceptable. Also we found point zero charge for carbon active made by mazot ash by using  $KNO_3$  0.01 N solutions, the zero point charge is at pH 6.9. Hence the optimum pH of Ba(II) adsorption was taken as 7.95 while 7.43 of Fe(II) adsorption onto activated carbon. The study indicated that activated carbon produced from mazot ash could be used as an effective adsorbent material for the treatment of barium and iron in aqueous solution. The adsorption of barium and iron on activated carbon was influenced by various parameters such as initial pH, initial metal ion concentration and dose of adsorbents. Adsorption was increased with increasing dose of adsorbent and decreased with increasing initial metal ion concentration. The maximum adsorption capacity of barium and iron metal ions was calculated from Langmuir isotherm and found to be 10.62 and 83.96 mg/g, respectively. The dimensionless separation factor  $SF$  and surface coverage,  $\theta$ , showed that the activated carbon could be used for the removal of barium and iron ion from aqueous solution. The characteristic parameters for each isotherm and related correlation coefficients,  $R^2$  were determined.

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