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Studies on Removal of Heavy Metals Cr, Cu and Zn from Waste Water Using Carrot Residues.

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ABSTRACT

The removal of chromium (III), copper (II) and zinc (II) from aqueous solution by adsorption on carrot residues (CR) was studied. Biosorption of chromium (III), copper (II) and zinc (II) on CR were compared. It was shown that CR has high metal removal efficiency. The Freundlich and Langmuir model can describe the adsorption equilibrium of chromium (III), copper (II) and zinc (II) on CR. The Freundlich and Langmuir constants for biosorption of chromium (III), copper (II) and zinc (II) on CR were determined. The effect of solution pH on biosorption was studied.
Keywords: Isotherm, Biosorption, Equilibrium, Kinetics

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INTRODUCTION

Biosorption of heavy metal or radionuclides by various biological materials have been studied extensively in the last decade due to its potential, particularly in wastewater treat-ment [1,2]. Recovery of metals from solution would be beneficial since the metal recovered may be subsequently described from the biomass and recovered for reused; and release of potentially toxic metals into the environment would be restricted [3]. Heavy metals such as chromium (III), cadmium (II), copper (II), zinc (II), etc., in wastewater are hazardous to the environment [4]. Biosorption involves the use of biomass [5] or natural substrates such as agri-cultural residues [6], forestry waste products [6], microor-ganisms [7], casein [8] and sugar beet pulp [9]. Because carrot residues (CR) are readily available, their use as biosorbents seems appropriate. In the present study, CR was used as a biosorbent for the removal of heavy metals. The cation exchange properties of these residues can be attributed to the presence of carboxylic and phenolic functional groups, which exist in either the cellulosic matrix or in the materials associated with cellulose, such as hemicellu-lose and lignin [10-14]. The objective of the present study was to explore the feasibility of using the CR for the removal of toxic heavy metals from wastewaters. Batch experiments were carried out to investigate metal biosorption properties of CR. The effects of pH on the biosorption were studied.

MATERIALS AND APPARATUS

Biosorbent preparation

Carrot residue was used as a biosorbent for the removal of heavy metals. It contained upto 12% of the weight of the original fruit. Carrot residue is composed mainly of cellulose and lignin, both with the capacity to bind metal cations due to carboxylic and phenolic groups. Carrot residue was dried overnight at 60 8C in a convection oven, ground in a ball mill, and sieved into different fractions. In order to eliminate soluble components such as tannins, resins, reducing sugars and coloring agents, the residues were successively washed with 0.5 M HCl and distilled water until a constant pH was achieved.

EXPERIMENTAL PROCEDURE:

Preparation of single metal ion solutions

The stock solution of chromium (III), copper (II) and zinc (II) were prepared by dissolving their nitrate salts in distilled water separately. The test solutions containing single chro-mium (III) or copper (II) or zinc (II) ions were prepared by diluting a 1 g/L stock metal ion solution. The initial metal ion concentration ranged from 20 to 500 mg/L, in the case of copper and zinc and from 20 to 1350 mg/L in the case of chromium. The pH of each solution was adjusted to the required value with HCl or NaOH before mixing the bio-sorbent.

Biosorption studies

Experiments were carried out in an Erlenmeyer flask at the desired temperature and pH; the flasks were agitated on shaker for 24 h, which is more than ample time for biosorption equilibrium. The amount of metal adsorbed was determined by difference between the initial metal ion concentration and the final one after equilibrium was reached.

Analysis of metal ions

The concentration of chromium (III), copper (II) and zinc (II) ions in the liquid samples was determined using a Philips model PU9100 atomic absorption spectrophotometer before biosorbent addition and after equilibrium was reached.

Metal desorption and biosorbent regeneration

After saturation of the biosorbent, the adsorbed metal was recovered by elution with 0.5 M HCl. Carrot residues were reused by washing with water to eliminate any excess mineral acid.

Adsorption isotherms

Batch sorption tests were carried out at 25 8C on a rotary shaker for 24 h using 100 ml conical flasks. The test solution containing single metal ion (50 ml) were adjusted to optimum pH before addition at the biosorbent (10 g/L), the experiments were performed by varying the initial metal ion concentration between 20 and 500 mg/L for copper and zinc, and between 20 and 1350 mg/L for chromium.

RESULTS AND DISCUSSION

Sorption kinetics

Preliminary experiments were carried out to determine the time of equilibrium for biosorption. Fig. 1 typically shows the time profiles of dimensionless metal ion concen tration (C/Co) for biosorption of three kinds of metal ions i.e. chromium, copper, and zinc by CR. Fig. 1 shows that more than 75% of metal ion biosorption was completed within 10 min and equilibrium was reached after 70 min.

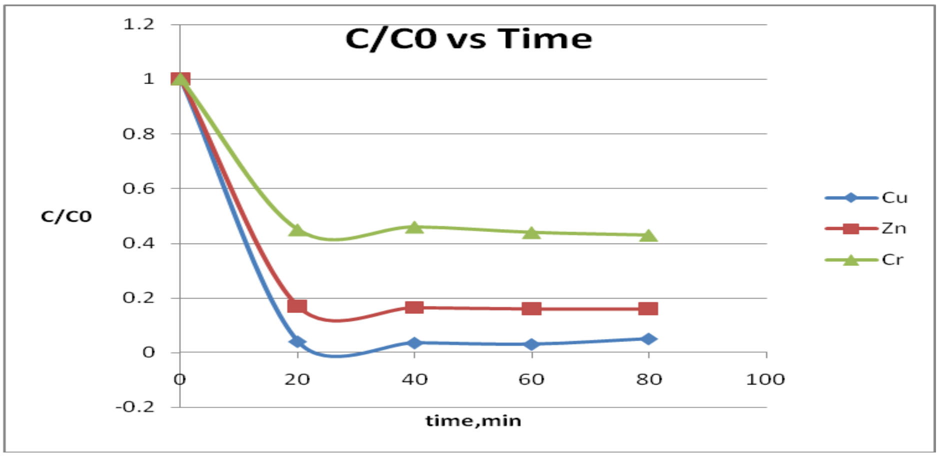


Fig. 1. Biosorption rate of metal ions by CR with initial optimum pH for each metal ion at 25 °C.

Effect of pH

The effect of initial pH on the biosorption of metal ion to the biosorbent was investigated. The effects of pH for chromium, copper, and zinc removal is shown in Figs. 2– 4. Metal ion biosorption by CR did not occur below pH 2, but increased above pH 2, metal adsorption between pH 2 and 5 is optimal. By the camparison of the result of Figs. 2–4 adsorption pH for chromium (III), copper (II) and zinc (II) were 4, 5, and 5, respectively. pH of 4.5 was selected for experiments.

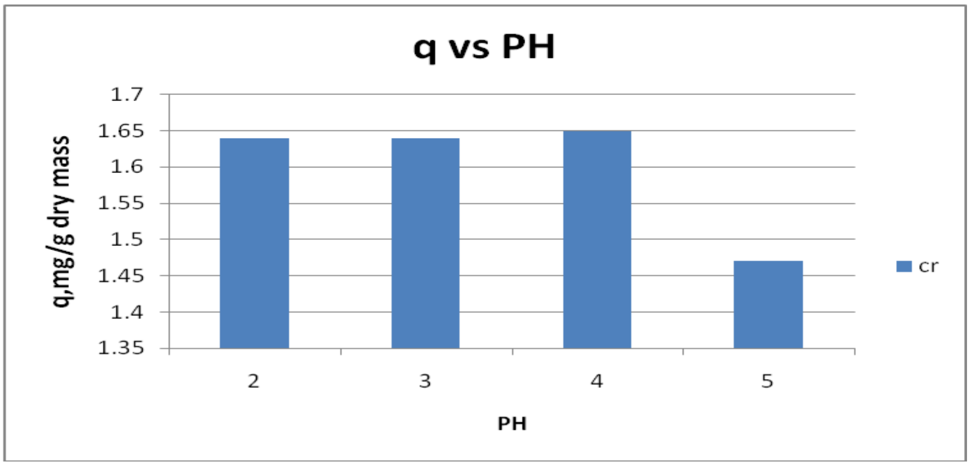


Fig. 2. Effect of initial pH on chromium (III) biosorption by CR. (C_o = 20 mg/L at 25 °C).

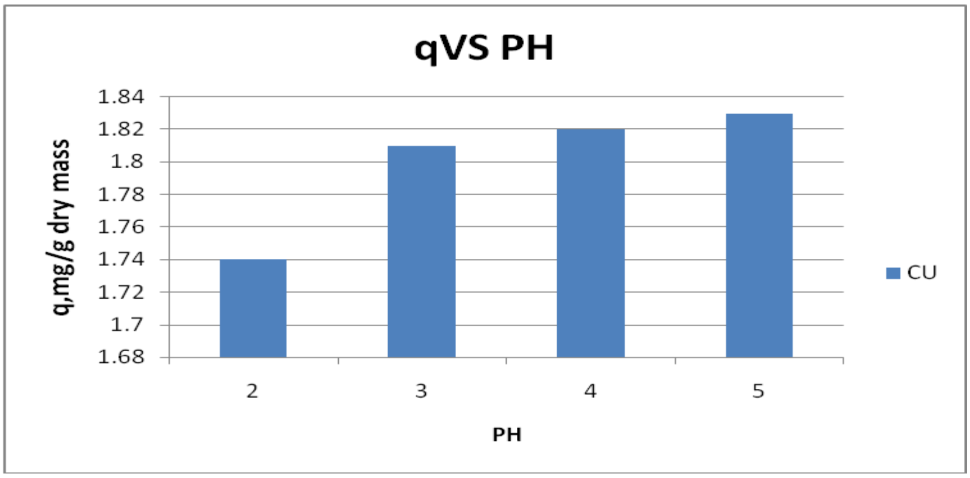


Fig. 3. Effect of initial pH on copper (II) biosorption by CR (Co = 20 mg/L at 25 °C).

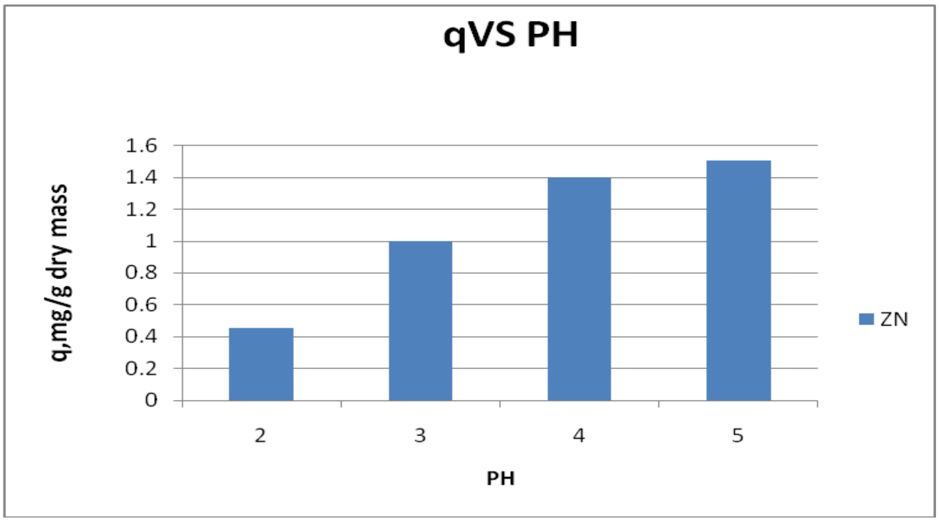


Fig. 4. Effect of initial pH on zinc (II) biosorption by CR (Co = 20 mg/L at 25 °C).

Equilibrium modeling camparison

Freundlich and Langmuir adsorption isotherm can describe the effect of metal ion concentration after equilibrium on the metal biosorption of CR. The Freundlich isotherm model has the form:

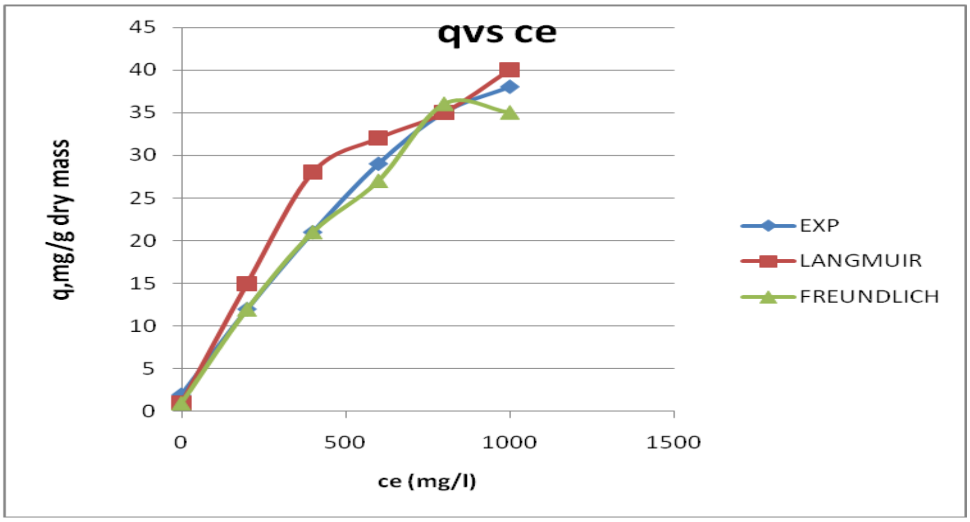
$$q=KCe^{1/n} \qquad (1)$$

In which q is the amount of adsorbate per unit weight of adsorbent in equilibrium with a solution concentration Ce. Where K and n are Freundlich constants and are indicating of adsorption capacity and adsorption intensity, respectively. The variables q and Ce also show the amount of metal adsorbed onto CR and the equilibrium concentration of metal, respectively.

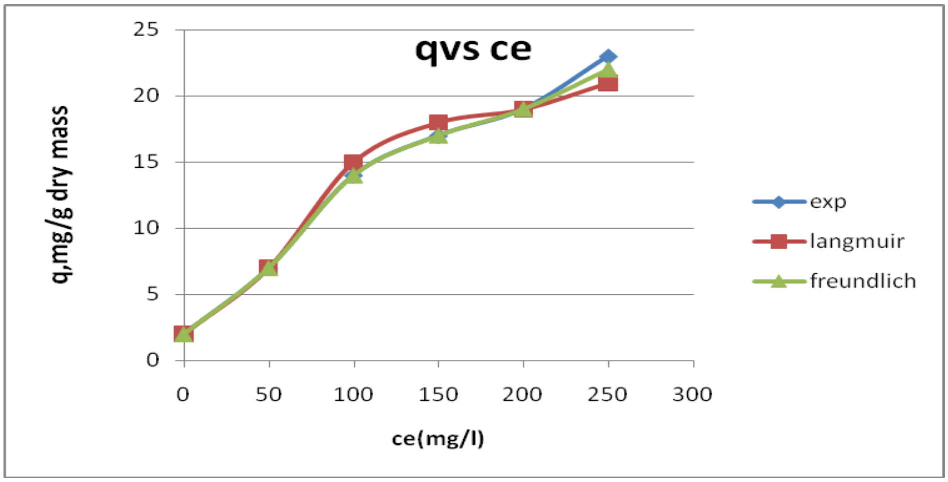
The Langmuir equation has general form:

$$q= q_{max}\, b\, Ce/1+bCe \qquad (2)$$

where qmax is the maximum sorbate (metal) uptake and b is the Langmuir constant, ratio of the adsorption rate constant to the desorption rate constant. Experimental Ce and q data were used to evaluate the constants K, n, qmax and b according to the least square fitting method. The curves in Fig. 5 were generated from Fruendlich and Langmuir model equations, respectively. As seen from Fig. 5, the Fruendlich model fitted the experimental data well. The values of Freundlich and Langmuir constants K, n, qmax and b resulting from equilibrium biosorption studied of Cr3+, Cu2+, and Zn2+ by CR are determined and listed in Table 1.



a)



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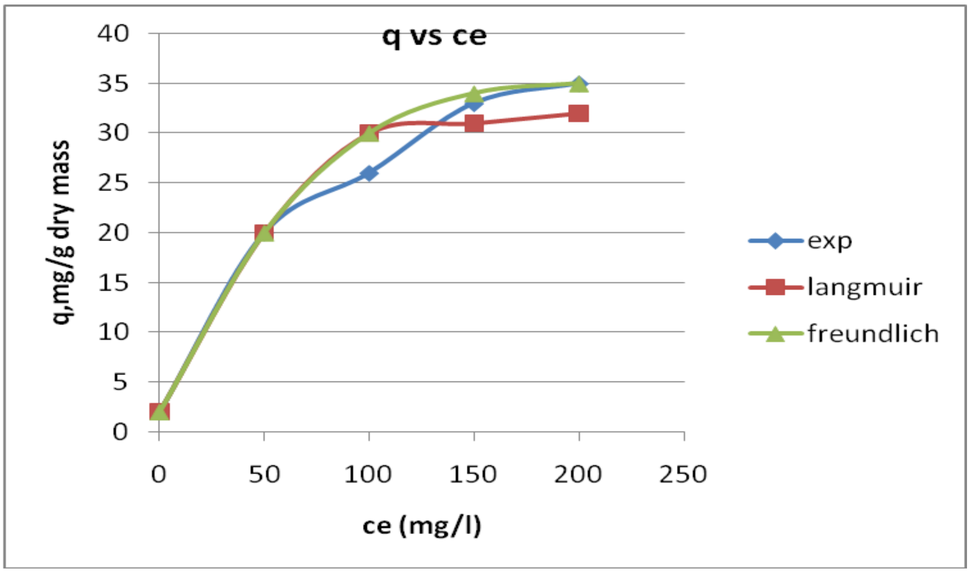

c)

Fig. 5. Application of equilibrium adsorption models by CR (T = 25 ^{0}C, pH 4.5). a-Cr;b-Zn;c-Cu

Table:1 : Freundlich and Langmuir model parameters for biosorption of metal ions by CR (T = 25 ^{0}C)

Metal ion	q_{max}	B	K	n
Cr^{+3}	45.09	0.004	0.6339	1.666
Cu^{+2}	32.74	00.1026	7.8578	3.5536
$_{Zn}$+2	29.61	00.0115	10.2013	1.8598

As a result of this investigation, the order of the sorption capacity was: Cu2+ > Zn2+ > Cr3+

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