

Original

Removing Copper from Contaminated Water Using Activated Carbon Sorbent by Continuous Flow

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Abstract

Introduction: A major concern of human being is accumulation and toxicity of heavy metals in their body. Copper is a heavy metal ion that in concentration of 2 mg/l can cause numerous complications. Different treatment methods have been proposed for removing metals from contaminated water by researchers. Among these methods, sorption seems a better method with high removal efficiency. In this study, conditions for removal of copper ions by activated carbon sorbent were studied with continuous flow.

Materials & Methods: This was a laboratory – experimental study. A 20mg/l solution of copper ions was prepared and passed through a 5 × 10 cm column with average output rate of 1.85 ml/min. Output of column was sampled every 30 minutes and the remaining amount of copper ion in each sample was measured by flame atomic absorption.

Results: The empty bed volume (EBV) was equal to 138 ml. The highest removal efficiency was 99.7 percent at 127 minutes. From equilibrium time, the removal efficiency was constant with time. The adsorption capacity of activated carbon was 0.25mg.g⁻¹. The isotherm study indicated that the sorption data can be obeyed by both Langmuir and Freundlich isotherms ($R^2 > 0.95$) but Langmuir model had higher agreement with this experimental data ($R^2 = 0.988$).

Conclusion: The binding of ions to the sorbent in the adsorption process is extremely important. For this column 62.5 minutes after filling was appropriate, so the highest removal efficiency was obtained. Equilibrium time was dependent on the speed of influent through the column in the continuous flow. For selected column, the rate of 1.85 ml/min is a good performance.

Keyword: Copper; Absorbent Pad ;Charcoal; Water Pollution, Water Pollution Chemical

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Introduction

Copper ions can be found in many wastewater sources including printed circuit board manufacturing, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, wood preservative using and printing operations. Typical concentrations vary from several thousand mg/l from plating bath waste to less than 1 ppm from copper cleaning operations.

Copper is a heavy metal that is naturally observed in the environment and in fragmented water resources. The discharge of wastewater including heavy metals increases the environmental pollution and toxic nature of Cu^{2+} affects water resources ^[1]. Various studies show that the copper ion concentration in drinking water has the range of less than 0.005 to more than 30 mg/l ^[2]. Copper ion in small amounts is used in agriculture and is an essential element for health of plants, animals and humans ^[3]. Copper deficiency can cause impaired growth in children and several metabolic problems in adults ^[4]. Copper is not biodegradable in environment, so it accumulates such as other heavy metals and may cause adverse effects. High concentration of copper compounds in drinking and agriculture water sources is the biggest threat to human health so that, in human it creates a kind of disease which is similar to flu ^[5-6]. It has been proved that drinking water including 30 grams of copper ion is fatal and the concentration of 1.3 mg/l of the this ion could be a reason for the relatively common diarrhea, abdominal cramps and nausea, especially in the infants ^[7]. According to WHO

standards, the maximum allowable concentration of copper in drinking water is 0.2 mg/l ^[8].

The use of treated wastewater (effluent) has been limited for different purposes due to the presence of copper ions. The maximum allowable concentration of copper ions in the Industrial Wastewater Treatment for discharge to surface waters and wells is 1 mg/l. This measure for trees and agriculture irrigation is 0.2 and 5 mg/l for long-term and short-term uses, respectively; and for ponds fish farming, it should be less than 2 mg/l ^[9].

In order to protect humans and the environment, removal of copper ions from environments such as water, sanitation and flood is important. Different methods were investigated for reducing heavy metal ions in industrial wastewater and contaminated factories, naming some of them: the use of coagulants, oxidizing agents, membranes, ion flotation ^[10], the use of nanoparticles ^[11], adsorption processes and electrochemical techniques. Since the sorption process is cheaper and simpler than other methods is more usable. Activated carbon has been recognized as the most common and efficient sorbent.

A simple, applied adsorption process in industrial scale and its use in industry is important. For this purpose, the dynamic behavior of natural systems simulated by fixed bed adsorption is necessary. Proper design processes to speed up transit time column on the dissolved contaminants from the column, the amount of contact with contaminated water absorbent (column length) and running conditions are optimized for more efficient removal.

In this study, our aim was to use activated carbon as a sorbent for copper ions by utilizing the continuous flow technique (with conditions more similar to real life water treatment system) to improve the efficiency and applicability of the removal process. The continuous flow technique was carried out by using columns packed.

Material & Methods

Chemicals and instruments

All laboratory tests were done in 2011 at chemistry laboratory of Shahid Sadoughi University of Medical Sciences. All substances used in the decomposition of pure material were purchased from Merck. Standard and contaminated solutions of copper ions were made from copper sulfate ($\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$) salt. Activated carbon was used as granula (mesh 8×30). Chemicals were weighed with precision of ± 0.0001 g with Mettler digital laboratory scale. Solution pH was measured by a session 3 model digital pH meter. Column using a 5×15 cm glass was purchased from the Pyrex fan company. For blocking of sorbent, two filters made of silicon with fine pores laser was used. The amount of copper ions was measured by atomic absorption spectrophotometer (20AA) in the laboratory of the Yazd Environmental Health School. Data was analyzed by SPSS software.

Column preparation

A schematic diagram of column system used in this study is depicted in figure 1. The column was filled with 20 grams of activated carbon sorbent. Two filters were initially put in the beginning and end of the 5×10 column. Some glass beads were filled two sides of the filter to ensure homogenous distribution of influent solution from the top to the bottom. Before feeding the column with an influent

solution containing Cu^{2+} , the column was run with pure distilled water for 2 hours to get wet and preserve the equilibrium between the water and sorbent. Due to uniform distribution of solution, the pressure gradient is reduced and canalization of the sorbent is decreased. So, sorbent particles quickly participate in practice and absorb. It increases the absorption rate.

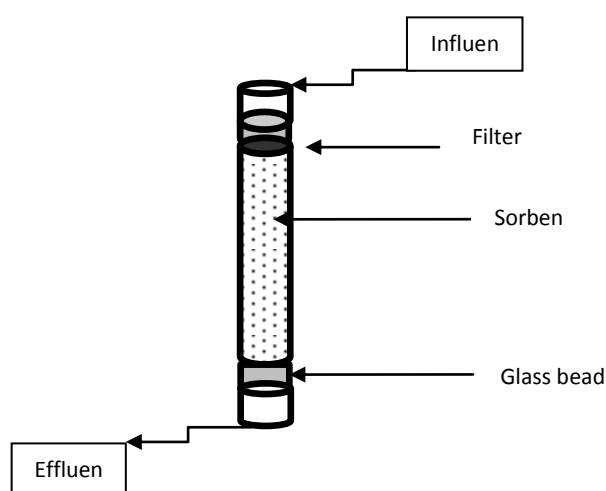


Figure 1. schematic diagram of the column

Testing and sampling

pH of the feeder copper ion solution was 6.5. Effective concentration of copper ions was 20 mg/l. The experiments were performed by continuous flow. Regular flow of the discharge volume of the solution was measured at given times. Volume of 500 ml of solution containing copper ions passed through the column. Then 5ml samples were collected at 30 minute intervals from column output in an average speed of 1.85 ml/min. pH of all collected samples was adjusted to 1.5 - 2 by HNO_3 1 M, immediately. Then solution sample was stored to measure Cu^{2+} .

Measuring the Copper ions concentration

A standard solution of 100 mg/l of copper ions was prepared. Series of standard solutions with

concentrations of 1, 3 and 5 mg/l as well as concentrations of 5, 10 and 20 mg/l of copper ions were prepared. Absorption wavelength of 324.7 nm of each solution was measured using a flame mode. To achieve accuracy in the measurement, all measurements were repeated 3 times and the relative standard deviation (RSD) of less than 0.4 was selected. Copper ion concentration for each sample was determined by flame atomic absorption. Additional effluent samples were stored and copper ion concentration was also measured.

Data analysis

Average amount of retained copper ion concentration was obtained by readout of atomic absorption. The removal efficiency of copper ions was calculated using this formula:

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

The amount of copper ion in the adsorbent phase (q_e ; mg.g^{-1}) was calculated by using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

Where C_0 and C_e are the initial and equilibrium concentration of Cu^{2+} (mg/l) at any time, V is the volume of solution (L) and W is the mass of the adsorbent (g) [12].

Generally the Langmuir equation applies to the cases of adsorption on completely homogeneous surfaces where interactions between adsorbed molecules are negligible [13]. The linear form of the Langmuir is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (3)$$

Where q_{max} is the monolayer capacity of the adsorbent (mg.g^{-1}) and K_L is the Langmuir constant ($\text{dm}^3.\text{mg}$) and related to the free energy of adsorption. The plots of C_e/q_e versus C_e (Langmuir) for the adsorption of copper ions onto activated carbon give a straight line [14-15].

Results

The empty bed contact time (EBCT) was calculated according to flow rate. Feed solution temperature was $25 \pm 2^\circ\text{C}$. The summary of obtained data is shown in table 1.

Table 1. The summary of the column data

Empty bed contact time	65
Average flow rate(ml/min)	1.85
Inflow pH	6.5
Initial Cu concentration(mg/l)	20
Average temperature($^\circ\text{C}$)	25
Max. removal time(min.)	127
Max. Cu removal (%)	99.7

Removal efficiency was plotted in time of running using SPSS software. Figure 2 shows the percentage of removal as a function of time. This figure shows that highest removal was achieved at 62.5 minutes after performance.

Several isotherm equations are available for adsorption process. Langmuir, Freundlich and Tempkin are three adsorption isotherm equations that were used in this study. The parameters and R^2 for three models are shown in table 2.

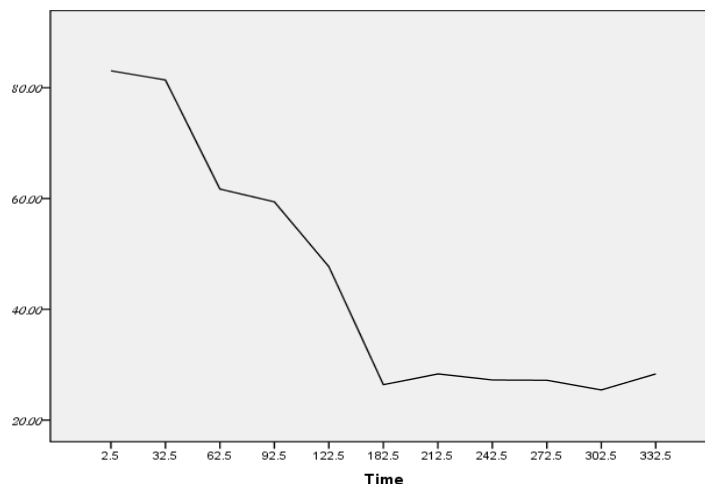


Figure 2. Removal efficiency at time of running, V= 1.85 ml/min, pH=6.5

Table2. Characteristics of adsorption isotherms (C₀=20 mg/l)

Langmuir isotherm		Freundlich isotherm		Temkin isotherm	
K _L (dm ³ .mg)	0.045	K _F (dm ³ .g)	0.018	A(L.g)	0.042
q _{max} (mg/g)	0.0258	1/n	1.207	b _t (J.mol)	0.024
R _L	0.525	R ²	0.95	R ²	0.644
R ²	0.988				

The Langmuir isotherm model had the highest values of regression coefficients (R² = 0.988). Figure 3 shows the plots of this model.

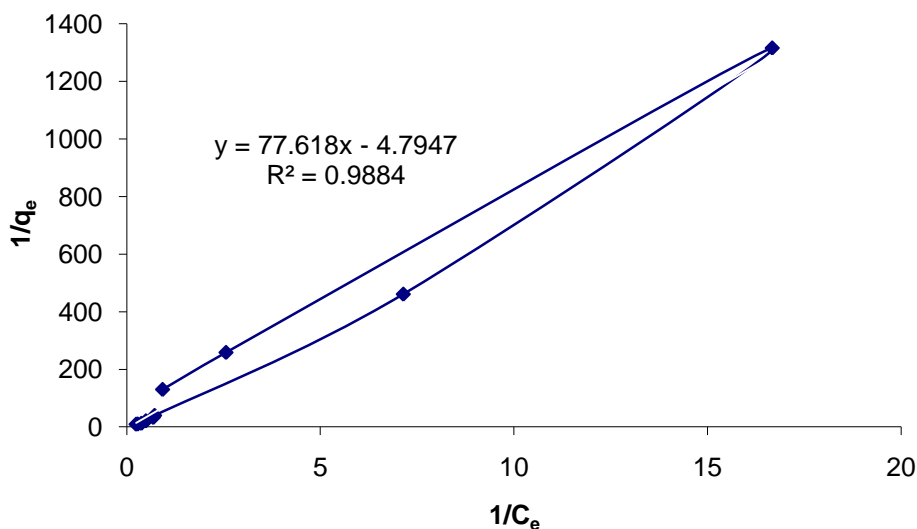


Figure 3. Langmuir isotherm for removal of Cu²⁺ by activated carbon

Discussion

It is believed that quite promising results were obtained in the present research by adsorption removal of copper ions from contaminated water. Empty bed volume (EBV) was equal to 138 ml and the highest removal efficiency (99.7%) was observed at 127 min after starting or the maximum removal efficiency has appeared at 62.5 minutes after the running. In a study by Murat Teker, Mustafa Imamo-glu (1999) the equilibrium was attained after shaking for 60 min for Cu^{2+} and 80 min for Cd^{2+} . So in each experiment the shaking period was selected as 60 min for Copper^[7] which is consistent with the results of the current study.

The contact time is inevitably a fundamental parameter in all transfer phenomena such as adsorption. Figure 1 showed the influence of contact time on the adsorption of copper ions onto activated carbon. From this figure, 62.5 minutes after filling the column was an appropriate time with the highest removal efficiency^[16]. This time in the continuous flow of solution through the column strongly depends on the speed. Then, the rate of 1.85 ml/min for selected adsorbent showed acceptable performance. A study for cadmium removal by Vimala (2011) showed that percent removal of cadmium decreased with increase of flow rate and removal of 68.27% was reported in flow rate of 5 ml/min^[17].

The effect of equilibrium time on the sorption by adsorbent shows that the adsorption process onto the adsorbent is relatively fast or slow. Figure 1 showed that 62.5 min was a sufficient time for completed removal of copper ions by adsorption onto the activated carbon. This result indicated that the adsorption process was fast. So, the fast adsorption

at the initial stage was probably due to the number of vacant sites available on the GAC surface at the beginning. The fast metal uptake by the sorbents may be attributed to their highly porous and mesh structure, which provides ready access and a large surface area for the sorption of the metal ions onto the binding sites. This result is in accordance with the results of Mousavi et al. study (2010). They found that contact time (2h) have maximum effect on the removal of Cu^{2+} from aqueous solution by the batch adsorption technique using waste tire rubber ash^[18].

It is important to consider the capacity of retention of copper by activated carbon. According to figure 2, the adsorbed amount of Cu^{2+} on amount of activated carbon (q_e) at 62.5 min was 0.25mg.g^{-1} . This result shows that surface area of activated sorbent was very much and the particles had high contribution in the adsorption process. Since ion binding to the adsorbent in the adsorption process is extremely important^[8]. In addition, the attainment of equilibrium adsorption may be due to the limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of GAC. The amount of the adsorbed Cu^{2+} , increased as the time lapses. The similar case was recorded by Onundi et al. They studied the adsorption of copper, nickel and lead ions from synthetic semiconductor industry wastewater by palm shell activated carbon. In their study, the adsorbent showed a rapid metal reduction for the first 5 min of contact time. The percentage of metal removal reached the equilibrium within 30 min for Pb and 75 min for Cu^{2+} and Ni^{2+} . It was assumed that the acidic groups on the GAC had affinity for all three metals; the higher initial

concentration of copper ion also favored copper over nickel in the percent uptake achieved by 75 min ^[19].

The equilibrium adsorption isotherms are important to understand the mechanism of the adsorption. Adsorption isotherm models describe the relationship between adsorbates and adsorbents at equilibrium. Several isotherm equations are available and three adsorption isotherm equations (Langmuir, Freundlich and Tempkin) were used in the present study. The applicability of the isotherm models to the adsorption study done was compared by judging the correlation coefficients values ^[12]. The Langmuir isotherm model had the highest values of regression coefficients ($R^2 = 0.988$) when compared to the rest of isotherm models, which

showed the homogeneous nature of the adsorbent. The calculated data of Langmuir isotherm which exhibited the highest regression correlation for Cu^{2+} described a better fitting model than of Freundlich and Temkin isotherms.

The essential feature of the Langmuir isotherm can be expressed by means of 'R_L', a dimensionless constant referred to as separation factor or equilibrium parameter (R_L) is calculated using the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

As the R_L values lie between 0 and 1, the related adsorption process is favorable ^[14, 15]. The R_L value in this study was 0.525 which indicates that the adsorption process is favorable.

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