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Application of soy hull biomass in removal of Cr(VI) from contaminated waters. Kinetic, thermodynamic and continuous sorption studies

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ABSTRACT

Soy hull was evaluated as a new material for Cr(VI) removal from aqueous solutions. Cr(VI) removal was associated to a redox mechanism, in which Cr(VI) was reduced to Cr(III) by the biomass. The redox capacity of soy hull was 1.12 mmol g^{-1}. A kinetic model that considers the redox reaction between Cr(VI) and the biomass surface was proposed. The maximum sorption capacity was 7.286 mg g^{-1} at 20 °C and pH 1.5. Activation parameters and mean free energies suggest that the sorption process follows a mechanism of chemical sorption. Thermodynamic parameters show that Cr(VI) removal was spontaneous. The isosteric heat of sorption indicated that soy hull has an energetically homogeneous surface. XPS spectra showed that chromium bound on the biomass was Cr(III). These results were confirmed by XANES and EXAFS experiments. EPR spectra showed the presence of Cr(V)-soy hull at short contact time and only a signal corresponding to Cr(III)-soy hull at long contact times. Continuous sorption data were fitted to Thomas and modified dose–response models. The bed depth service time (BDST) model was used to scale-up the continuous sorption experiments.

1. Introduction

Chromium is a very toxic heavy metal, and it is discharged in the effluents from many industries, including steel plants, electroplating, tannery, and pigment and dye industries [1]. Most chromium exists in the environment as Cr(VI) and Cr(III). Compared with Cr(III), Cr(VI) is a highly toxic heavy metal, which is able to cause cancer in humans and animals, thus it has been designated as one of the top-priority toxic pollutants by the U.S. EPA. The allowed limit given by US EPA for Cr discharged is 0.1 mg L^{-1} [2]. Besides, Cr(III) is susceptible to precipitation in soil strata while Cr(VI) is mobile and always leached out by groundwater. Thus, removal of Cr(VI) from wastewater or soil to avoid Cr pollution is a key step when designing environmental friendly processes [3].

Many different types of treatment processes have been used successfully to remove hexavalent chromium from polluted effluents, including ion exchange [4], chemical reduction [5], activated carbon [6], chemical absorption [7], membranes [8], and electrochemical processes [9]. Compared to other methods, sorption is one of the most popular and cost-efficient methods, and can be used for recovering Cr(VI) at low concentrations [10]. Many different materials have demonstrated their capacity to remove chromium, including carrot residues [11], eggshells [12], coir pitch [13], rice husk and citric peels [14], sawdust [15], activated neem bark [16]. To effectively apply these materials in sorption removal processes of heavy metals, it is essential to determine the parameters that affect metal sorption.

Soy is one of the major agricultural products in the world. Argentina stands as the third largest producer of soybeans, accounting for 18% of the world production. The oil and protein constituents of soybeans are the main products in soy cultivation while the hulls are usually discarded [17]. Soy hull is a by-product of the soybean oil industry. For each ton of soy seed processed, about 2% of the total mass corresponds to this by-product [18]. Soy hulls constitute about 8% of the whole seed and contain about 86% complex carbohydrates. The insoluble carbohydrate fraction of soy

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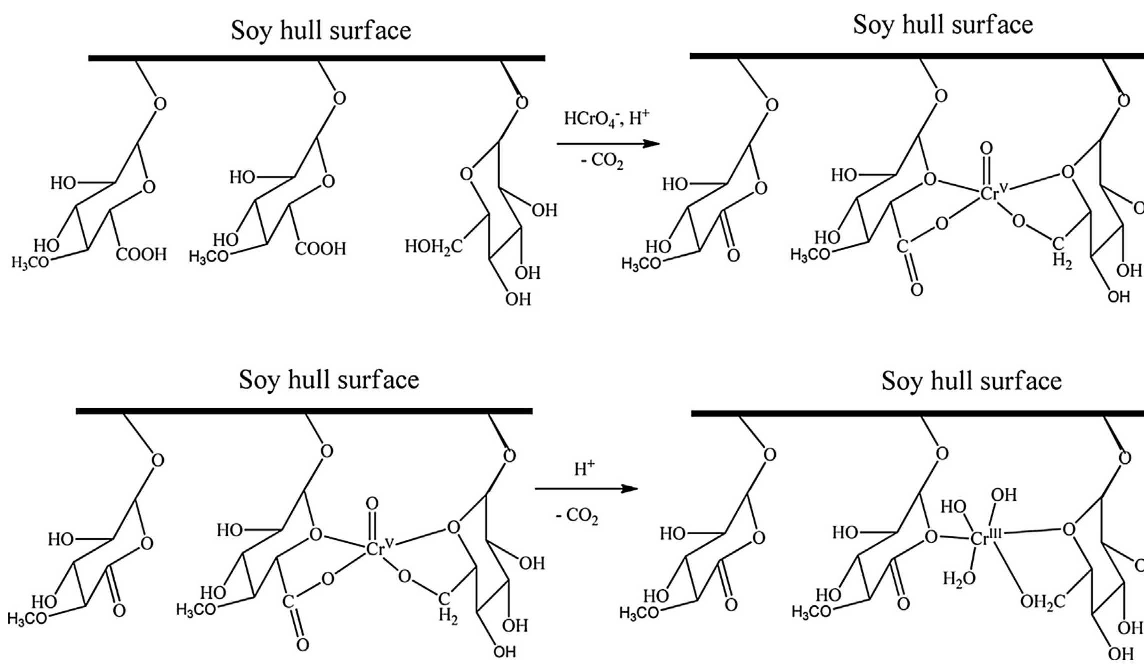

Scheme 1. Proposed mechanism for Cr^{VI} removal by soy hull biomass.

hull consists of 30% pectin, 50% hemicellulose, and 20% cellulose [19]. This fact makes soy hull a suitable biomass for metal biosorption. Soy hulls are an agro-industrial by-product available in great quantities in many countries, which could be used in waste-waters treatment processes. Additionally, it is a very cheap material lowering the costs involved.

The aim of the present work was to evaluate Cr(VI) removal from aqueous solution in batch and continuous systems using soy hull biomass. This biomass was chosen because it is obtained in great quantities, it is a cheap material and it contains a large number of biopolymers in its surface capable of binding and reducing Cr(VI) species. These characteristics make this biomass suitable for being employed in remediation of Cr(VI) contaminated waters. In this work we evaluated optimal conditions for batch removal of Cr(VI), kinetic and isotherm profiles, gathered spectroscopic evidence of a redox removal mechanism and analyzed the application of fixed bed columns in continuous Cr (VI) sorption removal.

2. Materials and methods

$K_2Cr_2O_7$ (Mallinckrodt, p.a.), $HClO_4$ (δ = 1.67 g mL^{-1}, 70% P/P) (Merck), NaOH (Cicarelli, p.a.), H_2SO_4 (δ = 1.84 g cm^{-3}, 98% P/P) (Merck), ethanol (Cicarelli, p.a.), K_2CO_3 (Sigma, p.a.), Na_2CO_3 (Sigma, p.a.), $AgNO_3$ (Cicarelli, p.a.), $K_2S_2O_8$ (Mallinckrodt, p.a.), H_2O_2(ac) 100 vol. (Cicarelli, p.a.), 1,5-diphenylcarbazide (Sigma, p. a.), diphenylpicryllhydrazyl (dpph) (Sigma, 99.9%), ehba = 2-ethyl-hydroxybutanoic acid (Aldrich 99.0%), $Cr(NO_3)_3 \cdot 9H_2O$ (Sigma, p.a.), were used without further purification. $Na[Cr^{(V)}O(ehba)_2] \cdot H_2O(s)$ was synthesized as described in literature [20].

Aqueous solutions were prepared in milli *Q* deionized water. For experiments performed in the 1.00–4.00 pH range, the pH of the solutions was adjusted by addition of $HClO_4$. The concentration of stock solutions of perchloric acid was determined by titration employing standard analytical methods.

Caution: $K_2Cr_2O_7$, $Na[Cr^VO(ehba)_2] \cdot H_2O$, and dpph are human carcinogens. Contact with skin and inhalation must be avoided.

2.1. Preparation of the biomass

Soy hulls were collected from a neighboring harvest zone of Rosario, Santa Fe Province, Argentina. The biomass was submitted to mechanical milling in order to obtain 0.3–0.5 mm-sized pieces, washed with deionized–distilled water several times and then air-dried for several days. To determine the pH value at point of zero charge (pHzpc), 2.0 g of biomass was put into contact with 100 mL 0.10 M $NaNO_3$ solution with different pH values (2.0–9.0) at T = 25 °C. The suspensions were stirred for 48 h (250 rpm). The change of pH (ΔpH) was calculated as a difference between the initial pH and the equilibrium pH values. The pHzpc was identified as the initial pH with minimum ΔpH [21].

2.2. Experimental design strategy. Response surface design

The response surface approach is desirable to find a mathematical model capable of predicting the response. The optimized model was obtained by using the Central Composite Design (CCD) [22]. To do this, one should measure the response at some points of the working domain. The selection of these experimental points

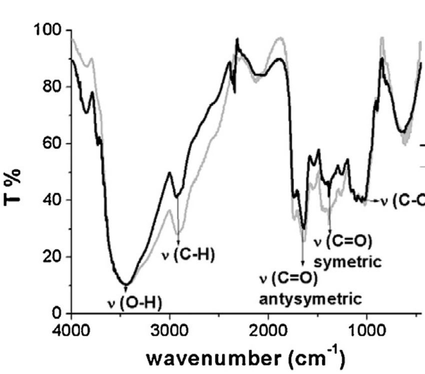

Fig. 1. FTIR spectra of (a) native soy hull, (b) Cr loaded soy hull.