



Biosorption of chromium onto native and immobilized sugarcane bagasse waste biomass



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ARTICLE INFO

Article history:

Received 28 March 2013

Received in revised form 12 June 2013

Accepted 5 July 2013

Available online 14 August 2013

Keywords:

Heavy metals

Kinetics

Isotherms

Tannery wastewater

SEM

EDX analysis

ABSTRACT

Adsorption experiments were carried out using sugarcane bagasse native and immobilized biomasses as a function of initial concentration, biomass dose, pH and contact time for the removal of Cr(III) and Cr(VI) form simulated and tannery wastewater stream. The equilibrium biosorption data was analyzed using pseudo-first order and pseudo-second order kinetic models and Langmuir and Freundlich isotherm models. The immobilized biomass furnished considerably high adsorption capacity of both chromium ions versus native biomass. Maximum uptake of 80.6% and 41.5% was observed for Cr(VI) and Cr(III) onto immobilized biomass and at optimized conditions, up to 73% chromium adsorption was observed onto immobilized sugarcane bagasse biomass. The sorption capacity of sugarcane bagasse biomass varies greatly with initial pH, biosorbent dose, initial metal ions concentration and contact time. Langmuir model fitted well to the data and the pseudo-second order could best describe the biosorption kinetics.

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1. Introduction

Heavy metals are discharged into environment from various sources such as textile, pigments, plastics, mining, electroplating and metallurgical processes (Han et al., 2006; Iyer et al., 2005), and are considered persistent environmental contaminants, because they cannot degraded naturally (Montazer-Rahmati et al., 2011). Due to their toxic effect and accumulation tendency throughout the food chain, the heavy metals pollution represents an important problem with serious ecological and human health consequences (Bulgariu and Bulgariu, 2011).

The chromium enters into water bodies due to indiscriminate disposal of wastes from the industries (Lakshmanraj et al., 2009). A survey report published by Pakistan Council of Research in Water Resources revealed that 23 major cities groundwater of Pakistan has been contaminated with chromium. Various authors individually reported that the chromium concentration has been exceeds the safe limits of WHO standards (0.05 mg/L). Analysis of drinking water samples from the residential area of Kasur, Khyber Pukhtoonkhwa, Lahore, Gujarat, Sialkot and Karachi showed chromium concentration beyond the permissible limits in drinking water. The reason of elevated concentration of chromium in water is the leather and tanneries industries located in these

areas (Azizullah et al., 2011). While studying the concentration of chromium in effluents of tanneries, soil and drinking water in Sialkot District, Pakistan, the concentration of total chromium was found to be in the range of 16.12–36.83 mg/L, 1.0483–3.1824 mg/L and 3.45–11.43 mg/kg, respectively (Mahmood, 2010).

Due to toxic nature and environmental impacts of chromium, there are growing concern for the removal of this metal from wastewaters (Bulgariu and Bulgariu, 2011; Chaisuwan et al., 2011). Various methods have been used for heavy metal removal, including chemical precipitation, neutralization, membrane filtration and adsorption. Among these techniques, biosorption using agricultural waste has gained considerable attention because of high efficiency, low cost, more availability and ease of handling (Chaisuwan et al., 2011). Biosorption utilizes biological materials as adsorbents and this method has been studied by several researchers as an alternative to conventional methods for the removal of heavy metals from wastewater (Bhatti and Amin, 2013; Inyang et al., 2012; Omorogie et al., 2012; Saqib et al., 2013; Zuo et al., 2012). The use of non-living biomaterial containing metal-binding functional groups would have the advantage of not requiring utmost care and maintenance as well as being useful in remediating areas with high levels of heavy metal contamination (Iqbal et al., 2013; Vijayaraghavan et al., 2012; Witek-Krowiak et al., 2011).

Sugarcane bagasse (*Saccharum officinarum* L.) is the fibrous material left after the crushing of the cane stalk and juice extracting. Structurally, sugarcane is composed of an outer rind and inner pith. The majority of sucrose together with bundles of small fibers is

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found in the inner pith. The outer rind contains longer and finer fibers, in a random arrangement throughout the stem and bound together by lignin and hemicelluloses. Sugarcane bagasse is a lignocellulosic plant waste which composed approximately of 40% cellulose, 24% hemicellulose, and 25% lignin (Lee et al., 2009). The sugarcane secondary wall consists of three layers (S1, S2, and S3) surrounded by a thin primary wall. The S2 and S3 layers contain mainly amorphous cellulose and hemicelluloses material, while S1 layer contains crystalline cellulose. Crystalline regions are shaped by linear hydrogen bonding in a highly ordered manner. However, amorphous regions also exist in the cellulose form. Amorphous cellulose, hemicellulose and lignin are present between the layers S1, S2 and S3. These three biological polymers have many functional groups that can be used for the adsorption of heavy metals from aqueous medium (Homagai et al., 2010; Karnitz et al., 2007).

The sugarcane bagasse rind and pith waste biomass (SCBR-sugarcane bagasse rind, SCBP-sugarcane bagasse pith, SCBRB-sugarcane bagasse rind beads and SCBPB-sugarcane bagasse pith beads), after the extraction of juice, was used for the removal of Cr(III) and Cr(VI) ions from aqueous solution and tannery wastewater stream. The ability of native and immobilized sugarcane bagasse rind and pith to remove Cr(III) and Cr(VI) was investigated as a function of initial metal ions concentration, contact time, pH and biosorbent dose. The equilibrium and kinetic data of biosorption studies were tested using two isotherm models (Langmuir and Freundlich) and two kinetic models (pseudo-first order and pseudo-second order). The SEM and EDX-analysis before and after sorption of chromium onto sugarcane bagasse was also performed to evaluate the mechanism of adsorption.

2. Experimental

2.1. Reagents

All chemicals and reagents used were of analytical grade; $K_2Cr_2O_7$, $Cr(NO_3)_3$, HCl, NaOH (Merck), acetone, $CaCl_2$, Na-alginate and Cr(III) and Cr(VI) standards were purchase from Fluka and Merck. Stock solutions of Cr(III) and Cr(VI) were prepared by dissolving salts of $Cr(NO_3)_3$ and $K_2Cr_2O_7$, respectively in double distilled water. The working solutions were obtained by diluting the stock solutions with double distilled water.

2.2. Biomass collection and preparation

Sugarcane bagasse biomass was collected from Shakarganj Sugar Mill Limited, Jhang, Pakistan, dried in sunlight followed by oven dried at 50 °C for 72 h. The dried biomass sieved through Octagon Siever (OCT-DIGITAL 4527-01) for the removal of uneven particle and to obtain adsorbent with a uniform and known particle size. The fraction with 0.25 mm diameter was selected and used for sorption experiments. The sieved material was stored in airtight plastic containers until experimentation.

2.3. Immobilization of biomass

Na-alginate (2%, w/v) solution was prepared in hot distilled water (60 °C) with constant stirring to avoid the formation of lumps. The slurry was then cooled to room temperature (25 °C) and 1 g of sugarcane bagasse waste biomass was added under stirring conditions to obtain a uniform mixture. The alginate–biomass slurry was then extruded into 0.1 M $CaCl_2$ solution. The resultant Ca-alginate beads (3 mm) were allowed to cure for 2 h at 4 °C and washed thoroughly with deionized distilled water. The immobilized sugarcane

bagasse wastes biomasses were used to study biosorption of Cr(III) and Cr(VI) from aqueous solution and tannery wastewater stream.

2.4. Biosorption experiment

To study the adsorption as a function of pH, 1–6 pH for Cr(III) and 1–7 pH for Cr(VI) were considered and biomass dose (0.1 g), contact time (24 h) and initial metal ions concentration (100 mg/L) were kept constant. To evaluate the initial metal concentration, 25–1000 mg/L concentrations were used, while 0.1 g biomass dose, contact time 24 h were constant and pH of 5 and 2 were adjusted for Cr(III) and Cr(VI), respectively. The contact time ranging from 10 to 1440 min was used to evaluate kinetic study, while dose (0.1 g), initial concentration (100 mg/L) and pH (5 and 2 for Cr(III) and Cr(VI), respectively) were constant. The volume of solution (100 mL) and biosorbent particle size (0.25 mm), shaking (100 rpm) and temperature (25 °C) were constant in all batches. The Cr(III) and Cr(VI) concentration were determined using A Analyst 30, Perkin Elmer equipped with single element hollow cathode lamp and acetylene air source. The amount of metals adsorbed onto biomass was calculated by the simple concentration difference method. The biosorption capacities of sugarcane bagasse waste biomass (native and immobilized) of Cr(III) and Cr(VI) were estimated using the amount of ions retained on unit mass of biomass (Eq. (1)) (Manzoor et al., 2013).

$$q = \frac{(C_0 - C) \times (V/1000)}{m} \quad (1)$$

where C_0 is the initial concentration of chromium (mg/L), C is the equilibrium concentration (mg/L), V is the volume of solution (mL) and m is the biosorbent mass (g).

2.5. SEM and EDX analysis

The sample of sugarcane bagasse biomass before and after biosorption were coated under vacuum with a thin layer of gold and examined by SEM for surface analysis (JEOL, JSM-6400, Japan). The surface elemental analysis of sugarcane bagasse biomass was also carried out by energy dispersive X-ray spectroscopy. The samples were gold sputtered to increase the electrical conductivity of a sample and protect the sample structure from electron beam damage and dehydration in vacuum while recording the spectra (Bhatti et al., 2010).

2.6. Statistical analysis

The data represents the mean of three independent experiments and is represented by mean \pm SD values. The regression coefficient (R^2) values of the linear form of Langmuir isotherm, Freundlich isotherm, pseudo-first-order and pseudo-second-order models were also determined using statistical functions of Microsoft Excel, 2007 (version Office XP, Microsoft Corporation, USA) (Manzoor et al., 2013).

3. Results and discussion

3.1. Effect of pH

It is well known that the adsorption of metallic ion from aqueous media is pH dependent. The efficiency of the process is expressed by removal efficiency versus pH plots (Fig. 1). The effect of pH on Cr(III) and Cr(VI) removal was tested from 1 to 6 pH for Cr(III) and 1–7 pH for Cr(VI). The other operating conditions such as initial metal ions concentration (100 mg/L), contact time (24 h) and biosorbent dose (0.1 g) were constant. The chromium removal efficiency was found

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