

Full Length Research Paper

A comparative study of copper (ii) removal on iron oxide, aluminum oxide and activated carbon by continuous down flow method

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The adsorption capacities of iron oxide, aluminum oxide, and activated carbon sorbents for the removal of copper ions were compared by down flow method. For this purpose, the 20 mg L⁻¹ aqueous solution of Cu (II) with initial pH of 6.5 was fed through three different packed columns at bed depth of 10 cm and flow rate of 1.85 ml min⁻¹. The experimental breakthrough curves were drawn from the adsorption data of packed bed columns. The breakthrough time comparison of the three columns revealed that the uptake capacity of Cu (II) was highest for activated carbon (16.24 mg g⁻¹) followed by aluminum oxide (5.60 mg g⁻¹) and iron oxide (5.41 mg g⁻¹). The maximum amounts of Cu (II) removal were attained as follows: 94.0% for aluminum oxide, 95.2% for iron oxide, and 99.7% for activated carbon. The computed adsorption capacity per unit bed volume (N_0) and the kinetic constant (K_{AB}) were, respectively 1202, 1045 (mg L⁻¹) and 3×10^{-4} , 4×10^{-4} (L mg⁻¹ min⁻¹) for iron oxide and aluminum oxide. Regression coefficient value (0.98) indicated that Thomas model fitted well with the experimental data for the iron oxide and aluminum oxide sorbents. The theoretical adsorption capacities obtained by Thomas model were in good agreement with experimental capacities determined by adsorption data. In a short time after running the experiment, the equilibrium concentration of Cu (II) reached to 1.2 mg L⁻¹ using these sorbents. Hence, the packed bed column with continuous down flow method can be successfully applied for the removal of heavy metals from contaminated waters in practical use.

Key words: Adsorption, breakthrough curve, continuous down flow, copper (II), packed bed column, Thomas model, Bohart-Adams, Yoon-Nelson.

INTRODUCTION

Heavy metals when released into nature posed a significant threat to the environment and public health because of their toxic and persistent nature. The contamination of wastewaters and surface waters by toxic heavy metals is a worldwide environmental problem (Seiler et al., 1998).

Copper ions, like other heavy metals, are released into natural waters by industrial and domestic wastewaters including printed circuit board manufacturing, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, wood preservatives, and printing

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operations (Karvele et al., 2003). Copper is an essential nutrient for human. Although the large concentration of Cu (II) in the blood system may produce reactive free oxygen species and damage the proteins (Brewer, 2010). According to World Health Organization (WHO) standards, the maximum allowable concentration of Cu (II) in drinking water is 2 mg L^{-1} (WHO, 2010). It has been proved that drinking water containing 30 mg L^{-1} of copper ion or more is fatal, and the copper ion concentration greater than 1.3 mg L^{-1} can be a cause of diarrhea, abdominal cramps and nausea, especially in the infant (Olivares et al., 1998). The most commonly applied physico-chemical methods for Cu removal from contaminated waters are those employed for heavy metals. These methods are: (i) precipitation as hydroxides, carbonates or sulfides and subsequent flotation or filtration; (ii) adsorption; (iii) membrane process; (iv) electronic recovery and; (v) liquid-liquid extraction (Qdais and Moussa, 2004; Lazaridis and Peleca, 2004; Salmani et al., 2013). These existing methods, although usually effective, have some individual limitations like defects in application, restrictions in techniques and economically unviable (Bhattachaya and Venkobacher, 1984).

New practices have been focused on the study of processes based on adsorption approaches. Adsorption process is arguably one of the most popular methods for removal of heavy metal ions because of its simplicity, convenience, and high removal efficiency (Sanastos and Olivera, 2003; Wang and Chen, 2009). Different materials have been studied in this respect. These can be classified into two groups: (i) minerals, such as iron oxide and aluminum oxide, and (ii) bio-materials, such as activated carbon and agricultural by-products. The adsorption process with iron oxide, aluminum oxide, and activated carbon is attractive to many scientists (Akill et al., 2004; Ceryera et al., 2003; Asgari et al., 2008) because of the effectiveness of the removal of heavy metal ions at trace concentrations.

Most of the earlier investigations on heavy metal adsorption were restricted to batch studies. The capacity of sorbent obtained from batch experiments is useful in providing fundamental information about the effectiveness of adsorption system. In spite of that, the data may not be applicable to most treatment systems where contact times are not sufficient for the attainment of the equilibrium (Chu, 2004). However, to improve their adsorption with conditions closer to real life water treatment system and to enhance the adsorption capacity, the designs of natural process are still necessary. A packed bed column is considered as an effective process for continuous wastewater treatment for a number of reasons: it makes the best use of the concentration difference known to be a driving force for heavy metal adsorption; it allows more efficient utilization of adsorption capacity, and results in better quality of the

effluent. Therefore, it is necessary to perform equilibrium studies for heavy metals removal by using packed column. Previous studies demonstrate that biosorbents are prominent sorbents for heavy metal removals in fixed bed column (Genc-Fuhrman et al., 2007; Sankaramakrishnan et al., 2008).

The objective of the present study is to develop some basic data for the comparison of Cu (II) removal from contaminated solution in a fixed bed system. Accordingly, the continuous down flow technique was studied by using activated carbon, aluminum oxide and iron oxide in different packed columns to improve the efficiency and applicability of the removal and separation process.

MATERIALS AND METHODS

Chemical reagents and apparatus

A stock copper (II) solution of 1000 mg L^{-1} concentration was prepared by dissolving 0.3906 g analytical grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 100 ml of distilled water. The 2 L working solution with effective concentration of 20 mg L^{-1} and 50 ml standard solutions $2, 5, 10, 15$ and 20 mg L^{-1} were made by diluting the stock solution. Similar particle sizes of the sorbent material used as particle size may have an effect on the removal efficiency. A varian model 20AA of flame atomic absorption spectrometer (AAS) was applied to measure the concentration of ions in the solutions. Chemical substances were weighed at precision of $\pm 0.0001 \text{ g}$ with a Mettler model digital laboratory scale. The pH of the inlet and outlet solutions was measured by a Sension 3 model digital pH meter.

Column preparation

Packed bed column studies were conducted using glass columns of 5 cm internal diameter and 15 cm length. A suitable known amount of each sorbent was mixed with a suitable amount of moist sand. After obtaining a homogenous mixture, a known amount of prepared mixture (containing 20 g sorbent) was transferred to the column cell, so that the total depth of packed column was made up to 10 cm within two supporting silicon filters with porosity 0.5μ and some glass beads. The schematic diagram of the study column is shown in Figure 1. The column was charged with initial concentration of 20 mg L^{-1} Cu (II) solution in down flow mode with mean flow rate of 1.85 ml min^{-1} . After filling the bed volume, samples were collected at regular 30 min intervals to determine the residual Cu (II) concentration using AAS.

Data analysis

All experimental data from output of AA were the average of triplicate experiments so that the relative standard deviation (RSD) of the data was less than 1.4% . The time and the mean concentration of Cu (II) in the outlet liquid from output of AAS was saved in data statistical package for social sciences (SPSS) file and the parameters for three columns were calculated in SPSS version-16 and then saved. The breakthrough time and the exhaust time corresponding to C/C_0 equal 0.1 and 0.9 were calculated from the experimental data. These parameters were used to evaluate the mass transfer zone given by Equation (1):

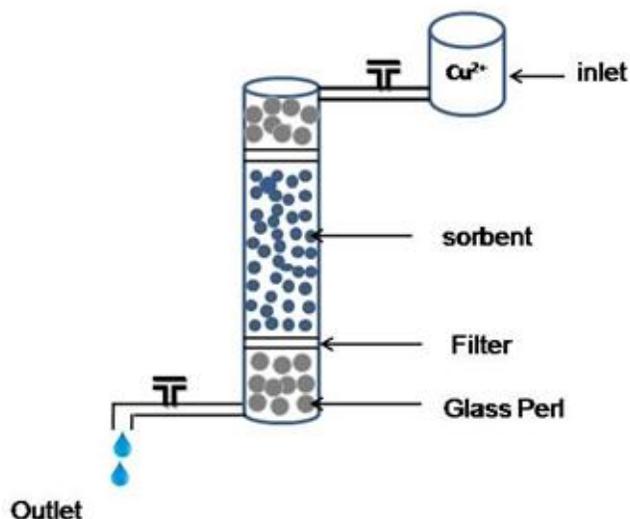


Figure 1. A schematic of study fixed bed column for Cu (II) adsorption.

Table 1. Physical controlled parameters in a packed bed column.

Physical controlled parameter	Value
Empty bed contact time (min)	65
flow rate (ml min ⁻¹)	1.85
Inflow pH	6.5
Initial Cu (II) concentration (mg L ⁻¹)	20
Temperature (°K)	298
Bed height (cm)	10
Mass of sorber (g)	20

$$\Delta t = t_e - t_b \quad (1)$$

The amount of metal sent to column with respect to flow rate (F) can be calculated from Equation (2):

$$m_t = C_0 F.t \quad (2)$$

The metal removal percent was determined from the relationship (3):

$$\%R = [(C_0 - C) F.t / m_t] \times 100 \quad (3)$$

The metal adsorption capacity value at time t expressed in mg g⁻¹ was obtained from Equation (4):

$$q = (C_0 - C) F.t / (M \times 1000) \quad (4)$$

In order to control the adsorption mechanism and kinetic model, the experimental data were tested by various mathematical models that have been used to describe the fixed bed column adsorption. The models reported by Bohart-Adams, Thomas and Yoon-Nelson are given in the following equations (5-7) (Bohart-Adams, 1920;

Thomas, 1948; Yoon and Nelson, 1984)

$$\text{Bohart-Adams} \quad \ln\left(\frac{C}{C_0}\right) = K_{AB} C_0 t - K_{AB} N_0 \frac{h}{u_0} \quad (5)$$

$$\text{Thomas} \quad \ln\left(\frac{C_0}{C} - 1\right) = \frac{K_{th} q_0 m}{F} - K_{th} C_0 t \quad (6)$$

$$\text{Yoon-Nelson} \quad \ln\left(\frac{C}{C_0 - C}\right) = K_{YN} t - \tau K_{YN} \quad (7)$$

To achieve the best adsorption equilibrium, different equations were tested and their parameters were determined from slope and intercept of the obtained straight line.

RESULTS AND DISCUSSION

The pH_{pzc} for these sorbents has been reported in the literature as 6 to 8 (Sperlich et al., 2005). pHs in the experiment adjusted on 6.5 based on the pH_{pzc} and the precipitation of Cu (II). Some physical parameters for the three columns were similar and their values are presented in Table 1. The dynamic behavior of a packed bed column is described in terms of breakthrough curve. A plot of effluent concentration versus time is referred as breakthrough curve, which has an S-shaped curve (Sperlich et al., 2005). The breakthrough profile of copper ions adsorption on studied different sorbents for a given flow rate and bed height are shown in Figure 2.

The success of a column adsorption process depends on the prediction of the concentration-time profile. A comparison of the breakthrough curves (Figure 2) demonstrates that the adsorption capacity of Cu (II) on the activated carbon was highest, and this results in a more efficient removal of this ion as well as a remarkable increase in the total mass which is transferred into the column by the effluent. A similar observation was made by Malkoc and Nuhoglu (2006) in the removal of Ni (II) using tea factory waste in a fixed bed study. It can also be observed that the slope of the breakthrough curves of adsorption on iron oxide, aluminum oxide and activated carbon decreased, respectively and this is probably due to an increase in the surface area of activated carbon adsorbent. This result is in agreement with Goyal et al. (2001) in the removal of Cu (II) by activated carbon and with Muhamad et al. (2009) in their study of batch and continuous fixed bed column biosorption of Cd (II) and Cu (II). The results in Table 2 present some of the calculated operational characteristics of the three sorbents packed bed columns at a bed height of 10 cm and a flow rate of 1.85 ml min⁻¹.

Breakthrough ion concentration is the point in the survey where the effluent concentration reaches its maximum allowable value. The time for the appearance of breakthrough and the shape of the breakthrough curve

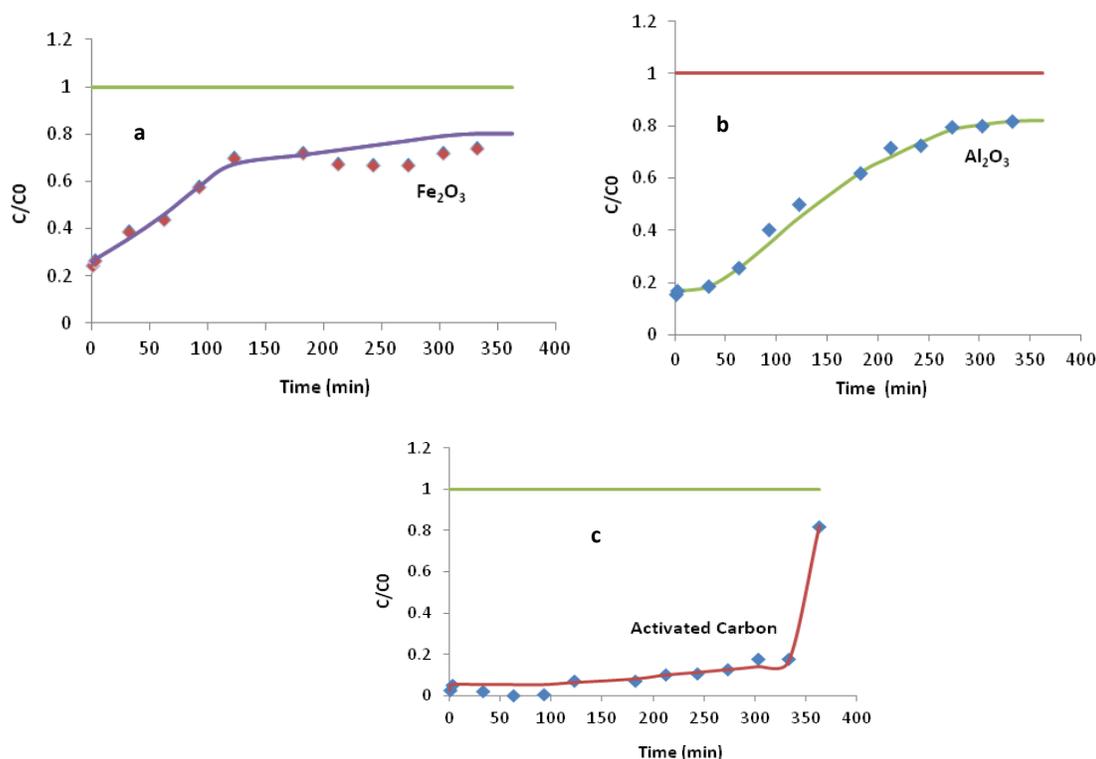


Figure 2. Experimental (♦) and calculated (□) breakthrough curves for adsorption of Cu (II) on: a) Fe_2O_3 b) Al_2O_3 and c) activated carbon at flow rate 1.85 mL min^{-1} and bed height 10 cm.

Table 2. Parameters obtained for Cu (II) removal by three sorbents.

Parameter	t_b	t_e	$q_{cal.}$	q_{exp}	V_b	V_e	Max. removal (%)
Sorbent							
Fe_2O_3	12.5	292.5	4.76	5.41	61	541.1	95.2
Al_2O_3	42.5	302.5	5.27	5.60	85	559.6	94.0
AC	212	----	---	16.24	392	---	99.7

are both important characteristics for determining the operation and the dynamic response of the adsorption column. These times for iron oxide, aluminum oxide, and activated carbon as represented in Table 2 are, respectively 12.5, 42.5, and 212 min. Generally, the breakthrough time depends on the capacity of column with respect to the initial concentration, bed height, and flow rate. However, these parameters were maintained constant in three columns, so the results showed that the breakthrough time of iron oxide is the shortest of all. It can be concluded that the packed column with iron oxide sorbent saturated the fastest. This time is very long for activated carbon in comparison to the other two sorbents. This illustrates that surface area of activated carbon sorbent is relatively extensive and the particles have high

contribution in the adsorption process (Gupta, 1998). In addition, this result suggests that internal diffusion to the adsorbent in the adsorption process is extremely important.

Modeling is a very good tool to understand the efficiency of continuous adsorption system. Various mathematical models are used to describe the breakthrough curves of adsorption in the packed bed column. To compare the removal ability of the sorbents, the parameter calculations of three models have been carried out. The information is listed in Tables 3 to 5.

The kinetic coefficient (K_{AB}) and saturation concentration (N_0) at a flow rate of 1.85 mL min^{-1} , initial Cu (II) concentration of 20 mg L^{-1} , and a bed height of 10 cm were 3×10^{-4} , 4×10^{-4} ($\text{L mg}^{-1} \text{ min}^{-1}$) and 1202, 1045

Table 3. Bohart-Adams model parameters.

Parameter	K_{AB}	N_0	R^2
Sorbent			
Fe ₂ O ₃	3×10^{-4}	1202	0.877
Al ₂ O ₃	4×10^{-4}	1045	0.830

Table 4. Yoon-Nelson model parameters.

Parameter	K_{YN}	τ	R^2
Sorbent Fe ₂ O ₃	1.8×10^{-2}	154	0.978
Al ₂ O ₃	1.8×10^{-2}	139	0.977

Table 5. Thomas model parameters.

Parameter	K_{Th}	$q_{0(Cal)}$	$q_{0(Exp)}$	R^2
Sorbent				
Fe ₂ O ₃	2.75	4.76	5.41	0.980
Al ₂ O ₃	2.69	5.27	5.60	0.980

(mg L⁻¹) for iron oxide and aluminum oxide, respectively. The above kinetic coefficient showed that the system kinetics was dominated by mass transfer at the initial of adsorption in the aluminum oxide and iron oxide columns (Goud et al., 2005). Whereas, the mass transfer zone of iron oxide (280 min) was higher than that aluminum oxide (260 min). Therefore, internal mass transfer resistant due to pore diffusion is high for iron oxide.

The Yoon-Nelson model is not only less complicated than the other models but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent, and the physical properties of the adsorption bed. The rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorption and the probability of adsorbate breakthrough on the adsorbent (Ghribi and Chlendi, 2011). The rate constant K_{YN} was similar for the two columns, but the time required for 50% adsorbate breakthrough (τ) for iron oxide was (154 min) more than aluminum oxide (139 min). This indicates that the probability of adsorption for each molecule to the adsorbate is higher for iron oxide sorbent.

Thomas equation is widely used to predict adsorption especially in column models. Similarly, here regression coefficient value (0.98) indicated that the experimental data were well fitted to Thomas model for determining Thomas rate constant (K_{th}) and maximum adsorption capacity for both iron oxide and aluminum oxide that are listed in Table 5. Higher value of Thomas rate constant K_{th} (2.96 L mg⁻¹ min⁻¹) for iron oxide compared to alumi-

num oxide (2.75 L mg⁻¹ min⁻¹) depict the internal diffusion of iron oxide is higher than the aluminum oxide. Previous study by Genc-Fuhrman et al. (2008) was performed on the removal of some heavy metals from polluted water using an iron based sorbent. Their findings revealed a percentage of 98.5% of Cu (II) removal, which approves Thomas model.

Conclusion

The continuous down flow process designed in this study for adsorption in order to remove the copper ions has a good potential to remove heavy metals from wastewater samples in practical application, because the high removal (more than 95%) of Cu (II) occurs in the flow rate of 1.85 ml min⁻¹ and bed height of 10 cm at the three columns. The maximum percentage of Cu (II) removal (99.7%) as well as breakthrough time (212 min) for activated carbon column was found to be high compared to other studied mineral sorbents. The 1.85 ml min⁻¹ is a suitable flow rate for both iron oxide and aluminum oxide, while the activated carbon can tolerate more speeds.

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ABBREVIATIONS

R, Metal removal efficiency; **t**, service time (min); **t_b**, breakthrough time (min); **t_e**, exhaust time (min); **τ** , 50% breakthrough time (min); **Δt** , mass transfer zone (min); **C₀**, inlet concentration of Cu (II) (mg L⁻¹); **C**, outlet mean concentration of Cu (II) at time t (mg L⁻¹); **M**, sorbent mass (g); **m_t**, total amount of Cu (II) sent to column (mg); **h**, bed height (cm); **F**, mean flow rate (ml min⁻¹); **q**, metal uptake capacity (mg g⁻¹); **q_{0cal}**, calculated uptake capacity (mg g⁻¹); **q_{0exp}**, experimental uptake capacity (mg g⁻¹); **V_b**, throughout volume of breakthrough (ml); **V_e**, throughout volume of exhaust (ml); **K_{AB}**, Bohart-Adams kinetic coefficient (L mg⁻¹ min⁻¹); **K_{th}**, Thomas rate constant (L mg⁻¹ min⁻¹); **K_{YN}**, Yoon-Nelson rate constant (min⁻¹); **N₀**, saturation concentration (mg L⁻¹).

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