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# Removal of copper from aqueous solution using newspaper pulp as an adsorbent

S. Chakravarty*, S. Pimple, Hema T. Chaturvedi, S. Singh, K.K. Gupta

*Analytical Chemistry Centre, National Metallurgical Laboratory, Jamshedpur 831007, India*

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ABSTRACT

Newspaper pulp was found to be a potential adsorbent for removal of copper from aqueous medium. Detail adsorption study of Cu on newspaper pulp was investigated. Batch adsorption study was carried out as a function of contact time, adsorbent dose, temperature (303–323 K). The experimental data was analyzed using Freundlich, Langmuir, Dubinin–Radushkevich (D–R) and Redlich-Peterson (R–P) isotherm models. It was found that Freundlich, Langmuir and R–P models fitted well. pH variation study revealed that the adsorption increased with increase in pH of the solution. Maximum loading capacity was found to be 30 mg $g^{-1}$ at 20 mg $L^{-1}$ of initial Cu concentration. Adsorption data were analyzed using two kinetic models, Lagergren first order and pseudo second order. It was observed that pseudo second order represented the best correlation. Langmuir isotherm was used to obtain the thermodynamic parameters such as free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) of adsorption. The negative value of free energy and positive value of enthalpy change indicate that the adsorption of Cu on newspaper pulp is a spontaneous process and endothermic. The results of activation energy also confirmed that the adsorption of Cu on newspaper pulp is physical in nature. Present investigation emphasized that newspaper pulp may be utilized as a low cost adsorbent for copper removal.



## 1. Introduction

Release of heavy metals such as Cr, Ni, Cd, Pb and Cu from industrial wastewater into the aquatic system is a major environmental concern. These heavy metals enter into the urban water system causing health problems. Soils irrigated by wastewater results in accumulation of heavy metals in the surface soils which further releases these contaminants upon saturation into groundwater and soil solution for plant uptake. Waste water irrigation further enhances the heavy metal content of the soils [1].

Copper is one of the major contaminants emanating from electrical, electroplating, and metal finishing industries. It is often found in high concentrations near mines, landfills and waste disposal sites. In human copper toxicity causes itching and dermatization, keratinization of the hands and soles of feet [2,3]. Severe gastro-intestinal irritation and possible changes in the liver and kidney occur due to intake of excessively large doses of copper [4]. Inhalation of copper spray increases the risk of lung cancer among exposed workers [5]. Maximum permissible concentrations of copper in drinking water by World Health Organization (WHO), United State Environmental Protection Agency (USEPA) are 1–2, and 1.3 mg $L^{-1}$, respectively [6]. The permissible level of copper for industrial waste water to be discharged to the surface water is 3 mg/L [7]. Hence the removal of copper from wastewater before its discharge into the aquatic system is extremely important and deserves immediate attention.

Coagulation, chemical precipitation, ion exchange, membrane filtration, electrochemical techniques are some of the most widely used techniques for the removal of heavy metals including copper [8]. Adsorption process is a simple cost effective method which has been extensively adopted. According to Babel and Kurniawan [8] low cost adsorbents having high adsorption capacity for heavy metals include chitosan, zeolites, waste slurry, clay, peat moss, fly ash, coal, blast furnace slag, lignin, etc. Of these only chitosan, zeolite, fly ash peat moss and waste slurry show mentionable adsorption of Cu(II). Maximum adsorption capacity of chitosan for Cu(II) was 222 mg $g^{-1}$, chabazite (zeoliote) 5.10 mg $g^{-1}$, fly ash-wollastonite 1.18 mg $g^{-1}$, eutrophic peat moss 19.56 mg $g^{-1}$ and waste slurry was 20.96 mg $g^{-1}$. Excepting chitosan none of the low cost adsorbents reviewed were effective for copper removal from industrial effluents. Of late biosorption has proven to be an effective technology for the removal of heavy metals. Bio-materials used to remove heavy metals include carrot residues [9], *Sargassum wighiti* [10], lentil, wheat, rice [5], tea industry waste [11], biomass of *Cladonia rangiformis hoffm* [12] and *Neorospora crassa* [13].

Cellulose is the most abundantly available natural biopolymer. Sorptive properties of cellulose towards metal are well documented [14,15]. Cellulose has better environmental acceptability in

* Corresponding author. Tel.: +91 657 2271709; fax: +91 657 2270527.
*E-mail address:* sanchita@nmlindia.org (S. Chakravarty).

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**Nomenclature**

| | |
|---|---|
| $A$ | Arrhenius factor |
| $b$ | Langmuir constant ($L\,mg^{-1}$) |
| $C_0$ | initial Cu concentration of the solution ($mg\,L^{-1}$) |
| $C_e$ | equilibrium Cu concentration ($mg\,L^{-1}$) after adsorption |
| $C'_e$ | equilibrium Cu concentration ($mg\,L^{-1}$) after desorption |
| $E$ | mean free energy of adsorption ($KJ\,mol^{-1}$) |
| $E_a$ | Arrhenius activation energy ($KJ\,mol^{-1}$) |
| $f$ | Redlich–Peterson constant |
| $\Delta G^\circ$ | free energy of adsorption |
| $\Delta H^\circ$ | standard enthalpy |
| $k$ | specific rate constant |
| $k_1$ | first order rate constant |
| $k_2$ | second order rate constant of adsorption ($g\,mg^{-1}\,min^{-1}$) |
| $k_d$ | D–R constant related to adsorption energy ($mol^2\,KJ^{-2}$) |
| $k_f$ | Freundlich constant |
| $k_r$ | Redlich–Peterson constant |
| $K_L$ | equilibrium constant corresponding to the Langmuir constant $b$ ($L\,mol^{-1}$) |
| $m$ | mass of the adsorbent |
| $n$ | Freundlich constant |
| $N$ | Redlich–Peterson constant |
| $q_e$ | amount of Cu(II) adsorbed at equilibrium ($mg\,g^{-1}$) |
| $q_t$ | amount of Cu adsorbed at time ($t$) |
| $Q_m$ | theoretical saturation capacity for D–R isotherm ($mg\,g^{-1}$) |
| $R$ | gas constant ($kJ\,mol^{-1}\,K^{-1}$) |
| $R^2$ | statistical linear coefficient of determination (the square of correlation coefficient) |
| $\Delta S^\circ$ | standard entropy |
| $T$ | temperature (K) |
| $V_m$ | saturated monolayer adsorption capacity ($mg\,g^{-1}$) |
| $X$ | $C_0 - C_e$ |
| $X/m$ | loading capacity |

*Greek letter*

| | |
|---|---|
| $\varepsilon$ | Polyani potential |

comparison to synthetic polymers with regard to biological compatibility and bio-decomposition. Waste newspaper pulp is a low cost cellulosic material. The present paper investigates, in detail, the adsorption of copper by processed newspaper pulp. Kinetics and thermodynamics of the adsorption process has been studied along with the conventional treatments of adsorption envelope, loading capacity and adsorption isotherm studies. The paper attempts to examine the reuse of newspaper as an adsorbent for the contaminated water bodies.

## 2. Experimental

### 2.1. Preparation of processed newspaper pulp

Old newspaper was treated with concentrated sodium bicarbonate solution for removing the foreign materials like, grease, black ink and the bleaching material (chlorine dioxide) which are usually present in the newspapers. The newspaper pulp was washed several times with distilled water till the pH of the supernatant water layer of the pulp was around 6.5–7. The pulp was gravity filtered through Whatman 40 filter paper, air dried and finely ground by mixer grinder to make it feathery. Characterization of the newspaper pulp has been detailed elsewhere [16].

### 2.2. Reagents

Analytical grade $CuSO_4{\cdot}7H_2O$ was dehydrated at 110 °C and was used for making stock solution of Cu(II) (1000 mg $L^{-1}$) in 18 MΩ ASTM grade water. The stock solution was diluted by serial dilution method as per requirement.

### 2.3. Batch adsorption experiments

Adsorption experiments were carried out in batches of 50 mL of 7.02 mg $L^{-1}$ of Cu(II) solution with known weights of newspaper pulp. pH of the solution was kept at $5.8 \pm 0.05$ for all experiments unless otherwise mentioned. The solutions were shaken in a mechanical shaker for a definite period of time. It was then filtered and Cu concentration was measured before and after adsorption by atomic absorption spectrophotometer (GBC AVANTA). Adsorption parameters such as adsorbent dose, shaking time were optimized by the method of continuous variation. The optimized parameters were found to be 0.1 g adsorbent dose and 30 min contact time to reach equilibrium for 7.02 mg $L^{-1}$ Cu(II) concentration.

### 2.4. pH variation study

To study the influence of pH on adsorption, the batch experiments were carried out in the pH range of 2.0–7.0. pH of the solution was adjusted using dilute NaOH and HCl. For desorption study, initially Cu(II) was adsorbed over the newspaper pulp at pH 5.8. The pH was then adjusted in the range of 2–7 using dilute NaOH and HCl and were shaken for half an hour. The percentage of desorption was calculated as follows.

$$\%\text{Desorption} = \left(\frac{C'_e - C_e}{C_0 - C_e}\right) \times 100$$

where $C_0$ is the initial Cu concentration of the solution ($mg\,L^{-1}$), $C_e$ is the equilibrium Cu concentration ($mg\,L^{-1}$) at a particular pH, $C_e'$ is the equilibrium Cu concentration ($mg\,L^{-1}$) at a particular pH after desorption.

### 2.5. Kinetic and thermodynamic study

Kinetic and thermodynamic studies were carried out for three different Cu(II) concentrations at temperature of 30, 40 and 50 °C.

### 2.6. Instrumentation

Cu(II) was analyzed using atomic absorption spectrophotometer, GBC AVANTA, chloride, fluoride, phosphate and nitrate was measured using ion chromatography (Metrohm Ion Chromatograph).

## 3. Results and discussion

### 3.1. Effect of adsorbent dose

Fig. 1 shows the adsorption of Cu(II) with varying weight of the adsorbent at pH $5.8 \pm 0.05$.

It indicates that the uptake of Cu(II) increases as the adsorbent dose increases from 0.01 to 0.2 g in 50 mL of Cu(II) solution. Beyond 0.2 g of the adsorbent the Cu(II) removal becomes more or less constant over the concentration range of 7.02–24.39 mg $L^{-1}$. The adsorbent dose of 0.2 g was able to adsorb 94.2% Cu(II) from 50 mL of 7.02 mg $L^{-1}$ Cu(II) solution. This increase of Cu(II) removal may be attributed to the active site of the adsorbent surface.