

“Research Note”

REMOVAL OF HEAVY METALS FROM AQUEOUS
SOLUTION BY CARROT RESIDUES*

T. ESLAMZADEH^{1**}, B. NASERNEJAD² B. BONAKDAR POUR²,
A. ZAMANI² AND M. ESMAAIL BYGI²

¹ Department of Biology, Shiraz University, Shiraz, I. R. of Iran 71454, Email: tesslam2@yahoo.com

² Department of Chemical Engineering, Amirkabir University of Technology,
No. 424, Hafez Ave., Tehran, I. R. of Iran Email: nasernejad@yahoo.com

Abstract – The removal of copper (II), zinc (II), and chromium (III) from wastewater by carrot residues (CR) was investigated to evaluate cation exchange capacity. The effects of solution pH and co-ions were studied in batch experiments. Adsorption equilibria were initially rapidly established, and then decreased markedly after 10 min. Column experiments were carried out in a glass column filled with CR to evaluate the metal removal capacity. The influences of the feed concentration and feed rate were also studied in order to compare the dynamic capacity for metal binding in different feed concentrations.

Keywords – Carrot residues, heavy metals, metal binding, and removal

1. INTRODUCTION

Contaminated soils and waters pose a major environmental and human health problem [1]. Man's awareness of the hazards of heavy metals now covers a wide spectrum of metals such as lead, cadmium, chromium, copper and zinc [2]. Among these, chromium and lead poisoning in humans cause disfunction of the kidneys, reproductive system, liver and central nervous system [3]. If Locoweed (*Astragalus*) is eaten by livestock, the large amounts of selenium in these plants affect the animal's nervous system causing an illness called “blind stagger”, which often kills livestock [4]. Similarly, bees that harvest pollen from locoweed often produce honey containing large amounts of selenium [4]. To remove heavy metals effectively from metal laden waste water, engineers and scientists have developed processes and measurements, namely chemical precipitation, ion exchange, membrane separation, chelation and adsorption.[5-9].

Plants possess a range of potential cellular mechanisms that may be involved in the detoxification of heavy metals and tolerance to metal stress. These include roles for binding to cell walls and extracellular exudates for chelation of metals by peptides such as phytochelatin, and by metallothioneins [6-8].

Compartmentation of metals in the vacuole by tonoplast located transporters is a tolerance mechanism [8]. Although adsorption to the cell wall must be of limited capacity, [6] a heavy metal tolerant plant, *Silene vulgaris ssp. humilis* accumulates a large range of metals in the epidermal cell walls, either bound to a protein or as silicates. [9]. Root exudates have a variety of roles, including

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**Corresponding author

metal chelators that may enhance the uptake of certain metals [10-13].

Agricultural waste such as tree bark, peanut skin and hull, and growing plants (Tobacco and tomato root tissues) have been used to remove heavy metals from water [10-12]. Because carrot residues (CR) are readily available, their use as adsorbents seems appropriate.

In the present study, CR were used as an adsorbent for the removal of metals. The cation exchange and/or adsorptive properties of these residues can be attributed to the presence of carboxylic, phenolic, and other functional groups, which exist in either the cellulosic matrix or in the materials associated with cellulose such as hemicellulose, lignin and also in the peptides [8, 10, 12].

2. MATERIAL AND METHODS

Carrot residue for these experiments was obtained from a carrot - juice processing factory. Carrot residues were dried overnight at 60° C in a Jurgens WTC Binder model oven, ground in a ball mill, and sieved into different fractions. In order to eliminate soluble components such as tannin, resins reducing sugars and coloring substances, the residues were washed with 0.5 M HCl and distilled deionized water until a constant pH was achieved; The pH meter model was a Hanna 7010 Corning 2400E. Batch experiments were performed at room temperature. All glassware tubes were acid-cleaned and rinsed thoroughly before use with distilled deionized water. Various initial metal concentrations were prepared by serial dilution of 1000 ppm of standard solution. The PH in the solution was adjusted with 0.1 N/IN NaOH and 0.1 N/1N HCl to cover a PH range from 2 to 6. The test tubes were then sealed with caps and placed on a Kohner ISF-1-W rotary shaker. The test tubes were removed after 24 hour shaking and centrifuged for 5 minutes at 3000 rpm. The supernatant was analyzed using a flame atomic absorption spectrophotometer (Phillips PU 9100) for residual metal content. Kinetic studies of metal removal by CR were carried out with a 200 ml copper (II), zinc (II) and chromium (III) solution of 20 ppm with 0.5 g CR. Samples were taken periodically from the suspension and centrifuged immediately to remove adsorbents. Experiments were also carried out in a glass column of 4.13 cm internal diameter and 45 cm length filled with CR. The metal solution was percolated through the packed column at a flow rate 5, 10, 15 ml/min for zinc (II) and 10, 20, 30 ml/min for Copper (II). Effluent samples were collected every 1 hour and analyzed by flame atomic absorption. After exhaustion of the adsorbent, the adsorbed metal was recovered by elution with 0.5 N HCl. Carrot residues were reused by washing with water to eliminate any excess mineral acid. The experiments were repeated twice.

3. RESULTS AND DISCUSSION

a) Batch experiments

I. Sorption Kinetics: The adsorption Kinetics of the metals with time at an initial metal concentration of 20 ppm at PH= 5 for copper (II), Zinc (II) and chromium (III) are shown in Fig. 1. The rate of metal sorption was rapid initially, but decreased markedly after 10 min. The CR functional groups initially act as coordination sites for metal uptake [8, 10, 13]. A similar initial rapid uptake of cadmium by chitosan has been reported by Jha et al [14]. From these experimental results, an equilibrium contact time of 24 hours was used in all further experiments.

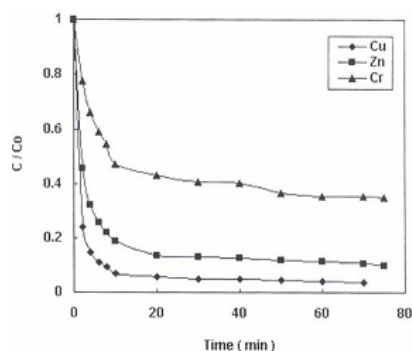


Fig. 1. Kinetics of metal removal by CR [CR: 0.5 g/200 ml]

II. Effect of PH: PH in solution has been identified as the most variable governing metal adsorption on biosorbents. This is partly due to the fact that hydrogen ions themselves are strongly competing adsorbents. The PH solution influences the specification of metal ions and the ionization of surface functional groups [8, 13, 15, 16]. The effects of pH for Copper (II), Zinc (II) and Chromium (III) removal are shown in Figs. 2, 3 and 4, respectively. The maximum removal was 97% for Copper (II), 90% for zinc (II) and 65% for chromium (III). These experimental results indicate that the binding of Zinc (II) is more PH- dependent than those of Chromium (III) and Copper (II).

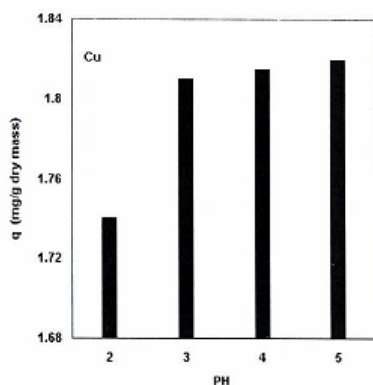


Fig. 2. Effect of PH on removal of Copper by CR [metal con .20 ppm]

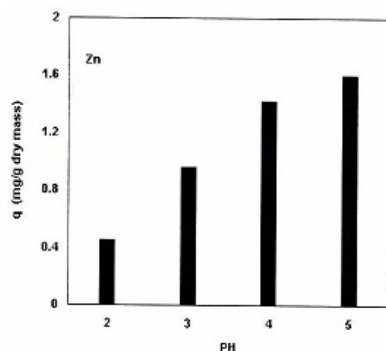


Fig. 3. Effect of PH on removal of Zinc by CR [metal con .20 ppm]

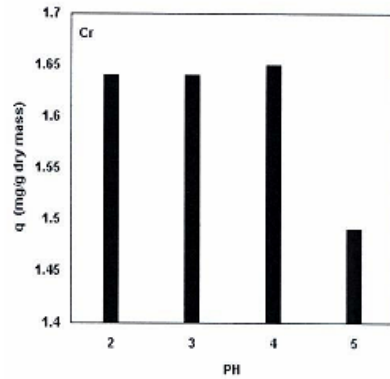


Fig. 4. Effect of PH on removal of chromium by CR [metal con.20 ppm]

III. Effect of co-ion: The effects of co-ions [Zn (II) & Cr (III)] on Copper and [Zn (II) & Cu (II)] on Zinc(II) removal by CR are indicated in Figs.5-7.

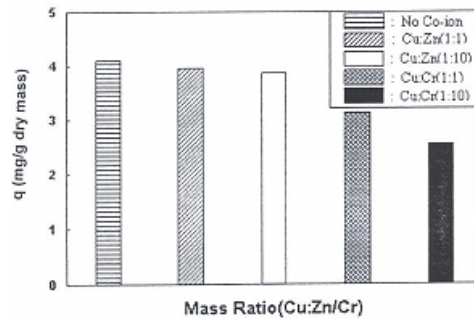


Fig. 5. Effect of co-ion (Zn, Cr) on the removal of Copper [Cu: 20 ppm, PH=5]

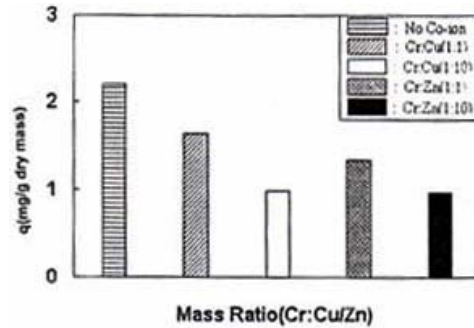


Fig. 6. Effect of co-ion (Zn, Cu) on the removal of Chromium [Cr: 20 ppm, PH=4]

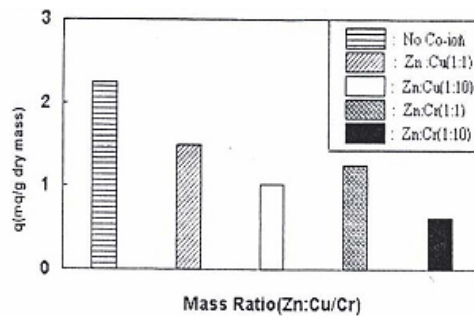


Fig. 7. Effect of co-ion (Cu, Cr) on the removal of Zinc [Cu: 20 ppm, PH=51]

b) Column experiments

Effect of feed concentration and flow rate: The experiments concerning the effect of feed concentration on the removal of copper (II) and zinc (II) were carried out in a continuous glass column and the results are shown in (Figs. 8-13). The flow rate of the feed metal solution was 20ml/min for Copper (II). The pH of the feed solution was maintained at 5. A breakthrough occurred at 5 hr, when the Copper (II) concentration was 50 ppm, while at 2.15 hr it appeared when the Copper (II) concentration was 100 ppm, and it appeared at 1 hr when the Copper (II) concentration was 200 ppm. The dynamic capacity was 9.375 mg Cu/g CR when the feed concentration was 50 ppm. However, the capacity decreased to 8.062 mg Cu/g CR and 7.5 mg Cu/g CR when the feed concentration was increased from 100 to 200 ppm. Dynamic capacity is defined as the amount of metal ion taken up prior to the breakthrough point [18]. Similar results were obtained for Zinc (II) removal. The flow rate of the feed metal solution was 10 ml/min. when the feed concentration was 50 ppm. Breakthrough occurred at 2.5 hr compared to a breakthrough point of 1 hr and 20 min with a Zinc (II) concentration of 100 and 200 ppm, respectively. The dynamic capacity was 2.3 44 mg Zn/g CR when the feed concentration was 50 ppm. The capacity decreased from 1.875 to 1.250 mg Zn/g CR when the feed concentration was increased to 100 and 200 ppm. The dynamic capacity of the CR ion exchanged column therefore decreased with an increase in feed concentration.

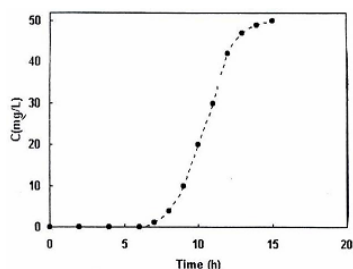


Fig. 8. Effect of feed concentration on removal of Copper by CR [PH= 5 C = 50 ppm]

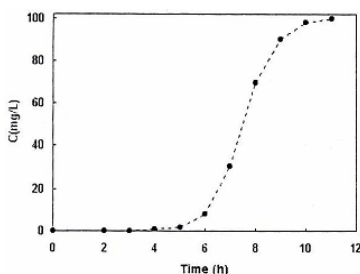


Fig. 9. Effect of feed concentration on removal of Copper by CR [PH= 5 C = 100 ppm]

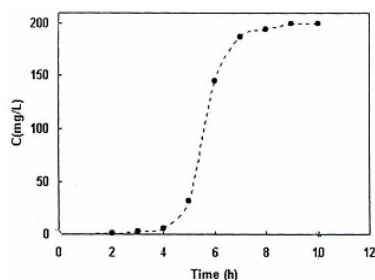


Fig. 10. Effect of feed concentration on removal of Copper by CR [PH= 5 C = 200 ppm]

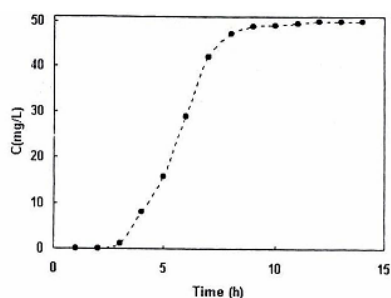


Fig. 11. Effect of feed concentration on removal of Zinc by CR [PH= 5, C = 50]

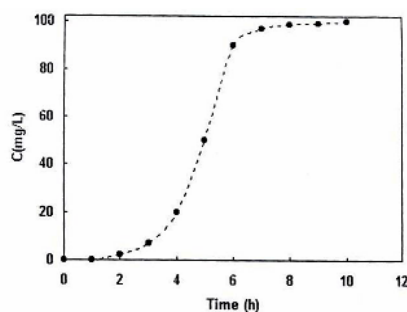


Fig. 12. Effect of feed concentration on removal of Zinc by CR [PH= 5 C = 100]

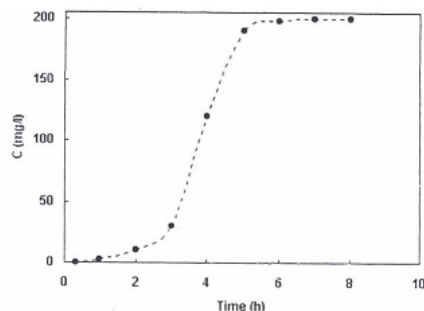


Fig. 13. Effect of feed concentration of removal of Zinc by CR [PH= 5, C = 200]

The effect of feed flow rate on the removal of Copper (II) by CR is shown in Fig. 14. The feed concentration was 50 ppm. The PH of the feed solution was maintained at 5. A breakthrough occurred at 2 hr when the Copper feed flow rate was 30 ml/ min., while at 5 hr and 11 hr it appeared when the Copper (II) flow rate was 20 and 10 ml/ min. Dynamic capacity was 10.31 mg/g CR when the feed flow rate was 10 ml/min. However, the capacity decreased to 9.375 mg/g CR and 5.625 mg/g /CR when the feed flow rate was increased to 20 and 30 ml/ min. The dynamic capacities were 2.1, 2.344 and 2.813 mg/g CR when the feed flow rates were 15.10 and 5 ml/min, respectively. Thus the dynamic capacity of the CR ion exchange column decreased with an increase in flow rate.

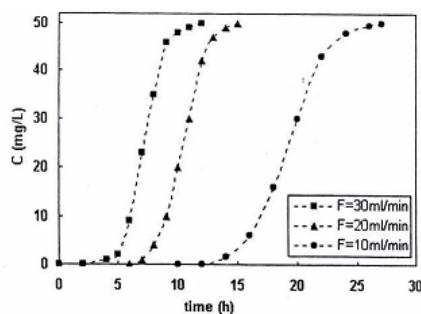


Fig. 14. Effect of feed flow rate on removal of Copper by CR [PH= 5]

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