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**Original article****Removal of copper from aqueous samples using modified sawdust****S. Elhami\*, B. Moghadasian***Department of Chemistry, Khouzeestan Science and Research Branch, Islamic Azad University, Ahvaz, Iran.*

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## ARTICLE INFO

## ABSTRACT

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The adsorption capacity regarding copper is low on sawdust which is a low cost adsorbent so in this research, modified sawdust with diethylenetriamine was used as efficient adsorbent for removal of copper from water samples. The effects of several parameters such as pH value of the copper solution, adsorbent dose, adsorption time and the initial copper concentration on the adsorption were investigated. DETA-sawdust had a high uptake capacity in room temperature and could remove Cu (II) of about 90 % with 3 g/L of adsorbent in 60 min for 50 mg /L of copper solution. The method was applied to the removal of copper in tap water and river water samples from different parts of Khouzeestan, Iran.

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**1. Introduction**

Nowadays, the removal of toxic substances from aqueous medium such as effluents is of great interest for environmental and human health purposes. For this reason, the control and treatment of these effluents have become one of the most important steps of the productive process. In this scenario, the application of solid phase extraction (SPE) procedures has increased in last few years, especially due to its efficiency and low requirements in terms of cost (Ageena, 2010). Removal of heavy metals in wastewater is normally achieved by advanced technologies such as ion exchange (Yasemin and Zeki, 2007), chemical precipitation (Srinivasa, et al., 2007), electroplating (ShirzadSiboni, et al., 2011), chemical coagulation (Laasri, et al., 2011) and membrane separation (ShirzadSiboni, et al., 2011). But these technologies do not seem to be economically feasible because of their

relatively high costs and that developing countries may not afford such technologies. Therefore, there is a need to look into alternatives to investigate a low-cost method, which is effective and economical. To overcome this difficulty there is a strong need to develop cheap adsorbents which can be used in developing countries.

Adsorption by natural materials is another alternative method to solve this kind of problems.

The natural materials form complexes with metal ions using their ligand or functional groups.

Process for metal removal like adsorption has been suggested as being cheaper and more effective than the other technologies (Ahmad, et al., 2009).

Copper (Cu) is an essential trace element that plays an important role in carbohydrate and lipid metabolism as well as the maintenance of heart and blood vessel activity (Ince, et al., 2008). Conversely, copper can be toxic to humans and animals if they are exposed to it at high concentrations. Because of its relatively high toxicity and widespread use, copper is the subject of much concern (Ince, et al., 2008). Excess copper in water is not only harmful to human beings, but also interferes with the self-purification of bulk water and exerts an adverse effect on the microbiological treatment of wastewater. Therefore, from the viewpoints of pollution, environmental chemistry, geochemistry, marine biology and analytical control in industrial, food, agricultural, pharmaceutical and clinical areas, it is necessary to establish a rapid, simple, sensitive and accurate procedure for the selective concentration of Cu<sup>2+</sup> prior to its determination (Ghazy, et al., 2006).

In the present study, sawdust was modified by diethylenetriamine. Then, modified sawdust was used for the removal of copper from aqueous solutions. The effect of pH, adsorbent dose, and contact time and agitation rate on the removal of copper was studied in order to establish optimum conditions .

## **2. Materials and methods**

### **2.1. Material**

All the used chemicals had an analytical grade and doubled distilled water was used throughout the study. A stock solution of 1000 mg/L of copper was prepared by dissolving 3.801 g of the Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O (Merck) in water and diluting to as much as 1000 mL in a volumetric flask. The desired concentrations were obtained by successive dilutions.

### **2.2. Preparation of adsorbent**

The sawdust supplied by a local wood processing factory was washed with distilled water to remove impurity, and then dried overnight at 60 °C. The dried sawdust was sieved to retain the 0.5 mm fractions for further chemical synthesis. 140 mL of HCl concentrated (Merck) was added to 10 gr of sawdust. After 2 h, 60mL of diethylenetriamine (Merck) was added too. Then, the product was filtered, washed with distilled water, and dried in oven at 40 °C for 24 h.

### **2.3. General procedure**

In each adsorption experiment, 100 mL of Cu (II) solution of known concentration and pH was added to the modified adsorbent in a 250 mL erlenmeyer flask in room temperature (25±1 °C) and it was agitated by a shaker at 100 rpm. After 60 min, the mixture was filtered and the concentration of Cu (II) in the solution was measured by the spectrometric method to be at 324.8 nm with thermo scientific Atomic Absorption Spectrometer (model: 3000ICE). The percentage of Cu (II) removal was calculated based on the following equation:

$$\text{Removal(\%)} = \frac{C_0 - C_e}{C_0} \times 100$$

In this equation, C<sub>0</sub> is the initial Cu (II) concentration (before being mixed with the adsorbent), and C<sub>e</sub> is the equilibrium concentration (after being mixed with the adsorbent). The equilibrium concentration was obtained through a calibration curve for the Cu (II).

## **3. Results and discussion**

Modified sawdust with diethylenetriamine was chosen as an adsorbent for removal of copper from water samples. The preliminary experimental observations showed that modified sawdust removed copper from water more than 80%, while sawdust did not have this ability.

### 3.1. The effect of pH

The effect of pH of the sample solution was evaluated by adjusting the pH of a set of 100 mL solutions containing 50 mg L<sup>-1</sup> of Cu (II) in the pH range of 2.5-6.5 using HCl or NaOH. The removal of Cu (II) was maximum in the pH of 6 "Figure 1".

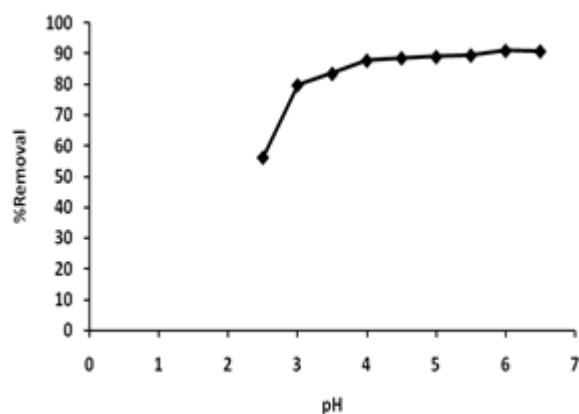


Fig. 1. Effect of pH on Cu (II) removal.

(Cu (II) initial conc. = 50 mg/L, adsorbent dose = 2 g/L, Time=60 min, shaker speed=100 rpm)

### 3.2. Effect of adsorbent dose

The effect of adsorbent dose on the removal of Cu (II) is shown in "Figure 2". The removal percentage increased with the adsorbent dose up to a certain limit and then it reached a constant value. The increase in the adsorption of Cu (II) with adsorbent dose was due to the availability of more surface area of the adsorbent for adsorption. The results showed that 3.0 g/L of modified sawdust was required for the 91% removal of Cu (II) from the initial concentrations of 50 mg/L.

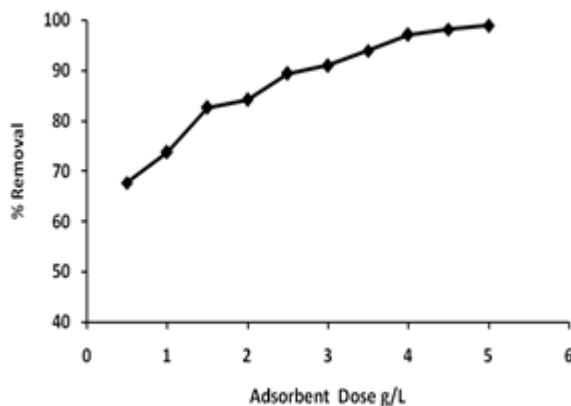


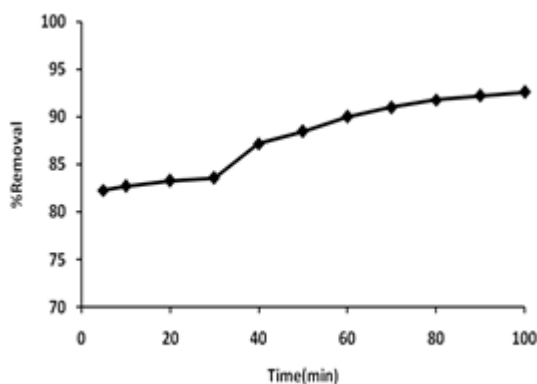
Fig. 2. Effect of adsorbent dose on Cu (II) removal.

(Cu (II) initial conc. = 50 mg/L, pH =6, Time= 60 min, shaker speed=100)

### 3.3. Effect of contact time and agitation rate

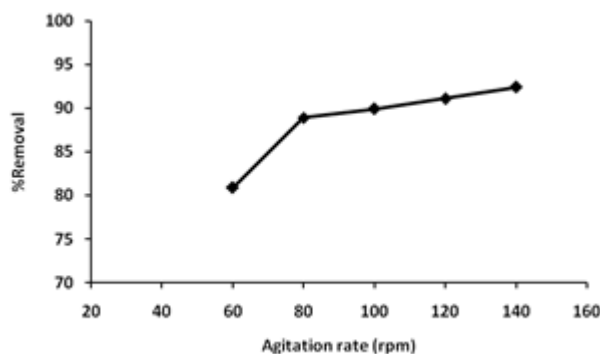
The effect of contact time in the range of 5-100 min was studied. The results showed that, in a interval of 60 minutes, more than 90.0% of the Cu was removed "Figure 3". However, for a removal of about 92.6%, a time interval of 100 minutes was needed.

The agitation speed ranging between 60 and 140 rpm was maintained. According to the "figure4", the speed had little effect. The stirring speed of 100 rpm was chosen in the next experiments. The small effect of agitation showed that external mass transfer was not the rate limiting step.



**Fig. 3.** Effect of time on Cu (II) removal.

(Cu (II) initial conc. = 50 mg/L, pH =6, adsorbent dose=3g /L, shaker speed=100 rpm)



**Fig. 4.** Effect of agitation rate on Cu (II) removal.

(Cu (II) initial conc. = 50 mg/L, pH =6, adsorbent dose=3g /L, time =60 min)

### 3.4. Initial concentration

The effect of the initial Cu (II) concentration on the removal using the above optimum concentrations was investigated. The results presented in "Table 1" show that for Cu (II) concentration of 500 mg/L about 96%, removal is possible. For concentrations up to 500 mg/L, Cu (II) quantitative removal (95.8%) was achieved. This is a relatively large range (20-500 mg/L) and the percentage of removal in this range was significant.

### 3.5. Application

In order to test the reliability of the proposed removal methodology, different concentrations of Cu (II) from tap water, Dezful river water and industrial water of Mahshahr petro chemistry samples were applied in order to check the removal. For this purpose, 50 mL of each of the samples was treated under the general procedure. Spiking Cu (II) to the samples indicated the validity of the procedure "Table 2".

**Table 1**  
Effect of Cu (II) initial concentration on the removal.

Cu (II) initial Concentration (mg/L)	Removal (%)
20	83.8
50	89.5
100	90.0
150	91.2
200	92.9
250	93.0
300	93.1
350	93.8
400	97.2
450	97.2
500	95.8

**Table 2**  
Real samples.

sample	Added Cu(II) (mg/L)	Remained Cu(II) (mg/L)	Removal (%)
Tap water	20	1.9	90.5
	50	4.7	90.7
	100	8.4	91.6
River water	20	1.9	90.4
	50	5.5	88.9
	100	9.4	90.6
Industrial wastewater	20	2.1	89.7
	50	5.3	89.5
	100	9.8	90.2

#### 4. Conclusion

The present investigation evaluated the fact that the chemically modified sawdust with diethylenetriamine can be used as an effective adsorbent for the removal of copper from different water samples. Contact time, adsorbent dosage and pH are the most effective parameters on adsorption of Cu (II). The effects of these parameters on the adsorption of Cu (II) were examined applying optimal experimental conditions. From the experimental results, it was found out that for Cu (II) concentrations ranging 20–500 mg/L, quantitative removal (more than 83%) was obtained in a single adsorption. The method was applied for the removal of copper from real samples of different waters such as industrial water, river water and tap water samples, in all of which removal was more than 88.

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