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Biosorption of chromium(VI) ion from aqueous solutions using walnut, hazelnut and almond shell

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Abstract

The potential to remove Cr(VI) ion from aqueous solutions through biosorption using, the shells of Walnut (WNS) *(Juglans regia)*, Hazelnut (HNS) *(Corylus avellana)* and Almond (AS) *(Prunus dulcis)* was investigated in batch experiments. The equilibrium adsorption level was determined to be a function of the solution contact time and concentration. Kinetic experiments revealed that the dilute chromium solutions reached equilibrium within 100 min. The biosorptive capacity of the shells was dependent on the pH of the chromium solution, with pH 3.5 being optimal. Adsorption of Cr(VI) ion uptake is in all cases pH-dependent showing a maximum at equilibrium pH values between 2.0 and 3.5, depending on the biomaterial, that correspond to equilibrium pH values of 3.5 for (WNS), 3.5 for (HNS) and 3.2 for (AS). The adsorption data fit well with the Langmuir isotherm model. The sorption process conformed to the Langmuir isotherm with maximum Cr(VI) ion sorption capacities of 8.01, 8.28, and 3.40 mg/g for WNS, HNS and AS, respectively. Percentage removal by WNS, HNS and AS was 85.32, 88.46 and 55.00%, respectively at a concentration of 0.5 mM. HNS presented the highest adsorption capacities for the Cr(VI) ion.

Keywords: Shell; Low-cost adsorbent; Batch model; Chromium; Adsorption; Walnut; Hazelnut; Almond

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1. Introduction

The discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades. They are extremely toxic elements, which can seriously affect plants and animals and have been involved in causing a large number of afflictions. Increased knowledge about toxicological effects of heavy metals on the environment is well recognized and therefore, it is inevitable to search for different methods to reduce water pollution [1]. The major sources of heavy metal contaminations are the industrial effluents. Due to their persistence in nature, it becomes essential to remove them from wastewaters [2]. Inorganic micro-pollutants are of considerable concern because they are non-biodegradable, highly toxic and have a probable carcinogenic effect [3,4].

An alternative method for the removal of heavy metals is considered based on the biological methods of metal removal and recovery. The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase containing a dissolved species to be sorbed (metal ions). Biosorption is a fast and reversible reaction of the heavy metals with biomass. The by-products obtained from biomaterial production are a cheap source of biosorbents. Several approaches have been studied and developed for the effective removal of heavy metals using biosorbents like peat, lignite and humic acids, treated activated carbons and coal-based natural adsorbents, chitosan-based polymeric surfactants, fly ash, microbial biomass and other agricultural by products, soya bean hulls, walnut hulls, cotton seed hulls and corn cobs, walnut skin, coconut fibre, cork biomass, defatted rice bran, rice hulls, soybean hulls and cotton seed hulls, wheat bran, cotton and mustard seed cakes, barks [5–34]. There are other systems for treating wastewaters containing toxic metal ions is today the use of micro-organisms such as bacteria, fungi and algae but as yet not suitable for applications on a large scale [35,36].

Conventional techniques have limitations [37] and often are neither effective nor economical especially for the removal of heavy metals at low concentrations. New separation methods are effective and environmentally acceptable at affordable cost [38]. Several methods are utilized to remove chromium from indus-

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trial wastewater. The commonly used procedures for removing metal ions from effluents include chemical precipitation, lime coagulation, reduction, activated carbon adsorption, electrolytic removal, ion exchange, reverse osmosis, membrane filtration and solvent extraction [39–46]. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimisation of chemical and or biological sludge regeneration of biosorbent; and the possibility of metal recovery. Developing countries suffer from water pollution; the high costs operating treatment systems make the major problems in these countries. The cost of these biomaterials is negligible compared with ion exchange resins. Synthetic ion exchange resins are marketed for US$ 30–50/kg. With the same performance, natural new biosorbents could cost less than US$ 5/kg [13,47]. The search for a cheaper alternative reveals that utilizing natural processes and materials can significantly reduce the cost.

Cr(VI) is a common pollutant introduced into natural waters from a variety of industrial wastewaters including those from the textile dyeing, leather tanning, electroplating and metal finishing industries. Cr(III) and Cr(VI) are the chromium oxidation states usually encountered in the environment. The hexavalent form is of particular concern because of its greater toxicity [48]. The untreated effluent from electroplating industry contains approximately 100 mg/L Cr(VI), which is much higher than the permissible limit of 0.05–1 mg/L [49]. Cr(VI) is typically present as an anion and its direct precipitation is not a usual practice. Instead, the anionic species are usually reduced to trivalent state form and then precipitated as chromic hydroxide using lime. However, this method is only effective at high chromium concentrations and has several disadvantages such as a significant sludge production; an ever increasing cost of landfill disposal, and most importantly, long-term environmental consequences. In the literature, the removal of Cr(VI) was achieved by different biomasses and the optimum pH for removal was reported to be in the 2.0–3.0 range [50–52].

This study reports the use of shells of WNS, HNS and AS as a biosorbent to remove toxic Cr(VI) ion from aqueous solutions and compare their performance. This will permit the evaluation of shells for their utilization as an adsorbent in the elimination of Cr(VI) ion from aqueous solution. The effect of time, initial concentration of the metal, solution pH and adsorbent dosage on the biosorption at room temperature are also studied and compared.

2. Materials and methods

2.1. Materials

Shells of Turkish WNS, HNS and AS species were ground in a ball mill and the resulting crumbs were sieved to obtain particle size under 100 μm. Before their use, all the sorbents were washed thoroughly with deionized water and oven dried at 100 °C for 24 h. All solutions were prepared from analytical grade chemicals and Mili-Q filtered deionized water. One millimolar of Cr(VI) stock solution was prepared by dissolving 0.1471 g of $K_2Cr_2O_7$ (from Merck). The working solutions with a concentration of 0.1–1 mM Cr(VI) were prepared by appropriate dilutions of the stock solution immediately prior to their use. The electrolyte used to modify the ionic strength in the adsorption experiments was 0.1 M KNO_3.

2.2. Batch adsorption

Shells were ground using a with Retsch RM 100 model grinding machine. The pH measurements were performed with an Orion 900S2 Model pH meter. A thermo stated shaker (GFL 3033 model) and magnetic stirrer (IKAMAG-RO15 model) were used for the sorption experiments. The sorption of Cr(VI) on shells was studied by batch technique. The general method used for this study is described as follows: 0.5 g shell was equilibrated with 20 mL of the 1 mM Cr(VI) solution in a stoppered pyrex glass flask at a fixed temperature in a thermostatic shaker bath. The initial pH of the solution was adjusted with diluted 0.1 M HNO_3 or 0.1 M NaOH solution and the stirring speed was 200 rpm to maintain the sorbent particles in suspension. The WNS, HNS and AS sorbents and solution were separated by filtration through a membrane filter. The shells were washed with distilled water and filtrate was collected in a separate beaker. The Cr(VI) ion concentrations in the solutions were determined by the standard colorimetric method with 1,5-diphenylcarbazide [53]. Metal concentration in the solution was analyzed with UV–vis Spectrophotometer (Schmadzu UV-1700) (λ: 540 nm). The concentration of chromium metal ions was calculated from the change in metal concentration in the aqueous solution before and after equilibrium sorption. In all cases, mass balance was confirmed.

Contact time adsorption experiments were conducted at 25 ± 1 °C in a well-mixed Pyrex glass vessel with a cover. Shells were added into deionized water having different initial pH (2–9) values. The test tubes were agitated intermittently for 2 h at room temperature, and then left for settling of shells. The final pH of the solution was measured. After equilibrium was reached, the pH of the solution was measured and recorded. Sorption isotherms were carried out with different initial metal concentrations varying from 0.1 to 1 mM while holding the sorbent amount at constant value at room temperature (25 ± 1 °C). The sorbent amount in the batch vessel was varied from 0.1 to 1 g for adsorption studies. The same measurements were repeated three times and average values have been taken as the remaining metal amount in the solution phase. The maximum deviation was 2.1%.

Total unadsorbed chromium (VI) was calculated by taking the difference of initial concentration and total hexavalent chromium concentration in the filtrate.

Cr(VI) sorbed = (initial chromium concentration) − (chromium concentration in the filtrate)

The kinetic data of adsorbed amount of metal at time t, q_t (in mg g^{-1} of adsorbent), were obtained by the mass balance [54]:

$$q_t = \frac{[(C_o - C_t)\, V]}{m} \tag{1}$$

where q is adsorbed metal (mmol/g adsorbent) on the sorbents, m is the weight of sorbents (g), V is volume of metal solution (L), C_o is initial metal concentration (mmol/L), and C_t is metal