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SCIENCE DIRECT®
Colloids and Surfaces B: Biointerfaces 50 (2006) 49–54
COLLOIDS AND SURFACES B
www.elsevier.com/locate/colsurfb

Adsorption of cadmium on husk of *Lathyrus sativus*: Physico-chemical study

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Received 23 January 2006; received in revised form 23 March 2006; accepted 29 March 2006

Abstract

Adsorption of cadmium (II) from aqueous solution by low-cost biosorbents was investigated. Husk of *Lathyrus sativus* (HLS) was found to be the most efficient in this respect and removed ~95% of the metal. The influence of pH, temperature, contact time and metal ion concentration on the adsorption process by HLS was studied. Hydrogen ion concentration of the solution greatly influenced the process with an optimum at pH 5.0–6.0, whereas temperature had no significant effect. The process was very fast and more than 90% of the total adsorption took place within the first 5 min and was found to follow pseudo-second order rate kinetics. The adsorption data can better be explained by Langmuir isotherm model and the calculated maximum adsorption capacity was 35 mg/g of HLS at pH 5.0 and 30 °C. Scanning electron micrographs showed that cadmium was present as micro precipitate on the surface of the adsorbent. Cadmium replaced calcium of the biomass as revealed from the EDX analysis indicating that the adsorption proceeds through ion exchange mechanism. Cadmium could be desorbed from the loaded biomass by lowering pH ~ 1.0 with mineral acid.

Keywords: *Lathyrus sativus*; Sorption; Isotherm; SEM-EDX; Desorption

1. Introduction

Industrial effluent containing toxic metals is a serious problem for the environment because of their ultimate accumulation in the food chain and in the ecosystem [1,2]. Cadmium has been recognized as one of toxic metals and comes into water bodies mainly from metallurgical, battery, metal plating, mining and alloy industries [3]. Toxic effects of cadmium on humans include both chronic and acute disorders like testicular atrophy, hypertension, damage to kidneys and bones, etc. [4]. Environmental regulation authority in India has set up the limit of cadmium for discharge into drinking water and in water bodies as 0.01 and 2.0 mg/l, respectively [5,6]. Therefore, many researches are carried out on the development of technology for the removal of cadmium ions from the effluent before discharging into water stream.

The most commonly used techniques for the removal of cadmium from wastewater include lime precipitation, ion exchange, ultrafiltration or reverse osmosis [2]; but these processes are either expensive or inadequate when the permissible concentration of the metal ion is low [7–9]. Moreover, they often generate huge amount of metal-bearing sludge causing difficulties in disposal.

Recently, much attention has been paid on the removal of metal ions through biosorption technique [10], which does not generate toxic sludge. Further, metal ions can be recovered from the loaded adsorbent for reuse. Activated carbon is the best choice in this regard and is being used for the treatment of municipal and industrial wastewater for many years [11]. But high cost of activated carbon restricted its use in many countries including India. This leads to the search for efficient, cost-effective and non-conventional adsorbents [12].

The objective of the present study was to search for low-cost locally available biosorbents with respect to their efficiency in the removal of cadmium from simulated contaminated samples. Since the performance of any biosorbent depends on biomass

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doi:10.1016/j.colsurfb.2006.03.022

characteristics and the microenvironment of target metal-solution, the effects of different physico-chemical parameters on the adsorption process [13] by the husk of *Lathyrus sativus*, the most efficient biosorbent in this regard, were also investigated.

2. Materials and methods

2.1. Chemicals

Cadmium sulphate ($CdSO_4 \cdot 8/3H_2O$) used in this study was purchased from Sigma, USA. All other reagents were of analytical reagent grade and procured from Merck, Germany.

2.2. Biosorbents

Rice husk, jute stick powder, water hyacinth, bagassee, jack fruit leaf and husk of *L. sativus* used in this study were collected locally. The materials were washed first with running water to remove adhering substances, then with deionised water, and finally dried at 80 °C for 24 h. Dried materials were then grounded to pass through a 50-mesh screen and kept in a desiccator until use.

2.3. Preparation of cadmium solution

Stock solution of cadmium (1000 mg/l) was prepared by dissolving required amount of cadmium sulphate in deionised and double distilled water. Standard solution of required concentrations were prepared by appropriate dilution.

2.4. Measurement of cadmium

Cadmium ion concentration was measured by Flame Atomic Absorption Spectrophotometer (Varian 2380). Amount of cadmium uptake by 1 g of the biosorbent was calculated from the following mass balance equation,

$$q = \frac{(C_i - C_f)V}{1000W}$$

where q is the amount of metal ion uptake, C_f the metal ion concentration after adsorption, C_i the initial metal ion concentration, W the amount of biosorbent and V the volume of the solution.

2.5. Selection of biosorbent

Each of the biosorbent (0.5 g) was added separately to 50 ml cadmium solution (100 mg/l, pH 3.0, 5.0 and 8.0) taken in different 250-ml Erlenmeyer flasks and agitated (120 rpm) at 30 °C for 24 h. Adsorbents were separated from the solution by filtration through glass wool. Cadmium ion concentration in the filtrate was measured.

2.6. Adsorption isotherm

This experiment was conducted with the husk of *L. sativus* (HLS) only as its adsorption capacity towards cadmium was found to be the highest. Other experimental conditions were the same as above except cadmium concentration in the solution was allowed to vary from 10 to 500 mg/l.

2.7. pH and temperature

The effect of pH on adsorption process was studied over a range 2.0–8.0 keeping other experimental parameters same as described earlier. This experiment was again repeated varying different incubation temperatures (10–40 °C) at the optimum pH.

2.8. Kinetic study

Kinetics was carried out with special interest to cadmium concentration of 10, 20 and 50 mg/l at pH 5.0 and 30 °C. Other experimental conditions were the same as for screening of biosorbents. Concentration of cadmium ion in the solution was determined at different time intervals up to 180 min. Each data point was obtained from individual flask and therefore no correction was necessary due to withdrawal of sampling volume.

2.9. SEM-EDX study

The surface morphologies of HLS biomass before and after adsorption of cadmium were examined with a field emission scanning electron microscope (JEOL JSM-6700F). Samples were platinum-coated by a vacuum electric sputter coater to a finest thickness before glue-mounted on it [14].

2.10. Chemical modification of HLS biomass and adsorption study

The dried and powdered HLS biomass was subjected to chemical treatments for modifications as described below. The modified HLS biomass was dried as mentioned in biosorbent preparation.

Methyl iodide: 1 g of biomass was stirred for 4 h at room temperature (30 °C) with 20 ml of methyl iodide.
Formaldehyde-formic acid: 1 g of HLS was refluxed for 4 h with 15 ml of formaldehyde and 30 ml of formic acid.
Triethyl phosphite-nitomethane: 1 g of HLS biomass was refluxed with 25 ml of triethyl phosphite and 20 ml of nitromethane for 6 h.

The modified HLS biomass was used for cadmium adsorption at pH 5.0 as described in Section 2.5.

2.11. Desorption experiment

Cadmium-loaded HLS biomass (0.5 g) after the adsorption isotherm experiment with 100 mg/l cadmium was taken in different 100-ml Erlenmeyer flasks and 10 ml of 0.1 M aqueous solution of EDTA, HCl, HNO_3, H_2SO_4 and Na_2CO_3 were added separately to either of the flasks. The flasks were agitated