



Alkaline treated carob shells as sustainable biosorbent for clean recovery of heavy metals: Kinetics, equilibrium, ions interference and process optimisation



M. Farnane^a, H. Tounsadi^a, R. Elmoubarki^a, F.Z. Mahjoubi^a, A. Elhalil^a, S. Saqrane^a, M. Abdennouri^a, S. Qourzal^b, N. Barka^{a,*}

^a Laboratoire des Sciences des Matériaux, des Milieux et de la Modélisation (LS3 M), FPK, Univ Hassan 1, B.P.: 145, 25000 Khouribga, Morocco

^b Equipe de Photocatalyse et Environnement, Département de Chimie, Faculté des Sciences, Université Ibn Zohr, B.P. 8106 Cité Dakhla, Agadir, Morocco

ARTICLE INFO

Article history:

Received 26 September 2016

Received in revised form 7 January 2017

Accepted 10 January 2017

Available online 17 January 2017

Keywords:

Biosorption
Remediation
Carob shells
Heavy metals
Optimisation

ABSTRACT

The aim of this work is to study the removal ability of cadmium(II) and cobalt(II) ions from aqueous solution by raw and chemically treated carob shells as an ecofriendly and sustainable biosorbents. The biosorbents were characterized by Fourier transform infrared spectroscopy (FT-IR), elemental analysis (CHNOS), scanning electron microscopy (SEM), Boehm titration and the point of zero charge (pH_{PZC}). Biosorption experiments were carried out as function of solution pH, biosorbents dosage, contact time, initial metal ions concentration and temperature. The effect of some major inorganic ions including Na⁺, K⁺, Ca²⁺, Mg²⁺ and Al³⁺ on the biosorption efficiency was also investigated. From this studies it can be concluded that chemical pretreatment of the raw carob shells with NaOH strongly enhances its biosorption potential for the selected metals. Experimental results show that maximum biosorption capacity occurred at neutral pH medium. Kinetic data were best fitted with pseudo-first-order kinetic model instead of pseudo-second-order. Biosorption isotherms were best correlated with Langmuir model than with Freundlich model. The temperature doesn't have much influence on the biosorption yield. Based on this preliminary study, full factorial experimental design with two levels (2⁴) was used for the optimisation of the process. Four independent variables, including solution pH, biosorbents dosage, initial metal concentration and treating agent were investigated. Thus, the optimal conditions for high biosorption of cadmium(II) and cobalt(II) were achieved at pH = 6, biosorbent dosage of 1 g/L, initial metal concentration of 50 mg/L for NaOH treated carob shells.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The industrial discharge of heavy metals in the aquatic environment is the main source of contamination with such pollutants, which significantly affects the ecosystems quality, and represents a high priority issue for environment safety. Various sources of heavy metals include soil erosion, natural weathering of the earth's crust, mining, industrial effluents, urban runoff, sewage discharge, insect or disease control agents applied to crops, and many others (Morais et al., 2012). The most commonly found heavy metals in wastewater include arsenic, cadmium, chromium, copper, lead, nickel, and zinc. These heavy metals have some toxicity to the aquatic ecosystem and humans, causing particular toxic effects on the nervous system

(Wuana and Okieimen, 2011; Clarkson, 1987), carcinogenic effects on the blood and bone marrow and kidney problems (Tchounwou et al., 2012).

Several methods were developed in the literature for efficient removal of heavy metals from aqueous solution in the context of environmental protection, namely chemical precipitation (Zhu et al., 2007), ion exchange (Wong et al., 2014), filtration (Ding et al., 2014), reverse osmosis (Petersková et al., 2012), electrochemical treatment (Sulaymon et al., 2011), liquid extraction (Fischer et al., 1939) and adsorption (Barka et al., 2012). This latter has been found to be superior to other water treatment techniques by its simplicity of design, ease of operation and flexibility (Tounsadi et al., 2016a). Despite that activated carbon has been popular choice as an adsorbent for heavy metals removal from wastewater due to its large specific surface area, low density, chemical stability, suitability for large scale production and variety of structural forms but its high cost poses an economical problem (Santhy and Selvapathy, 2004).

* Corresponding author.

E-mail address: barkanoureddine@yahoo.fr (N. Barka).

Therefore, many researches in recent years have focused on the use of various low-cost biosorbents instead of activated carbon such as olive stone and sugar cane bagasse (Moubarik and Grimi, 2015), leaves of *Arundo donax* reed (Ammari, 2014), tomato waste (Yargıç et al., 2015), *Opuntia ficus indica* (Barka et al., 2013), algae waste biomass (Bulgariu and Bulgariu, 2016), *Diplotaxis harra* and *Glebionis coronaria* L. (Tounsadi et al., 2015).

The carob tree (*Ceratonia siliqua* L.) is native to the Mediterranean region, including Southern Europe, Northern Africa, the larger Mediterranean islands, the Levant and Middle-East of Western Asia into Iran; and the Canary Islands and Macaronesia. It is of great socio-economic benefits to rural development and mountain economy. The fruit of carob is a pod, technically a legume 15–30 centimeters in length and fairly thick and broad. It contains a large majority of active components, that reveals currently the most profitable among the fruit and forest trees (Sidina et al., 2009). Multiple uses have been found for this component, for instance as chocolate substitute used in a huge variety of confectionery products and drinks as well as a general sweetener. Carob is also used to make flour, molasses, alcohol and a substitute for coffee and eggs.

The objective of this work was to test the ability of the chemically treated carob shells for the removal of cadmium(II) and cobalt(II) ions from aqueous solution by biosorption. Studies were carried out under various parameters such as solution pH, biosorbents dosage, contact time, initial metal ions concentration and temperature. The biosorption kinetic data were tested by pseudo-first-order and pseudo-second-order kinetic models. The equilibrium data were analyzed using Langmuir and Freundlich models.

This paper also investigated the combined effect of the most influencing parameters, which are pH, biosorbent dose, metal ions concentration and the treating agent. Full factorial experimental design with two levels (2^4) was used to acquire the optimal parameters for high removal efficiency.

2. Experimental

2.1. Materials

All the chemicals used in the present work were of analytical grade. $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (98%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%), NaCl (99.5%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\geq 98\%$), HCl (37%), Na_2CO_3 and NaHCO_3 were obtained from Sigma-Aldrich (Germany). $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (97%) was provided from SDS (France), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and HNO_3 (65%) from Scharlau (Spain) and NaOH (98%) was provided from Merck (Germany).

2.2. Preparation and characterization of the biosorbents

The carob shells were collected from the region of Khenifra in Morocco. Firstly it was washed several times with distilled water to remove impurities and then dried at 70°C for 24 h, crushed and sieved to the desired particle sizes $<160\ \mu\text{m}$ referred as Raw-carb. For the chemical treatment, 10 g of the Raw-carb was treated with 100 mL of 1 M solution of HCl or NaOH for 2 h. The suspension was then filtered and washed with distilled water until neutral pH. The pretreated biosorbents were then dried in an oven at 120°C for 24 h and stored in glass bottles under the following names HCl-carb and NaOH-carb for further use.

Functional groups of the biosorbents were examined using Fourier transform infrared spectroscopy (FTIR) in the region of $4000\text{--}400\ \text{cm}^{-1}$ by using a Scotech-SP-1 spectrophotometer. Basic and oxygenated acidic surface groups were quantified by Boehm titrations (Boehm, 2002). About 0.1 g of each sample was mixed with 50 mL of 0.01 M aqueous reactant solution (NaOH , Na_2CO_3 , NaHCO_3 or HCl). The mixtures were stirred at 500 rpm for 24 h

at room temperature. Then, the suspensions were filtered by a $0.45\ \mu\text{m}$ membrane filter. To determine the oxygenated groups content, back titrations of the filtrate (10 mL) were achieved with standard 0.01 M HCl solution. Basic groups contents were also determined by back titration of the filtrate with 0.01 M NaOH solution.

The elemental analysis was performed using a CHNS/O analyzer type Flash 2000 EA 1112 (Thermo Fisher Scientific). Before to the analysis, the samples were dried overnight at 105°C and cooled in a desiccator. Oxygen content was obtained by the difference between the total percentage (100 wt.%) and the sum of percentages (wt.% dry ash free) of nitrogen, carbon, hydrogen and sulfur. The morphological characteristics were analyzed by scanning electron microscopy using a FEI Quanta 200 model. Small amount of each sample was finely powdered and mounted directly onto aluminum sample holder using two-sided adhesive carbon model. The point of zero charge (pH_{PZC}) was determined by the pH drift according to the method proposed by Noh and Schwarz (1989). 0.05 g of each biosorbents were added to 50 mL of solution of NaCl (0.01 M). The initial pH of the solution was adjusted to defined values from 2.0 to 12.0 using HNO_3 and NaOH (1 M) solutions. The solutions were stirred for 6 h and the final pH was measured and plotted against the initial pH using a SensION+ PH31 pH meter. The pH_{PZC} was determined at the value for which $\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$.

2.3. Biosorption studies

Stock solutions of heavy metals were prepared by dissolving desired weight of each metal ion in distilled water and necessary concentrations were obtained by dilution. Biosorption experiments were performed in a series of 100 mL beakers containing the desired weight of each biosorbents and 50 mL of the metal ion solution at desired concentration. These experiments were carried out at a constant agitation (500 rpm) using a magnetic stirrer. The effect of solution pH was investigated in the range 2–7. Biosorbents dosage was varied from 0.5 to 5 g/L and the contact time from 5 to 180 min at room temperature with initial solution pH. Biosorption equilibrium was established for different metal ion initial concentrations between 20 and 200 mg/L. The effect of temperature was tested from 10 to 50°C using a thermostatically controlled incubator. The effect of some major inorganic ions including Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Al^{3+} on the biosorption efficiency was studied for each heavy metals at a constant initial metal concentration of 100 mg/L. The concentration of each ion was varied from 10 to 100 mg/L.

After each biosorption experiment completed, the solid phase was separated from the liquid phase by centrifugation at 3000 rpm for 10 min. The data obtained in the batch studies were used to calculate the metal biosorption capacity by using the following equations:

$$q_{t,e} = \frac{(C_0 - C_{t,e})}{R} \quad (1)$$

The removal efficiency (%) can be calculated as follows:

$$\% \text{ Removal} = \frac{(C_0 - C_{t,e})}{C_0} * 100 \quad (2)$$

where $q_{t,e}$ (mg/g) is the biosorbed quantity at any time or at equilibrium, C_0 (mg/L) is the initial metal ion concentration, $C_{t,e}$ (mg/L) is the metal ion concentration at a time t or at equilibrium, R (g/L) is the biosorbent dosage.

Kinetic and equilibrium parameters were estimated with the aid of the non-linear regression method using Origin 6.0 software.

Download English Version:

<https://daneshyari.com/en/article/5743910>

Download Persian Version:

<https://daneshyari.com/article/5743910>

[Daneshyari.com](https://daneshyari.com)