



## Removal of copper (II) from aqueous solutions by adsorption onto granular activated carbon in the presence of competitor ions

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### ABSTRACT

In this work, the removal of copper from an aqueous solution by granular activated carbon (GAC) in the presence of competitor ions was studied. A batch adsorption was carried out and different parameters such as pH, contact time, initial copper concentration and competitor ions concentration were changed to determine the optimum conditions for adsorption. The optimum pH required for maximum adsorption was found to be 4.5 for copper. Equilibrium was evaluated at 144 h at room temperature. The removal efficiency of Cu(II) was 71.12% at this time. The kinetics of copper adsorption on activated carbon followed the pseudo second-order model. The experimental equilibrium sorption data were tested using the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D-R) equations and the Langmuir model was found to be well fitted for copper adsorption onto GAC. The maximum adsorption capacity of the adsorbent for Cu(II) was calculated from the Langmuir isotherm and found to be 7.03 mg/g. Subsequently, the removal of copper by granular activated carbon in the presence of Ag<sup>1+</sup> and Mn<sup>2+</sup> as competitor ions was investigated. The removal efficiency of Cu(II) ions without the presence of the competitor ions was 46% at 6 h, while the removal efficiency of Cu(II) ions in the presence of competitor ions, Ag<sup>1+</sup> and Mn<sup>2+</sup>, was 34.76% and 31.73%, respectively.

### 1. Introduction

The contamination of water by toxic heavy metals is a worldwide environmental problem. For this reason, the discharge of industrial wastewaters contaminated with heavy metals into waterways or sewage systems is stringently regulated to reduce the environmental impact [1]. Heavy metals are toxic pollutants that are released into the environment from many industries such as petrochemical, leather, paint, metallurgical, battery and car radiator manufacturing, metal plating, and textile industries as well as from agricultural sources and mining operations [1-8]. Metals such as lead, cadmium, copper, arsenic, nickel, chromium, zinc and mercury have been recognized as hazardous heavy metals [9]. These metals tend to accumulate in ecological systems causing serious

soil and water pollution which can also be harmful to humans, animals, and plants, even in low concentrations [10]. Unlike biodegradable organic matter, metal ions are not eliminated from natural aqueous ecosystems by natural processes. As a result, scientists strive to develop novel methods to remove metal ions from water [11]. The presence of hazardous metals in water streams and marine water cause a significant health threat to the aquatic community, most commonly its damage to the gills of the fish [9]. Consequently, many countries have introduced stricter legislation to control water pollution. In addition, various regulatory bodies have set maximum prescribed limits for the discharge of toxic heavy metals into aquatic systems. However, metal ions are still being added to the water stream at a much higher concentration than the prescribed limits via industrial activities, thus leading to

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health hazards and environmental degradation [9]. The World Health Organization recommends a maximum acceptable concentration of Cu(II) in drinking water of less than 1.5mg/L [12]. Copper exists mainly as a divalent cation in aqueous solutions [13]. Copper is an essential metal for human metabolism because it acts as a cofactor for several cellular enzymes such as catalase (amineoxidase), cytochrome oxidase, dopamine b-hydroxylase, and peroxidase (galactose oxidase) [14]. In addition to being carcinogenic, high concentrations of Cu can be harmful or fatal to humans as well. Thus, it has been classified as one of the priority pollutants by the US EPA [15]. An excessive intake of copper by humans leads to nausea, vomiting, severe mucosal irritation, widespread capillary damage, hepatic and renal damage, headache, diarrhea, and central nervous problems followed by depression and gastrointestinal irritation [16-19]. Several methods have been proposed for the removal of copper ions from water and wastewaters including chemical precipitation, ion exchange, membrane filtration, electrolysis and adsorption [20, 21]. Each method has its limitations because of their cost, complexity, and efficiency as well as the secondary wastes they produce. For example, the electrolysis processes often have higher operational costs and chemical precipitation may generate secondary wastes [22]. In the case of membrane filtration, which is often guided by the pores in the membrane structure, it is inefficient in meeting the requirement of low metal concentration; another disadvantage is its high cost [21]. Adsorption is a highly effective and economical method to remove heavy metal ions from aqueous solutions [23] because of its high efficiency, easy handling, and the availability of different adsorbents [11]. Up to now, various materials like silica gels, activated alumina, oxides and hydroxides of metals, zeolite, clay minerals, sawdust, fly ash, kaolinite, bentonite, peanut hulls, polymeric materials, and activated carbons, etc. have been used as adsorbents [2, 16, 24-27]. Activated carbon is the most widely employed adsorbent used to remove various classes of compounds from contaminated streams [28]. It is mainly composed of carbonaceous material with various microporous structures. Its industrial usage can be found in the treatment process for flue gas, volatile solvents, etc. In the treatment of wastewater, it is used for purification, decolorization, and the removal of toxic organics and heavy metal ions [29]. Due to its porosity, large surface area, high adsorption capacity and surface reactivity [30], metals such as Cu(II) [12], Hg(II) [31], Pb(II) [32], Cd(II) [33], Ni(II) [34], Zn(II) [35], Cr(VI) [36], Co(II) [3], Mn(II) [37], and As(III) [38] can be removed using activated carbon. Commercial activated carbons are prepared from a variety of carbonaceous raw materials [39]. The qualities and characteristics of activated carbons depend on the physical and chemical properties of the starting materials and the activation methods used. Presently, lignite, peat, wood,

and coconut shell are the main common precursors for commercial activated carbons [39, 40]. The purpose of this paper was to study the removal of copper from aqueous solutions by granular activated carbon in the presence of competitor ions, and then compare it with the removal of copper without competitor ions. The effect of the solution pH, contact time and initial adsorbate concentration on the removal of Cu(II) was studied. The thermodynamic parameters for the adsorption of Cu(II) were also computed and discussed. The kinetics and factors controlling the adsorption process were also studied. Finally, the removal of copper ions in the presence of Ag(I) and Mn(II) ions were investigated.

## 2. Materials and methods

### 2.1. Materials and Batch adsorption experiments

The granular activated carbon obtained from the Merk Company was used as the adsorbent. The granular activated carbon (GAC) was used directly without any treatment. The mean diameter of the GAC particles was 1.5 mm. In Table 1, the physical characteristics of the granular activated carbon are presented. Stock solutions of  $\text{Cu}^{2+}$ ,  $\text{Ag}^{1+}$  and  $\text{Mn}^{2+}$  were prepared by dissolving given amounts of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{AgNO}_3$  and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , respectively, in distilled water. The solutions of different concentrations used in various experiments were obtained by diluting the stock solutions. All reagents used were of analytical reagent grade and purchased from Merck. Several experiments were done to identify the optimum values of pH and contact time. The experiment to remove copper ions from the aqueous solution was performed under optimal conditions in the presence of competitor ions. The pH values were adjusted at 2.5, 3.5, and 4.5 using a 1 M HCl solution; the initial pH of the copper solution was 4.5. The solution pH was adjusted using a 1 M HCl solution before adding the adsorbent to the batch. At the optimum pH, other experiments were done. Samples were collected at 0.25, 0.5, 1, 2, 4, 6, 12, 24, 48, 72, 96, 120, 144 and 168 h to determine the optimum value of time. Isotherm studies were carried out at 100, 250, 500, 750 and 1000 mg/L as initial  $\text{Cu}^{2+}$  concentration at optimum pH and equilibrium time. The experiments were carried out using a 100 mL conical flask filled with 50 mL of test solution. All adsorption experiments were carried out at room temperature (about 30 °C). The contents of the flasks were filtrated through filter paper. After adding 25%wt ammonia solution to the filtrate solution as the indicator, the copper residual concentration was measured at 615 nm using a UV/vis spectrophotometer (JENWAY 7315). A previously established linear Beer–Lambert relationship was used for the concentration determination. For each test run, the average of three replicates was reported. The equilibrium adsorption capacity ( $q_e$ , mg/g) and percentage removal (Re %) for copper were determined using

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

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

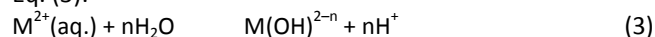
where  $C_0$  is the initial copper concentration (mg/L),  $C_e$  is the concentrations of copper at the equilibrium time (mg/L),  $m$  is the mass of adsorbent (g), and  $V$  is the volume of copper solution (L).

**Table 1.** Physical properties of adsorbent of granular activated carbon (GAC)

Provider	TFC Company of Korea
BET surface area (m <sup>2</sup> /g)	1261
Average pore diameter (mm)	1.5
Total pore volume (cm <sup>3</sup> /g)	0.610
Total volume of micropores (cm <sup>3</sup> /g)	0.473

## 2.2. Effect of pH

One of the most important parameters controlling the uptake of metal ions from an aqueous solution is pH. The pH determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. The pH of the solution controls the electrostatic interactions between the adsorbent and the adsorbate. It is known that the percent removal of heavy metal ions generally increases with pH. At low pH, the cations compete with the  $H^+$  ions in the solution for the sorption sites and therefore adsorption declines. In contrast, as the pH increases, the competition between proton and metal cation decreases which means that there are more negative groups available for the binding of metal ions and this results in greater metal uptake. On the other hand, at a higher pH, metal cations start to form hydroxide complexes or precipitate as their hydroxides, which decrease the adsorption of metal ions. In aqueous solutions, metal cations hydrolyze according to the generalized expression for divalent metals as presented in Eq. (3):



The distribution of various hydroxyl-metal complexes depends on the pH of the solution and the corresponding stability constants. Hydroxyl-metal complexes are known to adsorb with a higher affinity than the completely hydrated metals [10].

## 2.3. Adsorption kinetic studies

To evaluate the adsorption kinetics to  $Cu^{2+}$  ions, two different kinetic models were applied to the experimental data: the pseudo first-order model and pseudo second-order model. The pseudo first-order kinetic model is as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

where  $k_1$  (1/min) is the rate constant of the pseudo first-order sorption and  $q_t$  (mg/g) denotes the amount of sorption at time  $t$  (min).

After definite integration by the application of the conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$ , Eq. (3) becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (4)$$

The values of  $k_1$  and  $q_e$  can be obtained from the slopes and intercepts of  $\log(q_e - q_t)$  against the  $t$  plots [27,30].

The pseudo second-order equation can be written as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where  $k_2$  (g/mg min) is the rate constant. The integration of Eq. (5) and the application of the conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$  give

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2t \quad (6)$$

The following equation can be obtained by rearranging Eq. (6) into a linear form

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \quad (7)$$

The values of  $q_e$  and  $k_2$  can be gained from the slopes and the intercepts of the  $t/q_t$  versus  $t$  plots [27, 33, 41].

## 2.4. Adsorption isotherms

Adsorption isotherms are an important part of this study, as they can provide information about adsorption capacity as well as the surface properties and affinity of the adsorbent, thus providing a better understanding of how an adsorption system can be improved. In order to investigate the adsorption isotherm, four equilibrium models were analyzed. These included the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms.

### 2.4.1. Langmuir isotherm

The Langmuir isotherm assumes that adsorption occurs at specific homogeneous sites within the adsorbent without any interactions between the adsorbed substances. The Langmuir isotherm model is given by Eq. (8):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (8)$$

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (9)$$

where  $q_m$  (mg/g) is the maximum adsorption capacity and  $K_L$  (L/mg) is the Langmuir constant which is related to the adsorption energy [10,26,42].

The shape of the isotherm may be considered to predict if an adsorption system is favorable or unfavorable. The

essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor or an equilibrium parameter  $R$ , which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_e} \quad (10)$$

According to the value of  $R$ , the isotherm shape may be interpreted as follows:

- $R > 1$ : Unfavorable adsorption.
- $R = 1$ : Linear adsorption.
- $0 < R < 1$ : Favorable adsorption.
- $R = 0$ : Irreversible adsorption [43,44].

#### 2.4.2. Freundlich isotherm

The Freundlich model is empirical in nature and assumes that the uptake of ions occurs on a heterogeneous surface. The Freundlich isotherm model is given by Eq. (11):

$$q_e = K_F C_e^n \quad (11)$$

Eq. (11) can be linearized in logarithmic form and Freundlich constants can be determined.

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \quad (12)$$

where  $K_F$  is the intercept and  $n$  is the slope, which are the Freundlich constants representing the adsorption capacity and the adsorption intensity, respectively. In general, the greater the value of  $K_F$ , the greater the heterogeneity and the larger the value of  $n$  ( $n > 1$ ) and the more spontaneous the adsorption process is [10, 42].

#### 2.4.3. Temkin isotherm

Temkin considered the effects of some indirect adsorbent-adsorbate interaction on adsorption isotherms and suggested that the heat of adsorption of all the molecules in the layer would linearly decrease with coverage because of these interactions. The Temkin isotherm has been applied in the following form:

$$q_e = B \text{Ln } K_T + B \text{Ln } C_e \quad (13)$$

where,  $B = RT/b$ ,  $T$  (K) is the absolute temperature;  $R$  is the universal gas constant (8.314 J/mol K);  $K_T$  (L/mg) is the equilibrium binding constant that corresponds to the maximum binding energy; and  $b$  is the variation of adsorption energy (J/mol). The Temkin constants can be derived from the plot of  $q_e$  versus  $\text{Ln } C_e$  [26, 45].

#### 2.4.4. Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich (D-R) isotherm does not assume a homogeneous surface or constant adsorption potential. The linear form of the D–R isotherm model can be represented by the following equation:

$$\text{Ln } q_e = \text{Ln } q_m - \beta \epsilon^2 \quad (14)$$

where  $q_m$  (mg/g) is the maximum adsorption capacity,  $\beta$  ( $\text{mol}^2/\text{J}^2$ ) is a constant related to the mean free energy of

adsorption per mole of the metal, and  $\epsilon$  (J/mol) is the Polanyi potential, which is described in Eq. (15):

$$\epsilon = RT \text{Ln} \left( 1 + \frac{1}{C_e} \right) \quad (15)$$

where  $R$  (J/mol K) is the gas constant and  $T$  (K) is the absolute temperature. By plotting  $\text{Ln } q_e$  versus  $\epsilon^2$ , it is possible to generate the value of  $q_m$  (mg/g) from the intercept and the value of  $\beta$  from the slope. The mean free energy  $E$  (kJ/mol) describes free energy change when one mole of ion is transferred from the solution to the surface of the sorbent. The mean free energy  $E$  (kJ/mol) can be calculated from the following equation:

$$E = \frac{1}{2\beta} \quad (16)$$

In the D–R parameter, the mean free energy  $E$  (kJ/mol) gives an idea about the type of adsorption mechanism as to whether it is a chemical ion-exchange or physical adsorption. A magnitude of  $E$  between 8 and 16 kJ/mol corresponds to a chemical ion-exchange process. If  $E$  is less than 8 kJ/mol, the adsorption is physical in nature [10, 46].

### 3. Results and discussion

#### 3.1. pH

The solution pH plays a crucial role in affecting Cu adsorption. Figure 1 shows the results of the pH dependence of the adsorption. An increase of Cu adsorption was observed when the pH increased from 2.5 to 4.5. The reason for this increase has been explained in section 2.2. The maximum amount of Cu adsorption (46.08%) was observed at a pH = 4.5 which was the same as the initial pH of the copper solution. When NaOH solution was added to the copper solution in order to increase the pH to more than 4.5,  $\text{Cu}(\text{OH})_2$  precipitation was formed. Therefore, at a pH > 4.5, the adsorption of Cu ions was not only the result of adsorption.

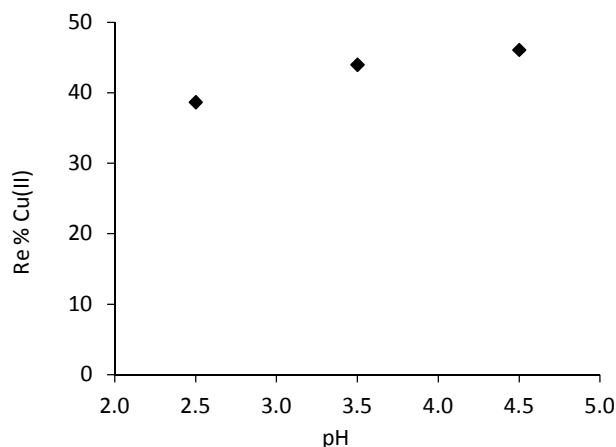
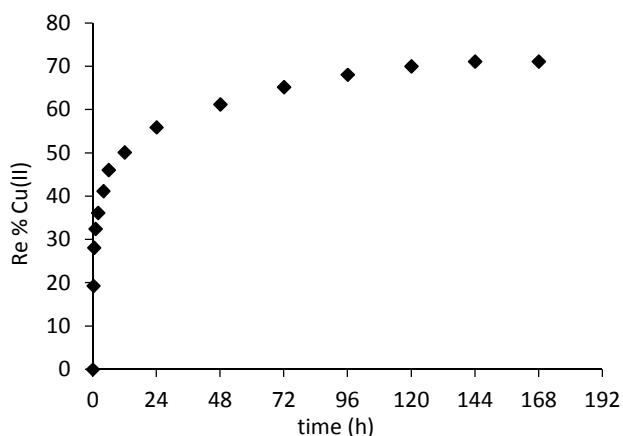


Fig. 1. Effect of pH on the removal of copper by GAC (initial Cu(II) concentration 1000 mg/L; adsorbent dose 100 g/L; contact time 6 h; temperature 30 °C).

### 3.2. Adsorption affected by contacting time

Figure 2 shows the extent of  $\text{Cu}^{2+}$  adsorption affected by contacting time. As shown, the uptake of  $\text{Cu}^{2+}$  by GAC was very rapid within the first 6 h. After 6 h, the uptake of Cu progressively decreased with time. Equilibrium was established at 144 h. It is interesting to note that there were two periods observed in the kinetic data: a fast adsorption and a progressive adsorption achieving equilibrium thereafter. In the fast adsorption stage, around 46% Cu removal occurred. The practical implication of the fast adsorption phenomenon can facilitate the design of the treatment process with energy saving expenditure by shortening the contacting time. The fast increase of  $\text{Cu}^{2+}$  adsorption rate at the beginning of the process was possibly due to a high availability of active surface sites on GAC surfaces. Since the readily available sites were mostly occupied, the subsequent slow adsorption is normally considered as being influenced by diffusion into the interior pore spaces of GAC.



**Fig. 2.** Effect of contact time on the removal of copper by GAC (initial Cu(II) concentration 1000 mg/L; adsorbent dose 100 g/L; pH 4.5; temperature 30 °C).

#### 3.2.1 Kinetic

The results showed that the correlation coefficient for the pseudo second-order kinetic model was more than 0.99. Therefore, the pseudo second-order kinetic model was selected to be the best-fit model and only the results from the pseudo second-order kinetics studies are presented (Table 2 and Figure 3). For the pseudo second-order kinetic model, the experimental  $q_{e(\text{exp})}$  corresponded to the calculated  $q_{e(\text{cal})}$  value. Furthermore, the linear regression value ( $R^2$ ) was higher than 0.99 which indicated that the kinetic of sorption can be well described by the pseudo second-order equation.

### 3.3. Effect of initial copper concentration

The experimental results for the removal of copper ions on the GAC adsorbent in the  $\text{Cu}^{2+}$  concentration range of 100–1000 mg/L at the optimum initial pH is shown in Figure 4.

The results showed that in the removal of copper by GAC, the sorption capacity  $q_e$  initially rose sharply. This indicated that specific adsorption sites were available for adsorbent sites of the metal ions. At higher initial metal concentrations, the adsorbent became saturated and no more sites were available for further sorption. The maximum sorption capacity of copper ( $q_{m,\text{exp}}$ ) by activated carbon was 7.11 mg/g.

#### 3.3.1. Adsorption isotherms

The constants of Langmuir, Freundlich, Temkin and Dubinin–Ruduskevich (D–R) isotherm were obtained from the linear plots of  $C_e/q_e$  versus  $C_e$ ,  $\log q_e$  versus  $\log C_e$ ,  $q_e$  versus  $\ln C_e$  and  $\ln q_e$  versus  $\epsilon^2$ , respectively (Fig. 5 and Table 3). The correlation coefficients, values of  $R^2$ , were regarded as a measure of the goodness-of-fit for experimental data (by the isotherms models). According to these values, the sorption of the studied copper by activated carbon fitted better to the Langmuir model than the Freundlich, Temkin and D–R isotherm models. It can be seen from Table 4 that the experimentally obtained values of  $q_{m,\text{exp}}$  were comparable to the maximum sorption obtained from the Langmuir adsorption isotherm ( $q_m$ ). This suggested the monolayer coverage of copper ions onto GAC. The maximum adsorption capacity of the adsorbent for Cu(II) was calculated from the Langmuir isotherm and found to be 7.03 mg/g. The Langmuir parameter  $R_L$  indicated the feasibility of the adsorption process: the adsorption process was unfavorable if  $R_L > 1$ ; linear when  $R_L = 1$ ; favorable in the range  $0 < R_L < 1$ ; or irreversible ( $R_L = 0$ ). Based on the results,  $R_L$  values lie between 0 and 1 for the studied copper, suggesting that the Langmuir model was favorable for adsorbents GAC (Table 4). Furthermore, higher  $R_L$  values at lower copper concentrations show that the adsorption was more favorable at lower copper concentrations. The results (Table 3) show that the mean free energy  $E$  (kJ/mol) values were lower than 8 kJ/mol in the study of the removal of copper by GAC. This indicated that the sorption process may be physical in nature.

### 3.4. The effect of competitor ions

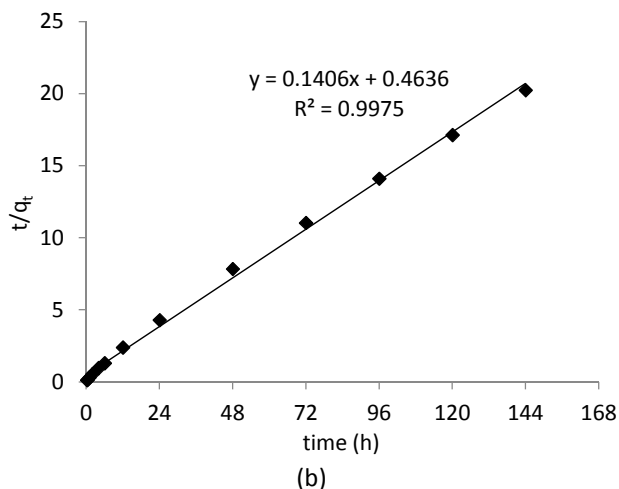
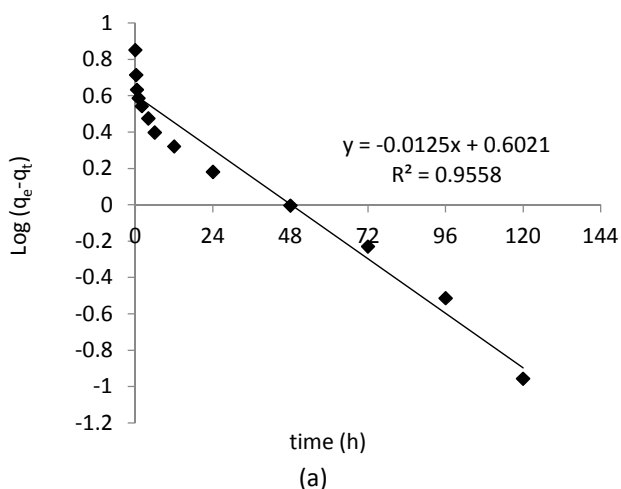
In this experiment, the removal of Cu(II) ions from an aqueous solution in the presence of  $\text{Ag}^{1+}$  and once again in the presence of  $\text{Mn}^{2+}$  ions was performed by activated carbon. The experiment was done under the following conditions: an initial Cu(II) concentration of 1000 mg/L; a contact time of 6 h; an adsorbent dose of 100 g/L; a pH of 4.5; and a temperature of 30 °C. In this experiment, the initial concentration of  $\text{Cu}^{2+}$  was constant and the competitor ion concentration was changed from 100 to 1000 mg/L. The results are shown in Table 5. In this table, CI is the symbol of the competitor ions. Figure 6 shows the effect of the competitor ions on the copper removal efficiency. As seen in the Figure 6, both silver and

manganese ions decreased the removal of Cu(II) from aqueous solutions by GAC; by increasing the value of competitor ions, the copper removal rate was reduced. These competitor ions occupied many activated sites of the adsorbent instead of the Cu<sup>2+</sup>. The behaviors of the two selected competitor ions were not the same. It can be seen that the Mn<sup>2+</sup> ions caused more trouble to remove the Cu<sup>2+</sup> by the activated carbon than the Ag<sup>1+</sup>. This may occur because the Mn<sup>2+</sup> ionic radius was smaller than that of the Ag<sup>1+</sup>. So the smaller Mn<sup>2+</sup> ions penetrated to the pores of the activated carbon more than the Ag<sup>1+</sup> ions and caused more occupation of the activated sites. Therefore, under the same conditions, the Cu<sup>2+</sup> removal percent was reduced from 46% to 31.7% in the presence of the Mn<sup>2+</sup>

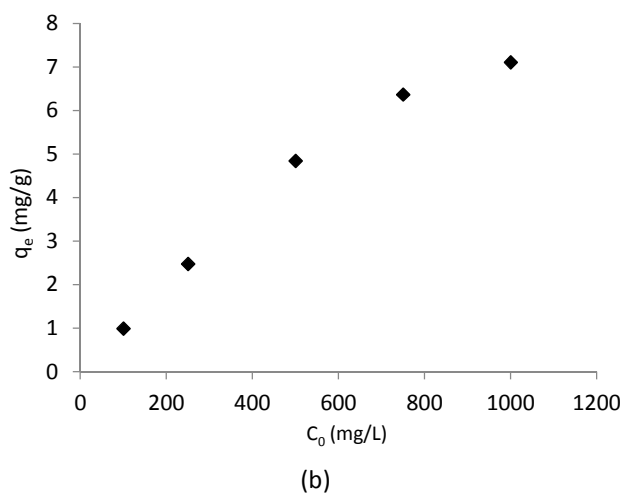
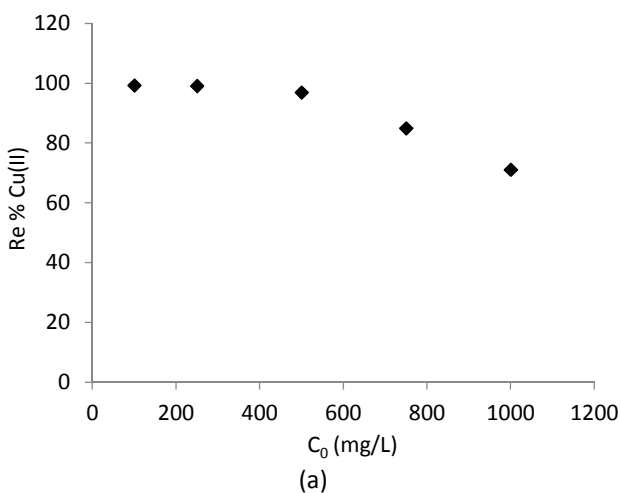
ion, but decreased from 46% to 34.8% with the Ag<sup>2+</sup> ion presence.

**Table 2.** Models rate constants for copper sorption kinetics by GAC

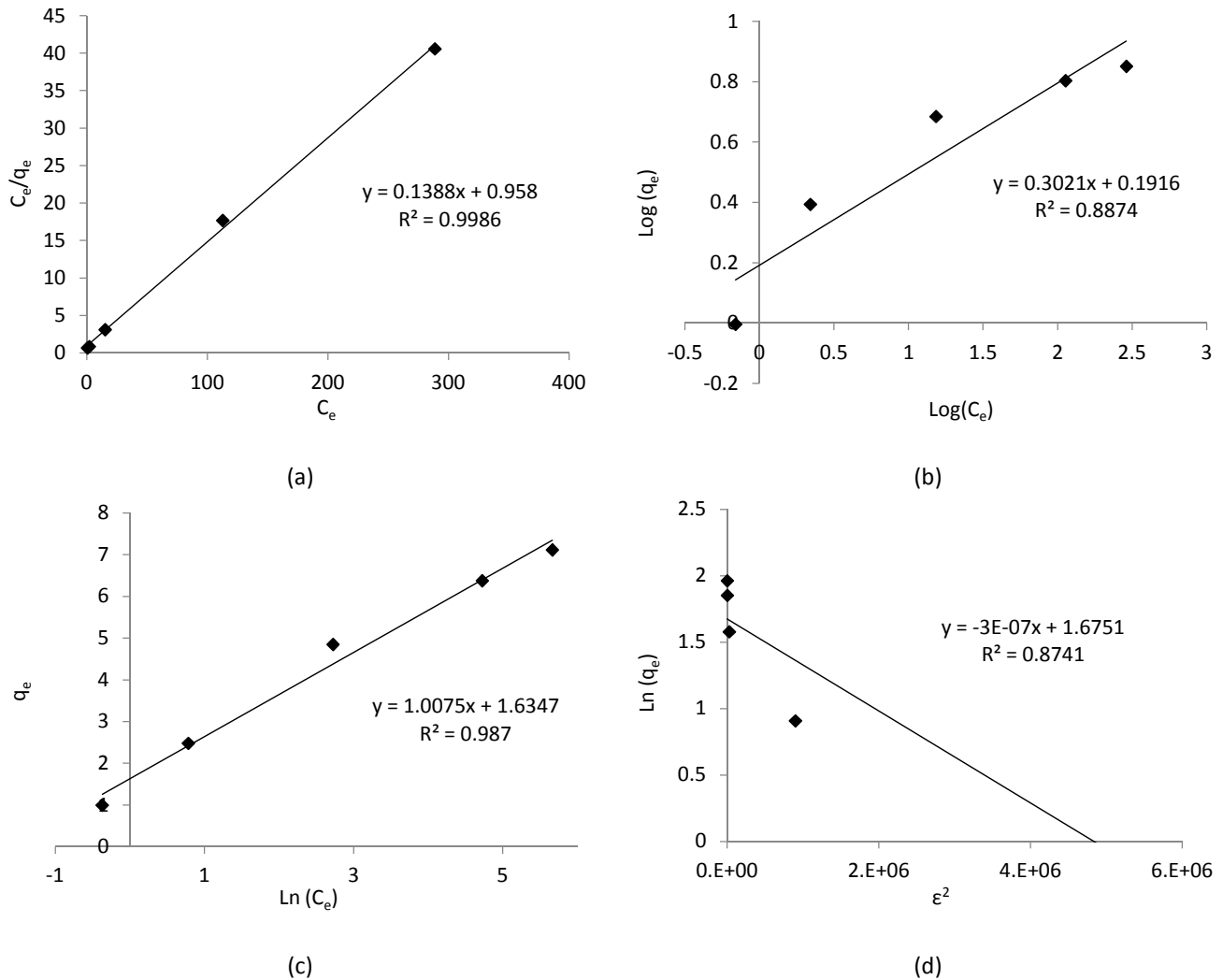
Pseudo-first-order rate model			
q <sub>e,exp</sub> (mg/g)	q <sub>e,cal</sub> (mg/g)	k <sub>1</sub> (×104 min <sup>-1</sup> )	R <sup>2</sup>
7.11	4	4.8	0.956
Pseudo-second-order rate model			
q <sub>e,exp</sub> (mg/g)	q <sub>e,cal</sub> (mg/g)	k <sub>2</sub> (×104 min <sup>-1</sup> )	R <sup>2</sup>
7.11	7.11	7.1	0.998



**Fig. 3.** Pseudo first-order (a) and pseudo second-order (b) for Cu(II) adsorption onto GAC (initial Cu(II) concentration 1000 mg/L; adsorbent dose 100 g/L; pH 4.5; temperature 30 C).



**Fig. 4.** The percentage of (a) removal and (b) adsorption capacity of various concentrations of copper (100–1000 mg/L) onto GAC under equilibrium condition (contact time 144 h; adsorbent dose 100 g/L; pH 4.5; temperature 30 C).



**Fig. 5.** Langmuir (a), Freundlich (b), Temkin (c) and Dubinin–Radushkevich (d) isotherms for Cu(II) adsorption onto GAC (contact time 144 h; adsorbent dose 100 g/L; pH 4.5; temperature 30 °C).

**Table 3.** Constants of models for copper sorption by GAC at pH=4.5

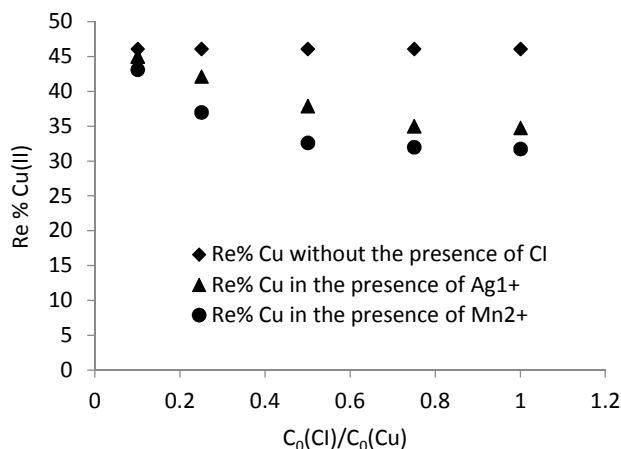
Langmuir			Freundlich		
$q_m$ (mg/L)	KL (L/mg)	$R^2$	$K_f$ (mg <sup>1-1/n</sup> L <sup>1/n</sup> /g)	n	$R^2$
7.20	0.14	0.998	1.57	3.31	0.881
Temkin			Dubinin–Radushkevich		
$K_T$ (L/mg)	B	$R^2$	$q_m$ (mg/L)	E (KJ/mol)	$R^2$
5.07	1.01	0.987	5.34	1.29	0.945

**Table 4.** RL values at different concentrations of copper ions

CO (mg/L)	100	250	500	750	1000
RL	0.065	0.027	0.014	0.009	0.007

**Table 5.** Copper removal efficiency in the presence of competitor ions  $\text{Ag}^{1+}$  and  $\text{Mn}^{2+}$ 

$C_0(\text{Cu}^{2+})$ [mg/L]	$C_0(\text{Ag}^{1+})$ [mg/L]	$C_0(\text{Mn}^{2+})$ [mg/L]	Re% $\text{Cu}^{2+}$ without the presence of Cl	Re% $\text{Cu}^{2+}$ in the presence of $\text{Ag}^{1+}$	Re% $\text{Cu}^{2+}$ in the presence of $\text{Mn}^{2+}$
1000	100	100	46	45	43.1
1000	250	250	46	42.1	37
1000	500	500	46	37.9	32.6
1000	750	750	46	35	32
1000	1000	1000	46	34.8	31.7



**Fig. 6.** The comparison of the copper removal efficiency without the presence of competitor ions and the presence of competitor ions  $\text{Ag}^{1+}$  and  $\text{Mn}^{2+}$  (initial  $\text{Cu}(\text{II})$  concentration 1000 mg/L; contact time 6 h; adsorbent dose 100 g/L; pH 4.5; temperature 30 °C)

#### 4. Conclusions

The results of the present study demonstrated the potential of granular activated carbon (GAC) for the removal of copper from aqueous solutions in the presence of competitor ions. The effects of pH value, contact time, initial concentration on adsorption were investigated. The optimum pH required for maximum adsorption was found to be 4.5 for copper which was also the pH of the solution. The results from the kinetic experiments showed that the adsorption rate of  $\text{Cu}(\text{II})$  ions onto the GAC was slow. The adsorption process can be well described by the pseudo second-order kinetic model. The equilibrium data correlated well with the Langmuir isotherm model. The presence of the competitor ions  $\text{Ag}^{1+}$  and  $\text{Mn}^{2+}$  reduced the amount of copper removed by GAC.

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