

## SORPTION POTENTIAL OF COPPER IONS FROM AQUEOUS SOLUTIONS ONTO *Cicer arietinum* HUSK

M. Sher, N. Parveen, N. Batool, M. A. Hussain, M. Ali, M. A. Shaheen, and S. Bashir\*

Department of Chemistry, University of Sargodha, Sargodha 40100, Pakistan

\*Department of Pharmacy, University of Sargodha, Sargodha 40100, Pakistan

Corresponding Author: e-mail: msherawan@yahoo.com

**ABSTRACT:** Efficient removal of copper from aqueous media was carried out using *Cicer arietinum* husk, a biosorbent. Sorption phenomenon was studied in detail by varying solution pH, contact time and sorbent dose. The results indicated the significant enhanced sorption of copper ions after thermal (100-800°C) treatments of biosorbent. About 100% removal of copper was achieved by thermally treated sorbent in 1.30 h, therefore, *C. arietinum* husk appears to be an efficient and cost effective biosorbent to remove copper ions from industrial effluents. The method used is convenient, efficient and free from interferences, hence it can be adopted for industrial waste water treatment.

**Keywords:** Atomic Absorption Spectroscopy; Biosorbent; *C. arietinum* husk; Heavy Metals

### INTRODUCTION

Metal ions generated during industrial activities pose a serious threat to the environment, aquatic life and human health. Toxic metals are often discharged in effluent water by several industries that significantly contaminate both the fresh and ground water and marine environment (Balkose and Baltacioglu, 1992).

A number of methods are available for the removal of heavy metals ions from industrial effluents; however, utilization of agricultural by-products to remove heavy metals from aqueous solutions is in forefronts. Sunflower stalk, (Gang and Weixing 1988), peanut skin (Randall *et al.*, 1975), tea waste (Amir *et al.*, 2005), coffee grounds (Macchi *et al.*, 1986), apple waste (Maranon and Sastre 1991), banana pith (Low *et al.*, 1995), chitosan (Saucedo *et al.*, 1993, Karthikeyan *et al.*, 2004), sugar-beet pulp (Reddad *et al.*, 2003), wheat bran (Dupond and Guillon, 2003), sugarcane bagasse (Krishnani *et al.*, 2004, Mall *et al.*, 2006), and cassava waste (Horsfall *et al.*, 2003) were studied and showed potential for the adsorption of heavy metal ions from aqueous solutions (Saeed *et al.*, 2005). As agricultural by-products are cost effective, naturally occurring, easily available and stable at elevated temperatures hence no complicated regeneration process, care and maintenance is required.

We wish to report the sorption potential of *C. arietinum* husk for the removal of copper because it is cheap and easily available agricultural waste product which is being exploited for the removal of copper ions from industrial effluents. Our intention was focused to explore the influence of all possible parameters for the sorption of copper onto bioadsorbent such as shaking time, adsorbent dose, pH, chemical and thermal treatment of sorbent.

### MATERIALS AND METHODS

All chemical used were of A. R grade manufactured by E. Merck/ BDH, Germany and used as received without further purification. Doubly distilled water was used for preparation of all solutions. Atomic absorption spectrophotometer, AA-6300, Shimadzu, Japan was used for the determination of copper contents. pH meter (Model No. 3510, JENWAY) was used to check the pH of the metal solutions. For continuous shaking, Shaker PA – 42/250 R P and for weighing electric balance of Shimadzu (AX 200) were used.

*C. arietinum* husk utilized for the current study was collected as a waste during the milling process. Sorbent was washed thoroughly with double distilled water to remove foreign impurities followed by soaking in boiling water for 15 minutes. Filtration was done and residue was sun dried followed by oven drying at 80°C for 01 hour to remove moisture. The sorbent was ground by electrical grinder, sieved and stored in contamination free atmosphere.

**Metal Analysis:** Stock solution (1000 ppm) of copper was prepared by dissolving 3.93 g of copper sulphate in 1000 mL distilled water. All experimental solutions were prepared by diluting the stock solution to the required concentration. The copper contents were measured by using atomic absorption spectrophotometer at 324.8 nm., slit width: 0.7 nm, Lamp mode: BGC-D2, Lamp current: 6mA, Burner height: 7 mm, Flame type: Air-Acetylene, Fuel gas flow: 1.8 Lminutes<sup>-1</sup> and Support gas flow: 15.0 Lminutes<sup>-1</sup>. The instrument was calibrated within the linear range of analysis and a correlation coefficient of 0.998 was obtained for the calibration curve. The instrument was periodically checked throughout the analysis with known standards. The amount bound onto the biomass was assumed to be the difference between

the initial metal concentration and that found in the supernatant. The copper uptake was calculated by the simple concentration difference method (Volesky and Holan 1995)

**Batch Adsorption Experiments:** Batch adsorption experiments were conducted at room temperature. For each experimental run, 25 mL of copper solution of known initial concentration were taken in a reagent bottle. A suitable adsorbent dose was added to the solution and the mixture was shaken at a constant agitation speed (100 rpm). Samples were withdrawn at appropriate time intervals (30-90 minutes) and then filtered. The filtrate was analyzed for residual copper concentration.

**Effect of Thermal Treatment :** Influence of thermal treatment of *C. arietinum* husk on elimination of copper from aqueous media was investigated by treating the sorbent at temperatures 100°C, 200,300°C, 400°C, 500°C, 600°C, 700°C and 800°C. Thermally treated husk (1 g) was mixed with 25 mL of 3 mgL<sup>-1</sup> solution of copper. The reagent bottles were shaken using shaking speed 100 rpm at room temperature for 90 minutes. Samples were withdrawn at time interval of 30, 60, and 90 minutes and then filtered. The filtrate was analyzed for residual copper concentration.

**Influence of Chemical Treatment:** The sorbent was washed with distilled water and dil. HNO<sub>3</sub> respectively and effect of water and acid treatment on sorption of copper onto husk was examined by shaking chemically treated sorbent (1 g) with 25 mL of 3 mgL<sup>-1</sup> solution of copper at shaking speed of 100 rpm at room temperature for 90 minutes. The effect of variation of pH from 2 to 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 on the rate of adsorption was investigated by using 25 mL of 3 mgL<sup>-1</sup> copper solutions and 1 g of sorbent. The adsorbent-adsorbate mixture was shaken at room temperature using agitation speed 100 rpm for 90 minutes to determine the concentration of copper in solution by using atomic absorption spectrophotometer.

**Sorbent Dose:** The effect of sorbent dose on the removal of copper was measured by contacting 25 mL of 3 mgL<sup>-1</sup> of copper solution with different amounts of *C. arietinum* husk (0.25-2 g) using shaking speed 100 rpm for 90 minutes. In all sets of experiments, reagent bottles were shaken at a speed of 100 rpm for 90 minutes. The solutions were then filtered off before analysis for copper concentration.

**Effect of Contact Time:** The effect of contact time on the removal of copper was determined by using 25 mL of 3 mgL<sup>-1</sup> of copper solution with 2 g of *C. arietinum* husk (0.25-2 g) at shaking speed 100 rpm for 30, 60 and 90 minutes. The solutions were then filtered and analyzed for copper concentration.

## RESULTS AND DISCUSSION

**Metal Analysis:** The metal adsorbed onto the biomass was determined by Atomic Absorption spectrophotometer and calculated as the difference between the initial concentration of metal in the solution and concentration of metal in the solution after adsorption. The metal adsorption onto biomass under different conditions are given in tables 1-3, figures 1-3 and have been discussed below.

**Batch Adsorption:** For each experiment 25 mL of unknown concentration of copper solution was used along with varying amount of adsorbent dose. The best dose of adsorbent for adsorption was found to be 2.0 g. Similarly the effect of time was also determined by measuring the concentration of copper from solution at different intervals (30-90 min). Best adsorption time was found to be 90 minutes. The results of the sorbents dose and contact time are given in figures 2 and 3 respectively.

**Effect of Thermal Treatment:** Effect of thermally treated *C. arietinum* husk for the removal of copper from aqueous media was studied in the temperature range of 100-800°C while keeping the concentration of sorbate (3 mgL<sup>-1</sup>) and quantity of sorbent (1 g) constant and shaking time 30, 60 and 90 minutes. The %age sorption obtained after 30, 60 and 90 minutes at different temperatures are given in table 1. Maximum sorption achieved at 800°C (97.67%) as compared to sorption obtained at low temperatures indicates that high temperature may activate the husk for enhanced metal adsorption (Inglezakis *et al.*, 2004.). The results differ significantly from each other as 72.14% sorption was noted at 100 °C and 97.67% at 800 °C.

**Influence of Chemical Treatment:** The chemical treatment of sorbent may or may not affect the sorption process. However, in general practice, acid treatment is used for the biosorbents to check its effects on metal uptake along with water-washing. Therefore, biosorbent was treated with nitric acid and distilled water and %age sorption of metal was studied after 30, 60 and 90 minutes (Table 2). Highest copper uptake (88.67%) was obtained by using distilled water treated sorbent. The results has shown that *C. arietinum* husk do not require acid treatment. Effect of pH on the sorption of copper using *C. arietinum* husk was studied at the pH range 2.0 - 12.0 by keeping all other relevant parameters constant. The results of % sorption are given in Table 3. The maximum sorption (85.67%) of copper was obtained at pH 9 with 90 minutes contact time of sorbant and sorbate. The effect of pH may be explained by the fact that at lower pH, there exist appreciable concentrations of H<sup>+</sup> ions that compete with already present Cu<sup>+2</sup> ions for available binding sites. As a result there is a decrease in the copper uptake. However, with the increase in pH at sorbate

solution, the number of  $H^+$  ions decreases and hence more sites are available for copper uptake (Bajpai and Rohit, 2007). The effect of pH on % sorption of copper onto biosorbent are given in table 3 which show that with different contact time maximum sorption was observed at pH 9.

**Table 1. Effect of thermal treatment of sorbent on % sorption of copper from water solution of known concentration**

Temperature (°C)	Sorption (%) after 30 min (±SD)	Sorption (%) after 60 min (±SD)	Sorption (%) after 90 min (±SD)
100	44.23±0.11	70.68±0.07	72.14±0.12
200	40.15±0.14	57.92±0.10	61.05±0.14
300	55.23±0.09	69.00±0.14	69.29±0.09
400	62.05±0.15	69.75±0.09	69.88±0.11
500	85.14±0.12	86.52±0.11	86.77±0.15
600	87.13±0.08	87.45±0.12	87.48±0.13
700	95.40±0.09	95.76±0.09	96.79±0.11
800	97.33±0.11	97.65±0.11	97.67±0.10

**Table 2. Effect of chemical treatment of sorbent on % sorption of copper**

Time (min)	% sorption (Nitric acid) (±SD)	% sorption (Distilled water) (±SD)
30	77.0 ±0.10	84.33±0.12
60	77.0±0.09	88.00±0.10
90	84.0±0.11	88.67±0.11

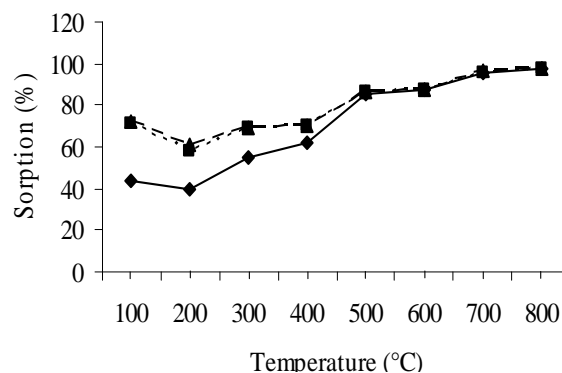
**Table 3. Effect of pH on % sorption of copper onto biosorbent**

pH	% sorption (30 min) (±SD)	% sorption (60 min) (±SD)	% sorption (90 min) (±SD)
2	20.0±0.10	30.0±0.13	35.0±0.09
3	30.5±0.09	61.4±0.10	63.1±0.14
4	42.5±0.11	70.2±0.12	75.4±0.12
5	70.15±0.10	76.9±0.11	77.0±0.10
6	72.2±0.12	78.3±0.09	79.0±0.11
7	80.0±0.11	80.0±0.11	80.5±0.08
8	78.5±0.10	79.15±0.12	80.12±0.10
9	84.33±0.09	85.33±0.11	85.67±0.11
10	51.5±0.12	61.2±0.10	63.4±0.12
11	52.0±0.11	58.5±0.13	60.2±0.10
12	10.4±0.13	20.2±0.10	25.0±0.11

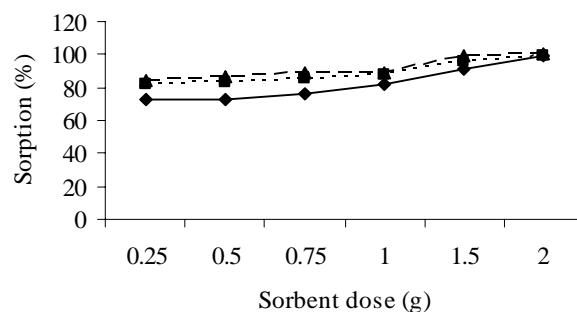
**Sorbent Dose:** The amount of sorbent was assorted from 0.25 g - 2.0 g to calculate %age sorption for 30, 60 and 90 minutes keeping all other conditions constant. Increase

in the adsorption with increasing dose of adsorbent was expected due to the increase in adsorbent surface area and the availability of more adsorption sites (Mall et al., 2006, Pandey *et al.*, 2007). Nevertheless, 2.0 g of sorbent was found sufficient to remove 99.73% of copper at contact time of 90 minutes (Figure 2).

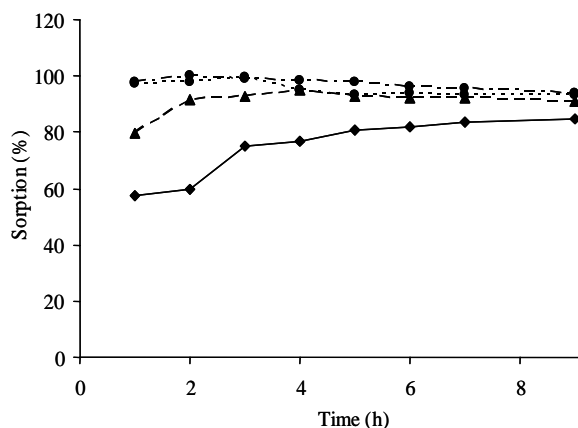
**Effect of Contact Time:** To observe the effect of contact time on sorption, time was varied from 30 minutes to 9 hours. For comparison purpose, %age sorption was studied for untreated sorbent, chemically treated sorbent, thermally treated sorbent and chemically plus thermally treated sorbent keeping all other conditions constant. For untreated sorbent maximum %age sorption obtained was 84.67% at 9 hours while for chemically treated sorbent maximum %age sorption obtained was 95 % at 4 hours. Thermally treated sorbent showed maximum %age sorption was 99.67% at 3 hours while about 100% sorption at 2 hours was attained for chemically plus thermally treated sorbent. Results are illustrated in Figure 3. The results obtained with chemically treated husk are found to be statistically different from those obtained with thermally treated husk and thermally treated plus chemically treated husk which clearly indicates enhanced sorption in the later case.



**Fig. 1. Effect of thermal treatment of sorbent on % sorption after 30 (—), 60 (---) and 90 min (----).**



**Fig. 2. Effect of sorbent dose on % sorption after 30 (—), 60 (---) and 90 min (----).**



**Fig.3. Effect of contact time on % sorption employing untreated (—), chemically treated (---), thermally treated (----) and chemically plus thermally treated (— · —) *C. arietinum* husk.**

**Conclusions:** Use of *C. arietinum* husk (biosorbent) for the removal of bivalent copper ions is an efficient, convenient and economical method. At room temperature, by applying said biosorbent with shaking speed of 100 rpm and at pH 9, maximum sorption of copper can be achieved in 1.30 h. High metal sorption capacity and satisfactory removal of copper by *C. arietinum* husk indicates that this method can easily be adopted by industries for the purification of industrial effluents polluted with copper metal.

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