Removal of Cr (VI) Through the Use of the Agroindustrial Residue of the Persea Americana Shell

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Abstract

We analyzed the Chromium (VI) removal capacity in aqueous solution by the Persea americana biomass, using the diphenyl carbazide method to evaluate the metal concentration. Biosorption at different pH (1, 2, 3, and 4) was evaluated for different times. We too studied the effect of temperature in the range of 28 to 60 °C and the removal at different initial concentrations of Cr (VI) of 200 to 1000mg/L. Therefore, the highest biosorption of the metal (50mg/L) occurs within 270 minutes, at pH of 1.0 and 28 °C. According to temperature, the highest removal was observing at 60 °C, in 45 minutes, when the metal is completely adsorbed. At the analyzed concentrations of Cr(VI), fungal biomass, showed excellent removal capacity, besides it removes efficiently the metal in situ (100% removal in earth and water contaminated, after 5 and 6 days of incubation, 5 and 10g of biomass, 10g of earth and 100 mL of water); so, it can be used to eliminate it from industrial wastewater.

Keywords: Chromium (VI); Removal; Shell biomass; Detoxification

Introduction

Currently, one of the main environmental problems is heavy metal pollution. These elements alter the equilibrium of ecosystems by persisting indefinitely in the environment, because they are not degrading by biological or chemical means [1]. Its accumulation in the organisms of the different links of the trophic chain, its mobility in natural aquatic ecosystems and its toxicity, make its elimination a global concern [2]. The introduction and redistribution of metal ions in the biosphere have their origin from natural and anthropogenic sources [3]. However, the main direct as well as indirect cause of the metal contamination are the urban sources, being the industrial operations with a deficient or absent treatment of its residual waters and solid waste, its main emitter. Some of the industries that generate waste contaminated with these elements are sugar, oil, brewing, textiles, cellulose and paper, metal finishing, copper and its alloys, tannery, food and of iron and steel, legally classified as point sources of pollution [2]. Hexavalent chromium [Cr (VI)] is an important water pollutant. Even at Cr (VI) levels measuring in the parts per billion (ppb), research has shown it to be toxic [4]. Cr (VI) can originate from different anthropogenic activities such as chromite mining, leather tanning, pigment synthesis, electroplating and metal finishing [4]. The primary forms of chromium found in nature are chromium (III) and chromium (VI) and these forms are convert to each other depending on environmental conditions [5]. Cr (VI) is consider the most toxic form of chromium is usually associated with oxygen as chromates (CrO₄²⁻) and dichromate (Cr₂O₇²⁻) [4].

It has been established now that various chromium compounds as oxides, chromates and dichromate, are environmental contaminants in water, soil, and industrial effluents, because this metal is widely used in various manufacturing, such as electrolytic plating, explosives manufacturing, leather tanning, metal alloy, dyes and pigments manufacturing, etc., [2,3,5]. There are studies of the current technologies that are being used to effectively reduce Cr (VI) present in aqueous solutions by means of chemical, electrochemical and biological methods, for example: ion exchange on resins, coagulation-flocculation, adsorption on activated carbon, reduction, chemical precipitation, sedimentation, etc., [6], which in most cases are expensive or inefficient, especially when the concentration of these ions is very low [7]. Therefore, arise emerging technologies such as biosorption, the process of attracting various chemical species by biomass (live or dead), by physicochemical mechanisms as adsorption or ion exchange [8]. Recently, varieties of low cost materials have been study for their ability to remove Cr (VI) from aqueous solution and promising results are shown. Among these low cost adsorbents are dead microorganisms, clay minerals, agricultural wastes, industrial wastes and various other...
low cost materials [4,6-9]. Thus, there is a need to develop or find innovative low cost adsorbents with an affinity towards metal ions for the removal of Cr (VI) from aqueous solution, which leads to high adsorption capacity [4,6-8]. The objective of this study was to analyze in vitro biosorption of Cr (VI) by Persea americana shell biomass.

Material and Methods

Biosorbent used

The Persea americana shell, was obtained from the fruits harvested and offered in the market place Republic, between the months of August to September in 2017, of the capital city of San Luis Potosí, S.L.P. México. To obtain the biomass, the shells was washed with tri de-ionized water during 72 hours at constant stirring, with water changes every 12 hours. Subsequently, it was boil 1 hour to removal traces of the fruit and dust and were dry at 80 °C for 12 hours in an oven, ground in blender and stored in amber vials until use.

Biosorption studies and determination of hexavalent, trivalent, and total chromium

For these studies, was used 1g of dried biomass mixed with 100mL of tri deionized water containing 50mg/L in an Erlenmeyer flask at the desired temperature and pH. The flasks were agitated on a shaking bath Yamato BT-25 model at different times. Samples of 5mL were taken at different times and centrifuged at 3000rpm for 5min. The supernatant liquid was separated and analyzed for Cr (VI) ions, which were quantifying by a Spectrophotometric method employing Diphenylcarbazide [10]. The information shown in the results section are the mean from three experiments carried out by triplicate.

Result and Discussion

Effect of incubation time and pH

The optimum time and pH for Cr (VI) removal for P. americana was 270 minutes and pH 1.0, at constant values of biosorbent dosage (1g/100 mL), with an initial metal concentration of 50mg/L, and a temperature of 28 °C (Figure 1). It was used a pH meter Corning Pinnacle 530 model and we use nitric acid 1M to maintain the pH. The literature [11], report an optimum time of 4 hours for the removal of Cr(VI) by Anamarantus caudatus, with 5g of biomass, 180 minutes for the Cucumis melo shell [12], 9 hours for sawdust of pine tree [13], 16, 60, 120, 180, and 480 minutes, respectively for Magnifica indica, Magnifica paradisisaca, Cucumis paradise, Cucumis melo, and Cucumis máxima shells [14,15] and pH 1.0, at constant values of biosorbent dosage (1g/100 mL), with an initial metal concentration of 50mg/L. Changes in the cell permeability of unknown origin, could partly explain the differences founded in the incubation time, providing greater or lesser exposure of the functional groups of the cell wall of the biomass analyzed [1,3,6-8].

Adsorption efficiency of Cr (VI) was observe a maximum at pH 1.0 with the biomass analyzed, and this is like to most reports [1,11-15]. This was due to the dominant species (CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$) of Cr ions in solution, which were expecting to interact more strongly with the ligands carrying positive charges [1,7,8].

**Figure 1:** Effect of incubation time and pH on Chromium (VI) removal by the biomass of P. americana shell. 50mg/L Cr (VI), 100rpm, 28 °C.

Effect of the temperature

Temperature was found to be a critical parameter in the bio adsorption of Cr (VI) (Figure 2). To maintain constant the temperature in all experiments, we use a shaking bath Yamato BT-25 model. The total removal was observed at 60 °C and 28 °C with 45 minutes and 64 hours of incubation. This results are coincident for tamarind shell with 95% of removal at 58 °C and 3 hours [16], for the adsorption of cadmium (II) from aqueous solution on natural and oxidized corncob (40 °C and 5 days) [17], but these are different for the mandarin waste [18], Caladium bicolor (wild cocoyam) biomass [19], and Saccharomyces cerevisiae [20]. The increase in temperature increases the rate of removal of Chromium (VI) and decrease the contact time required for complete removal of the metal, to increase the redox reaction rate [16].
Effect of initial metal concentration

At low metal concentrations (200mg/L), we observe the best results for removal, with the biomass analyzed, 28 °C, because the removal of the metal was 100% at 20 and 64 hours for 200 and 1000mg/L, respectively (Figure 3). In addition, we observe the development of a blue-green and white precipitate, which changes more rapidly at higher temperatures (date not shown). The results are coincident for C. reticulata and Tamarindus indica shell [12,16]. With respect to other biomasses, most authors report lower removal efficiencies of metal, for example: 45mg/L for eucalyptus bark [21], 13.4 and 17.2mg/L for bagasse and sugar cane pulp, 29mg/L coconut fibers, 8.66mg/L for wool [22], 25 and 250mg/L of chitin and chitosan [23], and 1mg/L for cellulose acetate [24]. The increase in initial concentration of Cr (VI), results in the increased uptake capacity and decreased in the percentage of removal of the metal. This was due to the increase in the number of ions competing for the available functional groups on the surface of biomass [16]. On the other hand, at 60 °C, 200 and 1000mg/L, they are eliminated at 60 and 120 minutes, respectively (Figure 4), which is similar to other reports in the literature, for the removal of the same metal concentration by different natural biomasses [11-16].

Figure 2: Effect of the temperature on Chromium (VI) removal by the biomass of P. americana shell, 50mg/L Cr (VI), pH 1.0, 100rpm.

Figure 3: Effect of initial metal concentration on Cr (VI) removal by biomass of P. americana shell. pH 1.0, 100rpm, 28 °C.

Figure 4: Effect of initial metal concentration on Cr (VI) removal by biomass of P. americana shell. pH 1.0, 100rpm, 60 °C.
Effect of bio sorbent dose

The influence of biomass concentration on the removal capacity of Cr (VI) is depicted in Figure 5. If we increase the amount of biomass, also increases the removal of the metal in solution, with more biosorption sites of the same, because the amount of added bio sorbent determines the number of binding sites available for metal biosorption [25]. Similar results have been reported for modified corn stalks [26], C. reticulata shell [27], and Mucor hiemalis and Rhizopus nigricans, although latter with 10g of biomass [18,28], but they are different from those reported for wastes biomass of mandarin (bagasse), with an optimal concentration of biomass of 100mg/L [29].

![Figure 5: Effect of biomass concentration of P. Americana on the removal of 50mg/L Cr (VI), 28 °C, pH 1.0, 100rpm.](image)

Removal of Cr (VI) in industrial wastes with biomass of P. americana shell

![Figure 6: Removal of Cr (VI) in industrial wastes incubated with 5 and 10g of P. americana biomass. 28 °C, 100rpm, 100mL of contaminated water, (50mg Cr (VI)/L (adjusted).](image)

![Figure 7: Removal of Cr (VI) in industrial wastes incubated with 5 and 10g of P. americana biomass. 28 °C, 100rpm, 10g of contaminated earth, (50mg Cr (VI)/g earth.](image)
We adapted a water-phase bioremediation assay to explore possible usefulness of this biomass for eliminating Cr (VI) from industrial wastes, the biomass (5 and 10g), was incubate with non-sterilized contaminated earth and water containing 50mg Cr (VI)/g and 50mg Cr(VI)/L (adjusted), suspended in tri deionized water to a final volume of 100mL. It was observing that in 5 and 6 days of incubation with the biomass, the Cr (VI) concentration of earth and water samples decrease fully in both (Figures 6 & 7), and the decrease level occurred without change significant in total Chromium content during the experiments. In the experiment carried out in the absence of the biomass, the Cr (VI) concentration of the earth samples decreased by about 18% (date not shown); this might be caused by indigenous microflora and (or) reducing components present in the soil [1,4,9,11]. The chromium removal abilities of this biomass are equal or better than those of other reported for example, T. indica, M. paradisiaca, C. limonium, and C. sinensis shells [30], maize leaf [31], C. melo shell [12], sawdust of pine tree [13], M. indica, M. paradisiaca, C. paradisi, C. melo y C. máxima shells [14,15].

Conclusion

The biomass analyzed, showed complete capacity of biosorption of 1.0g/L Cr (VI) in solution at different time of incubation, at 28 °C, 100rpm with 1g of biomass, besides this removal the metal in situ (5 and 6 days of incubation, with 5 and 10g of biomass), in earth and water contaminated. These results suggest their potential applicability for the remediation of Cr (VI) from polluted soils in the fields.

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References


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