Desalination 253 (2010) 78–87

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Efficacy of *Daucus carota* L. waste biomass for the removal of chromium from aqueous solutions

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ARTICLE INFO

Article history:
Received 30 October 2009
Received in revised form 17 November 2009
Accepted 18 November 2009
Available online 16 December 2009

Keywords:
Carrot
Cr(III)
Cr(VI)
Pretreatment
Kinetics
Sorption

ABSTRACT

In the present study the removal of Cr(III) and Cr(VI) using *Daucus carota* L. (carrot) waste biomass was investigated from aqueous solutions. Biosorption studies were determined as a function of contact time, pH, initial metal ion concentration, biosorbent size and biosorbent dose. Maximum uptake capacity of *D. carota* L. waste biomass for Cr(III) (86.65 mg/g) and Cr(VI) (88.27 mg/g) was observed at pH 1 and 5 respectively. Optimum biosorbent dose (0.1 g), biosorbent size (0.250 mm), initial concentration (100 mg/L), temperature (30 °C) and contact time (240 min) gave maximum biosorption. The sorption isotherms followed the Langmuir type suggesting monolayer sorption character. A high degree of correlation coefficient was obtained for the second-order kinetic model. To evaluate the effect of pretreatment on Cr(III) and Cr(VI) uptake by *D. carota* L., the waste biomass was physically as well as chemically pretreated. Maximum Cr(III) and Cr(VI) uptake was observed with acetone and *Moringa oleifera* extract pretreated *D. carota* L. waste biomass. The results also demonstrate that chromium uptake capacity of *D. carota* L. waste biomass was comparatively higher than most of early reported work.

1. Introduction

Chromium is a contaminant in certain water, soil, and sediments, occurring primarily in the trivalent or hexavalent form [1]. Cr(VI) is carcinogenic and mutagenic as well as being a strong oxidizing agent which irritates plant and animal tissues even in small quantities [2,3]. Biological membranes are impermeable to Cr(III) but Cr(VI) can penetrate through and may be reduced in the mitochondria, nuclei and cytoplasm to Cr(III) which readily forms insoluble chromium hydroxides at pH 7.5. Cr(III), which may be generated inside the cell, binds to protein and interacts with nucleic acids [4]. Various compounds of chromium have widespread industrial uses in steel production, wood preservation, leather tanning, metal corrosion inhibition, paint and pigments, metal plating, and other applications [5]. The guideline value of Cr as an inorganic constituent of health significance is 0.05 mg/L. According to Environmental Protection Agency (EPA), the permissible level for Cr(III) and Cr(VI) in drinking water is 0.1 mg/L.

The conventional technologies which have been used are: ion exchange, chemical precipitation, reverse osmosis, evaporative recovery, coagulation, ion exchange, membrane filters and adsorption by activated carbon. These methods are highly expensive and are ineffective especially when the heavy metals concentration is in the range of 1–100 mg/L [6]. It is therefore, necessary to search for alternative adsorbents which are of low cost, naturally occurring, easily available, and can be successfully used in the small scale industries. Biosorption is an alternative technology in waste water treatment based on the property of different kinds of inactive and dead biomasses to bind and concentrate heavy metals from dilute aqueous solutions. The major advantages of biosorption include low cost, high efficiency of heavy metal removal from dilute solution, regeneration of the biosorbent and possibility of metal recovery [7]. Carrot juice is widely marketed, especially as a health drink, either stand-alone or blended with other fruits and vegetables. Carrot waste biomass, a fiber-rich material, is available in large quantity during juice production. It is a waste material having no commercial significance. Because this waste material is easily available and not yet explored for the removal of chromium, its use as biosorbent seems appropriate. The purpose of the present study is to explore the feasibility of carrot waste biomass for the removal Cr(III) and Cr(VI) from synthetic effluents.

Hence the present study was undertaken with following objectives:

(i) To investigate the potential of *Daucus carota* L. (carrot) waste biomass as a biosorbent for Cr(III) and Cr(VI).
(ii) To study the effect of different experimental conditions such as pH, biosorbent dose, biosorbent size, initial metal concentration, temperature and shaking speed on sorption process.
(iii) To evaluate the effect of various pretreatment on biosorption capacity of this waste biomass.

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doi:10.1016/j.desal.2009.11.029

Table 1
Mineral composition of the *Daucus carota* L. (carrot) biomass.

Minerals	Concentration (mg/g)
Na	10.6 ± 0.23
K	48.9 ± 2.36
Li	0.8 ± 0.05
Cu	0.12 ± 0.09
Mn	2.14 ± 0.11
Pb	1.45 ± 0.09
Cr	4.21 ± 0.14
Co	0.38 ± 0.03
Fe	4.72 ± 0.14
Mg	2.99 ± 0.13

2. Materials and methods

2.1. Reagents

All the chemical reagents used in this study were of analytical grade, including $K_2Cr_2O_7$, $Cr_2(SO_4)_3$, Cr(III) and Cr(VI) atomic absorption spectrometry standard solutions (1000 mg/L), NaOH, $Al(OH)_3$, HCl, H_2SO_4, H_2O_2, C_6H_6, C_2H_5OH CH_3OH, HCHO, $(CH_3)_2CO$, $(NH_4)_2SO_4$, $CaCl_2$, EDTA, Triton X-100, sodium alginate, calcium alginate, PEI, glutaraldehyde, κ-carragnen and potash alum. *Moringa oleifera* seed powder was purchased from a local Super Market.

2.2. D. carota L. (carrot) waste biomass

D. carota L. was collected from vegetable area, Institute of Horticultural Sciences, University of Agriculture, Faisalabad, Pakistan. The lignocellulosic fiber left after the extraction of juice was selected as biosorbent for Cr(III) and Cr(VI). The sorbent was washed with distilled water to remove particulate matter from its surface and oven dried at 70 °C for 72 h. Dried biomass was ground, sieved and stored in air tight plastic bottles.

2.3. Digestion of the biomass

Approximately 1 g of finely powdered untreated biomass was digested with 20 mL conc. HNO_3. The mixture was heated slowly on the hot plate until half of the volume remained. Then H_2O_2 (5 mL) was added to it slowly and heated again till half of its volume. After cooling, the volume of the solution was made up to 50 mL in the volumetric flask using deionized distilled water (DDW). The digested sample was analyzed for Cr, Cu, Mn, Pb, Co, Fe, Mg, Na, K, and Li (Table 1).

2.4. Cr(III) and Cr(VI) solutions

Stock Cr(III) and Cr(VI) solutions (1000 mg/L) were prepared by dissolving 3.769 g of $Cr_2(SO_4)_3$ and 2.827 g of $K_2Cr_2O_7$ in 1000 mL of DDW. Solutions of different concentration were prepared by adequate dilution of the stock solutions with DDW.

2.5. Pretreatment of biosorbent

Biosorbent was physically modified using heating (5 g of biosorbent was heated in oven at 100 °C for 30 min) and boiling (5 g of biosorbent soaked in 100 mL of H_2O, boiled for 10 min). For chemical pretreatments, 5 g of biosorbent was soaked in 100 mL of 0.1 N HCl, 0.1 N HNO_3, 0.1 N H_2SO_4, (acidic treatments), 0.1 N NaOH, 0.1 N $Al(OH)_3$, 0.1 N $Ca(OH)_2$ (basic treatments), calcium alginate (2% solution/50 mL), sodium alginate (2% solution/50 mL), polyethyleneimine (PEI) + glutaraldehyde (2% solution in methanol/50 mL of reagent). κ-carragnen and Triton X-100 (surfactant pretreatment) (5 g of biomass/50 mL 0.1 N reagent). Biosorbent (5 g) was suspended in acetone, methanol, benzene, potash alum, formaldehyde, $CaCl_2$, EDTA (100 mL of 0.1 N reagent) and *M. oleifera* seed powder (100 mL of 1% extract) for 2 h [8,9]. Then suspensions were extensively washed with deionized distilled water (DDW) and filtered thoroughly. Finally the biomass was oven dried for 48 h until constant weight. The dried samples were grounded with a laboratory grinder and passed through laboratory vibro-sieving machine (Octagon siever: OCT-DIGITAL 4527-01) prior to their testing for metal biosorption. The fraction of particles between 0.25 and 1 mm was used in the study.

2.6. Batch biosorption studies

All glassware used for experimental purpose was washed in 10% (v/v) nitric acid and subsequently rinsed with DDW to remove any possible interference by other metals. In all sets of experiments fixed volume (100 mL) of Cr(III) and Cr(VI) solution was thoroughly mixed with desired biosorbent dose (0.1, 0.2, 0.3 and 0.4 g), size (<0.255 mm, 0.255 to 0.355 mm, 0.355 to 0.500 mm, 0.500 to 0.710 mm and 0.710 to 1 mm), pH (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10), initial metal concentration (25, 50, 100, 200, 400, and 800 mg/L) temperature (30–70 °C), shaking speed (0–150 rpm) and time (0–1440 min). The pH of the medium was recorded using pH meter (Hanna Instruments, HI 9813). For adjusting the pH of the medium 0.1 N of solution of NaOH/HCl was used. The flasks were placed on a rotating shaker (PA250/25. H) with constant shaking. At the end of each experiment, the flasks were removed from the shaker and the solutions were separated from the biomass by filtration through filter paper (Whatman no. 40, ashless) [6,9].

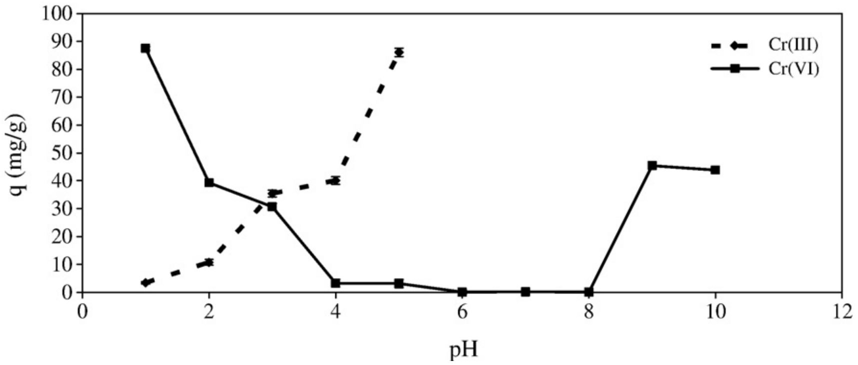

Fig. 1. Effect of pH on sorption of Cr(III) and Cr(VI) by *Daucus carota* L. waste biomass. (Biosorbent dose = 0.1 g; biosorbent size = 0.25 mm; temperature = 30 °C; shaking speed = 100 rpm).