

Mass Transfer in Adsorption Systems onto Granular Activated Carbon

Yousr E. Khater, Rehab M. Ali, Gihan F. Malash, Ahmed A. Zaatout

Abstract— Removal of copper ions Cu (II) from aqueous solutions by granular activated carbon GAC has been investigated. Batch adsorption processes were carried out to investigate the optimum operating condition of various parameters such as adsorption time, adsorbent dosage, temperature and initial copper ion concentration. The maximum adsorption amount of Cu (II) onto GAC was found to be 120 mg/g after 30 minutes at 0.05g GAC, 300 ppm initial copper concentration and temperature of 25°C. The adsorption kinetic models were studied using four models; pseudo first – order, pseudo second – order, Elovich and Intra – particle diffusion. The kinetic data were best fitted with pseudo second- order reaction model. The equilibrium data were tested using two isotherm models; Langmuir and Freundlich. The present equilibrium data were found to be best described by Freundlich isotherm model with a high correlation coefficient. This study convinced that GAC is a promising adsorbent for Cu (II) removal from aqueous solution.

Index Terms—Activated carbon, Adsorptions, Copper, Cu (II) removal, Heavy metal removal, Isotherms, Kinetics, Thermodynamics, Water treatment.

1. INTRODUCTION

Heavy metals are natural components of the Earth's crust. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain theme hoboism of the human body. However, at higher concentrations they can lead to poisoning [1,2,3].

Copper is one of the heavy metals that are toxic to humans. Copper may come from various industrial sources such as metal finishing, electroplating, mining, welding, electrical wiring, plumbing supplies (pipes, faucets, braces, and various forms of tubing), agricultural processes, gearwheel, air conditioning tubing and roofing etc. in addition to human activities [4]. Copper may lead to severe mucosal irritation, hepatic and renal damage, wide spread capillary damage and central nervous problems.

There are various methods for removing heavy metals such as chemical precipitation, membrane filtration, ion exchange and liquid extraction [5,6,7]. However, these methods are not widely used due to their high cost and low feasibility for small-scale industries [8,9]. Adsorption has been shown to be the most promising option for heavy metals removal[10].

Adsorption by activated carbon is the most widely used and effective method in industry. Activated carbon is utilized in this process due to its porous surface structure, which provides high surface area, harmlessness to the environment and ease in operation. Hence, this study aims to investigate the activated carbon efficiency of copper ion removal from wastewater. The effects of adsorbent dosage, initial metal ion concentration, temperature, and adsorption time were investigated. Thermodynamic parameters, mechanism of adsorption, kinetics and adsorption isotherm models were also calculated.

2. EXPERIMENTAL

2.1. Materials and methods

2.1.1 Metal solution (Adsorbate)

Stock solution (1000 ppm) of Cu (II) was prepared by dissolving copper sulfate pent hydrate, assay 99% produced by Chemajet chemical company in distilled water. The solution was further diluted to the required concentrations before use.

- Yousr E. M. Khater is currently pursuing Doctorate degree program in chemical engineering in Alexandria University, Egypt. E-mail: yousr.chem.au@gmail.com
- Rehab M. Ali is Assistant professor, Department of Fabrication Technology, Institute of Advanced Technology and New Materials, City of Scientific Researches and Technological Applications. E-mail: rehabmohamedali1983@gmail.com
- Gihan F. Malash and Ahmed A.Zaatout are professor in chemical engineering Alexandria University, Egypt. E-mail: gmalash@gmail.com

2.1.2 Activated carbon (Adsorbents)

Granular activated carbon GAC, from EL-Nasr pharmaceutical chemical company.

2.1.3 Batch experiment and analysis

Batch adsorption experiments were carried out by Cu (II) solutions of known concentration (100, 200, 300 and 400 ppm) were poured into flask (100 mL) containing accurately weighed amounts of the adsorbents. The GAC weight ranged from (0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 g per 100 ml of solutions). The flasks were shaken at 200 rpm using an electric shaker. Samples were withdrawn every 5 minutes until equilibrium take place. After filtration through the filter paper, remaining Cu (II) in the solutions were determined by iodometric titration.

The amount of metal ion adsorbed was calculated as follows:

$$\% \text{Adsorption} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of the adsorbate, respectively.

3. RESULTS AND DISCUSSION

3.1. Investigation of adsorption parameters

3.1.1. Effect of adsorption time

Figure 1. shows the effect of contact time on removal of Cu (II). Experimental studies were carried out with varying initial metal ion concentrations of Cu (II) ranging from 100-400 ppm using 0.05 g/100 ml Cu (II) solution. The figure shows that the adsorption of the heavy metal ions was increased by increasing the adsorption time. The rate of adsorption indicates that, the granular activated carbon adsorption process for Cu (II) takes place on the solid-liquid surface as the rapid adsorption on the surface at the initial stage followed by the slow adsorption in which metal cations in aqueous solution migrate and diffuse to the internal pores and channels of the GAC. With the adsorption time increased than 30 min, the removal rate of metal cations did not change significantly, indicating that adsorption was on dynamic equilibrium [11].

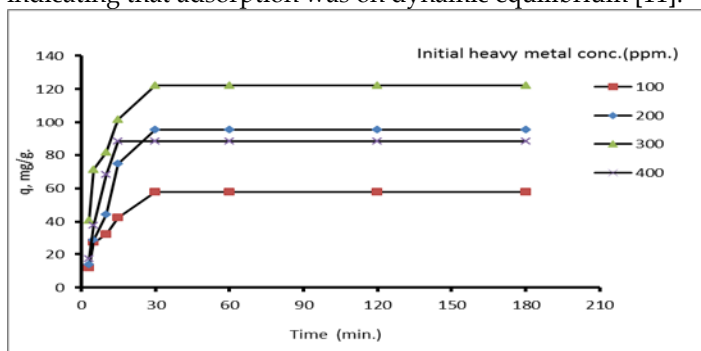


Fig. 1. Effect of time on Cu (II) adsorption. Temp. 25°C, amount of GAC. 0.05 g/100 ml Cu (II) solution, shaking speed.300 rpm.

3.1.2. Effect of adsorbent dosage

The effect of adsorbent dosage was studied at constant temperature and stirring rate 25 °C and 300 rpm and different initial Cu (II) concentrations from 100 to 400 ppm for 30 min. Figure 2. shows that, the amount of Cu (II) adsorbed (mg g^{-1}) was found to decrease with increasing adsorbent dosage. The adsorption capacity (mg g^{-1}) decrease with adsorbent dosage increase may be due to the high number of unsaturated adsorption sites. Hence, 0.05 g GAC/ 100 ml Cu (II) solution is the optimum dosage of GAC.

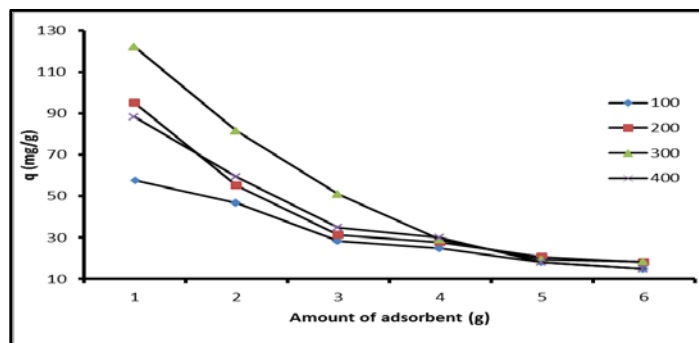


Fig. 2. Effect of adsorbent dosage on Cu (II) adsorption. Temp. 25°C, time. 30 min, shaking speed. 300rpm.

3.1.3. Effect of temperature

A decrease in the Cu (II) adsorption percentage is occurred by rising temperature, as shown in figure 3. This decrease may be due to the increasing tendency of Cu (II) to desorb from the interface to the solution. This result also indicated that the adsorption process of Cu (II) onto GAC was exothermic in nature [12]. The effective temperature in adsorption is 25°C. These results agree with Ahmet Sari [13].

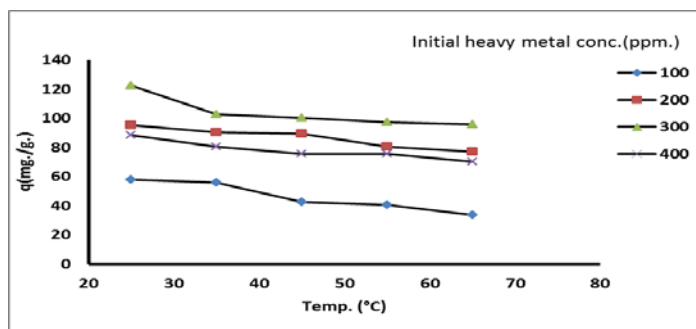


Fig. 3. Effect of temperature on Cu (II) adsorption. Amount of GAC 0.05 g/100 ml Cu (II) solution, time 30 min, shaking speed 300 rpm.

3.1.4. Effect of initial copper concentration

The effect of initial concentration on the Cu (II) removal, at concentration levels ranging from 100 to 400 ppm is shown in Figure 4. Batch experiments have been carried out with varying amount of GAC from 0.05 to 0.5g. The figure shows that the adsorption of the Cu (II) has been increased by increasing the Cu (II) initial concentration till 300 ppm, then it decreased. Hence, 300 ppm can be considered as the optimum Cu (II) initial concentration. Figure 4. also insured that 0.05 g GAC/ 100 ml Cu (II) solution is the optimum amount of GAC.

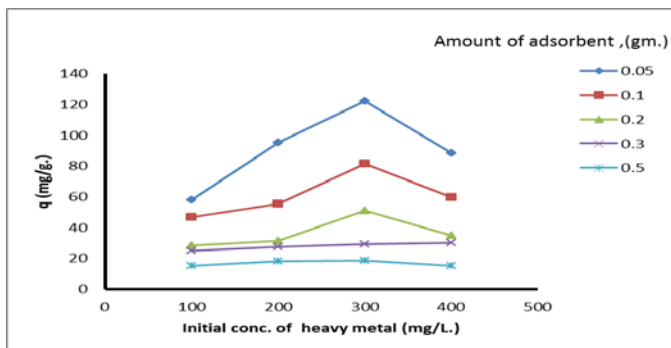


Fig. 4. Effect of Cu (II) initial concentration on Cu (II) adsorption. Temp. 25°C, time 30 min, shaking speed 300 rpm.

3.2. Adsorption kinetic study

The models of adsorption kinetics were correlated with the solution uptake rate; hence these models are important in water treatment process design for representing adsorption of heavy metals on GAC [14,15]. In order to elucidate the adsorption mechanism and potential rate controlling step, four kinds of kinetic models were used to test the experimental data. These are intraparticle diffusion models, Elovich equation, Lagergren first order equation and second order equation.

3.2.1. Lagergren- first order equation

The Lagergren first order is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

where q_e and q_t are the amount of metal sorbed per unit weight of sorbent at equilibrium and at any time t , respectively (mg g^{-1}) and k_1 is the rate constant of Lagergren first order sorption (min^{-1}). After integration and applying boundary conditions, for $t=0, q = 0$, the integrated form of equation (2) becomes equation (3)

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

Values of k_1 were calculated from the plots of $\log(q_e - q_t)$ versus t for different concentrations of the Cu (II) figure 5. The values of k_1 and q_e are given in Table (1).

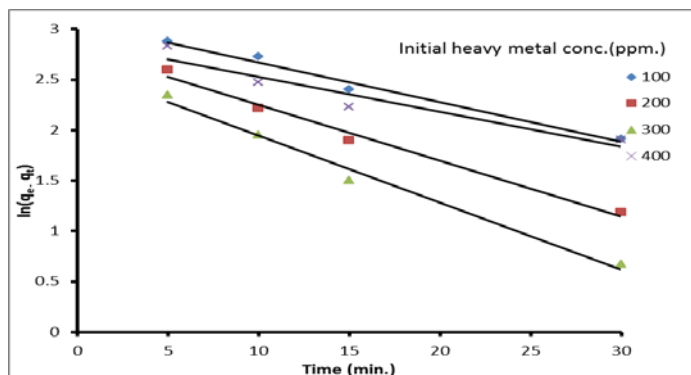


Fig. 5. Lagergren- first order sorption kinetics of Cu (II) on GAC at different concentrations.

3.2.2. Pseudo-second-order equation

The pseudo-second-order equation can be expressed as:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{4}$$

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (4) becomes the following:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

Where k_2 is the pseudo-second-order rate constant (g/mg min); q_t is the amount of adsorption (mg/g) at time t (min); q_e is the amount of adsorption equilibrium (mg/g) [16].

A plot of t/q_t versus t figure 6 should yield a linear relationship with a slope of $(1/q_e)$ and an intercept of $(1/k_2 q_e)$. The constants are listed in Table (1).

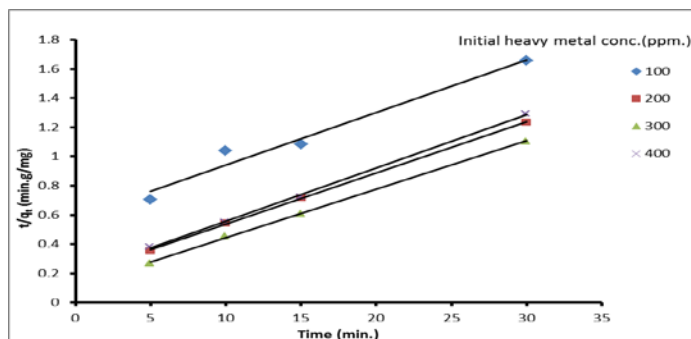


Fig. 6. Pseudo-second-order sorption kinetics of Cu (II) on GAC at different concentrations.

3.2.3. The Elovich equation

The Elovich model equation is generally expressed as:

$$\frac{dq}{dt} = \alpha \exp(-\beta q_t) \tag{6}$$

Where α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is the desorption constant (gmg^{-1}) during any one experiment.

To simplify the Elovich equation, $\alpha\beta \gg t$ is assumed and by applying the boundary conditions $qt = 0$ at $t = 0$ and $qt = q_t$ at $t = t$ equation becomes:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{7}$$

A plot of qt versus $\ln(t)$ figure 7 should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$. The constants are listed in Table (1).

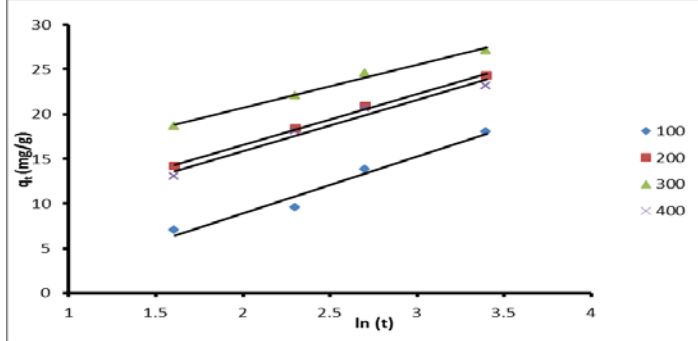


Fig. 7. Relation plots of qt and $\ln t$ for adsorption of Cu (II) by GAC. Temp 25°C, 0.5 g GAC/100 ml Cu (II) solution at different initial Cu (II) concentrations.

3.2.4. Intraparticle diffusion model

The intraparticle diffusion model can be expressed by the following equation:

$$q_t = k_i t^{1/2} + C \tag{8}$$

Where k_i is the intraparticle diffusion rate constant ($\text{mmol g}^{-1} \text{min}^{-1/2}$), C is the intercept. A plot of qt versus $t^{1/2}$ figure 8 should yield a linear relationship with a slope of k_i . The constants are listed in Table (1).

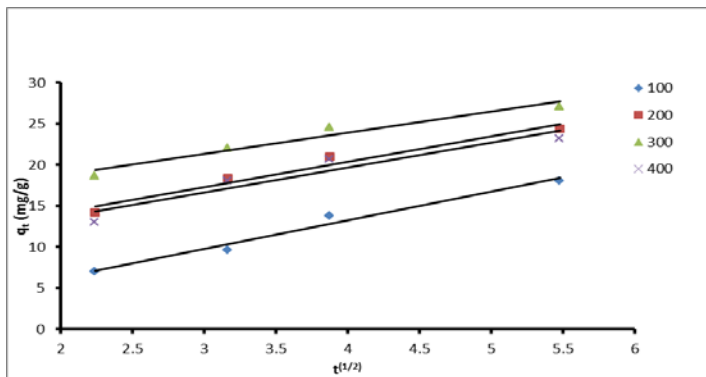


Fig. 8. Relation of qt and $t^{1/2}$ for Cu (II) adsorption by GAC. Temp 25°C, 0.5 g GAC/100 ml Cu (II) solution at 300 ppm initial Cu (II) concentrations.

TABLE 1

CONSTANTS AND CORRELATION COEFFICIENT OF PSEUDO FIRST ORDER, PSEUDO SECOND ORDER, INTRA-PARTICLE DIFFUSION, AND ELOVICH MODELS OF Cu (II) ADSORPTION ON GAC

Initial concentration (ppm)	$q_e(\text{exp})$ (mg/g)	Pseudo first order			Pseudo second order			Intra-particle diffusion		Elovich
		$q_e(\text{cal})$ (mg/g)	K_1 (min ⁻¹)	R^2	$q_e(\text{cal})$ (mg/g)	K_2 (g/mg.min)	R^2	K_{int} (mg/g min) ^{0.5}	R^2	R^2
100	24.82	14.5866	-0.0393	0.9829	27.7778	13.235044	0.9697	3.638	0.982	0.975
200	27.58	10.2009	-0.0551	0.9873	28.5714	12.609601	0.9996	3.551	0.948	0.997
300	29.08	7.47183	-0.0664	0.9877	30.1205	9.296401	0.9995	3.049	0.904	0.976
400	29.88	14.1827	-0.0345	0.9106	27.3224	9.4537801	0.9993	3.0747	0.897	0.977

From the table, various kinetic models were studied to describe the Cu (II) adsorption process kinetics onto GAC. It can be concluded that the adsorption of Cu (II) on GAC follows pseudo second order model. This model assumes that, the rate-controlling step may be chemical adsorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate [17,18].

3.3. Adsorption isotherm models

Two important isotherm models were selected in this study, which are; Langmuir and Freundlich isotherm models [19, 20]. Langmuir and Freundlich isotherm models are applied to establish the relationship between the amounts of Cu (II) adsorbed onto GAC and its equilibrium concentration in aqueous solution as shown in table (2).

TABLE 2

ISOTHERM AND THEIR LINEAR FORMS.

Isotherm	Linear form	Plot
Freundlich	$q_e = K_f C_e^{1/n}$	$\log(q_e) \text{ vs. } \log(C_e)$
Langmuir-1	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} \text{ vs. } C_e$
Langmuir-2		$\frac{1}{q_e} = \left(\frac{1}{K_L q_m} \right) \frac{1}{C_e} + \frac{1}{q_m}$
Langmuir-3		$q_e = q_m - \left(\frac{1}{K_L} \right) \frac{q_e}{C_e}$
Langmuir-4		$\frac{q_e}{C_e} = K_L q_m - K_L q_e$
Redlich-Peterson	$q_e = \frac{AC_e}{1 + BC_e}$	$\ln \left(\frac{C_e}{A - C_e} - 1 \right) = g \ln(C_e) + \ln(B)$

3.3.1. Langmuir adsorption isotherm

Langmuir adsorption isotherm is applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites and is represented in four linear forms:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m} \tag{9}$$

$$\frac{1}{q_e} = \left(\frac{1}{K_a q_m} \right) \frac{1}{C_e} + \frac{1}{q_m} \tag{10}$$

$$q_e = q_m - \left(\frac{1}{K_a} \right) \frac{q_e}{C_e} \tag{11}$$

$$\frac{q_e}{C_e} = K_a q_m - K_a q_e \tag{12}$$

Where C_e is equilibrium concentration of the metal (mg/L), q_e is the amount of the metal adsorbed (mg) by per unit of the adsorbent (g). q_m and K_L are Langmuir constant relating adsorption capacity (mg/g) and the energy of adsorption (L/g), respectively and listed in Table (3).

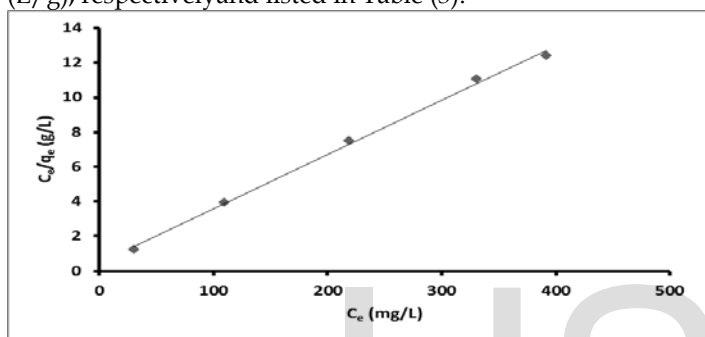


Fig. 9. Langmuir-1 isotherm plot for the adsorption of Cu (II) onto GAC. Adsorbent dosage 0.3 g, temperature 25°C.

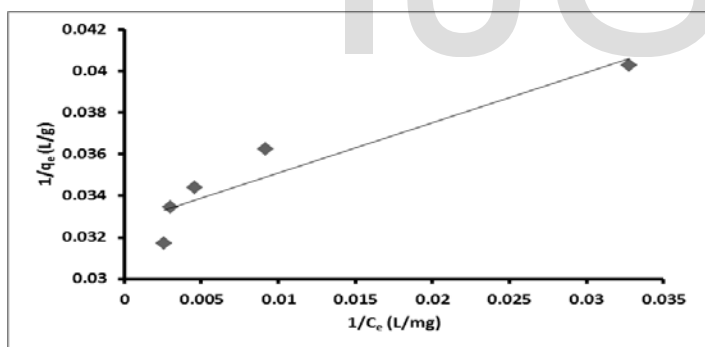


Fig. 10. Langmuir-2 isotherm plot for the adsorption of Cu (II) onto GAC. Adsorbent dosage: 0.3 g, temperature 25°C.

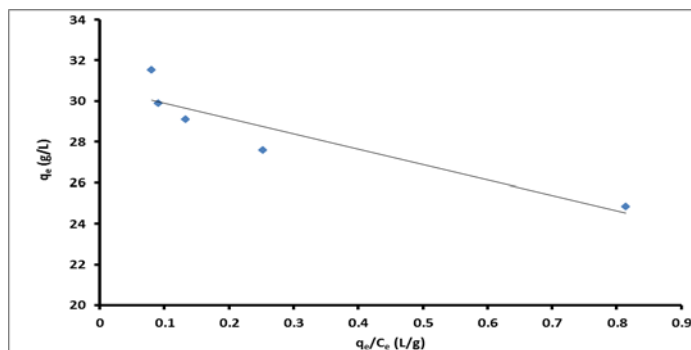


Fig. 11. Langmuir-3 isotherm plot for the adsorption of Cu (II) onto GAC. Adsorbent dosage: 0.3 g, initial Cu (II) concentration 300 ppm, temperature 25°C.

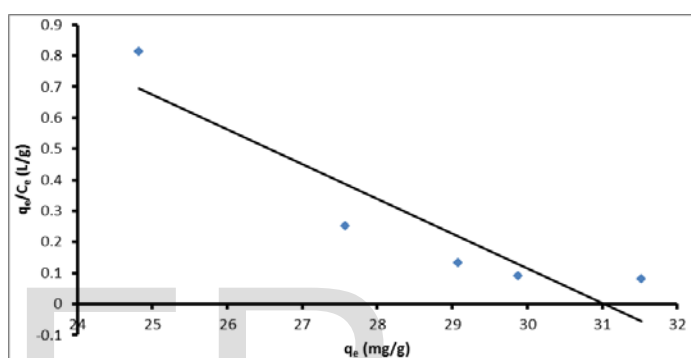


Fig. 12. Langmuir-4 isotherm plot for the adsorption of Cu (II) onto GAC. Adsorbent dosage: 0.3 g, temperature 25°C.

TABLE 3

ISOTHERM PARAMETERS OBTAINED USING THE LINEAR METHOD.

Isotherm	q_e (mg/g)	q_m (mg/g)	K_a (L/g)	R^2
Langmuir-1	30.23707	31.908	68.545	0.887
Langmuir-2	30.23707	30.57169	0.13566	0.887
Langmuir-3	30.23707	30.64	0.1326	0.8848
Langmuir-4	30.23707	31.016	0.112	0.8448

3.3.2. Freundlich adsorption isotherm

Freundlich adsorption isotherm, which is the earliest relationship known describing the adsorption equilibrium [21]. The Freundlich isotherm model is based on heterogeneous surface suggesting that binding sites are not equivalent and independent. Freundlich adsorption isotherm is expressed in linear form by the following equation:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{13}$$

where K_F (mg/g) and n are Freundlich constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption. These

constants are determined from the intercept and slope of linear plot of $\log q_e$ versus $\log C_e$ and listed in table (4)

After studying Langmuir and Freundlich isotherm plots, the models showed that the adsorption of Cu (II) on GAC obeys Freundlich isotherm. This suggests the heterogeneous nature of adsorption surface on GAC [22]

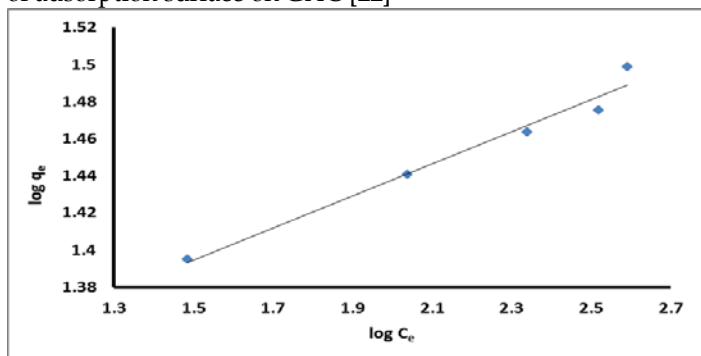


Fig. 13. Freundlich isotherm plot for the adsorption of Cu (II) onto GAC. Adsorbent dosage 0.3 g, temperature: 25 °C.

TABLE 4

ISOTHERM PARAMETERS OBTAINED USING FREUNDLICH METHOD

Isotherms	1/n	$K_f(L/g)$	R^2
Freundlich	0.08633	18.281	0.9741

1. 4. CONCLUSION

This study demonstrated that the GAC could be used as an effective adsorbent for the treatment of wastewater containing Cu (II). The adsorption process is dependent on several factors such as initial metal concentration, contact time, adsorbent dosage and temperature. The isotherm study indicates that adsorption data correlated well with Freundlich isotherm models. The kinetic data obeyed pseudo-second-order kinetic model better than the pseudo-first-order kinetic model.

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