Biosorption of Chromium (VI) by Cucumis Melo Shell

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Abstract—Cr (VI) is a toxic metal which belongs to the list of priority pollutants due to its mutagenic and carcinogenic properties, defined by the US EPA. Contamination with Cr (VI) comes from electroplating, leather tanning, textile dyeing and metal finishing industries. Recently, a variety of low cost materials has been studied for their ability to remove this metal from aqueous solution with promising results. We studied the Cr (VI) removal capacity in aqueous solution by the biomass of Cucumis melo shell, using the diphenylcarbazide method to evaluate the metal concentration in solution and obtaining the highest biosorption of the metal (50 mg/L) in 180 min, at pH of 1.0, and 28°C. The highest removal (100%), was observe at 60°C, at 40 min. At the analyzed concentrations of Cr (VI), biomass showed good removal capacity of 1.0 g/L of the metal (100%), 75 min at 60°C. If we increase the biosorbent concentration, increase the metal removal, with 100% at 25 min with 5 g of Cucumis melo biomass.

Keywords—Chromium (VI), Removal, Biomass, Shell, Detoxification

I. INTRODUCTION

Chromium (Cr) toxicity is used in the tanning of hides and leather, the manufacture of stainless steel, electroplating, textile dyeing and as a biocide in the cooling water of nuclear power plants. Discharges from these industries cause one of the major environmental pollution problems, due to the toxicity of this metal [1], which exists in nine valence states (from -2 to +6), but only the hexavalent Cr (VI) and trivalent Cr (III) forms have significance because they are the most stable in environment [2]. The discharges are spill into water bodies and wastewaters, so we found the Cr (VI) as chromate (CrO$_4^{2-}$) or dichromate (Cr$_2$O$_7^{2-}$), depending of the pH in the solution [3]. These two divalent oxyanions are very water soluble and poorly adsorbed by soil and organic matter, making them mobile in soil and groundwater [2], which represent acute and chronic risks to animals and human health, because they are extremely toxic, mutagenic, carcinogenic and teratogenic [4]. While Cr (III) species: predominantly hydroxides, oxides or sulphates, are less water soluble, mobile, 100 times less toxic [5], and 1000 times less mutagenic [6]. The principal techniques for recovering or removing Cr (VI) from wastewater are chemical reduction and precipitation, adsorption on activated carbon, ion exchange and reverse osmosis in a basic medium [7]. However, these methods have certain disadvantages: high cost, low efficiency, generation of toxic sludge and other wastes that require disposal and imply operational complexity [8]. In the recent years, several studies on the removal of Cr (VI), have been reported, using various low cost adsorbents such as wool [9], used tires [10], seaweed [11], fungal biomass [12], green algae [13], maple sawdust [14], sugar industry waste [15], etc. However, many of these naturally available adsorbents have low chromium adsorption capacity. 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 [16]. The objective of this study was to analyze in vitro biosorption of Cr (VI) by biomass of Cucumis melo shell.
II. EXPERIMENTAL

A. Biosorbent used

The *Cucumis melo* shell was obtained from the fruits harvested and offered in the market place Republic, between the months of June to September in 2013, of the capital city of San Luis Potosí, S.L.P. México. To obtain the biomass, *C. melo* rind was washed with trideionized water 72 hours under constant stirring, with water changes every 12 hours.

Subsequently, boiled 1 hour to remove traces of the fruit was dry at 80°C for 12 hours in the oven, ground in blender and stored in amber vials until use.

B. Biosorption studies and determination of hexavalent, trivalent, and total Cr

In these study, was used 1 g of dried biomass mixed with 100 mL, containing 50 mg/L of the metal bearing solution 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 5 mL were taken at different times and centrifuged at 3000 rpm for 5 min.

The supernatant liquid was separated and analyzed for Cr (VI) ions. Hexavalent Chromium and trivalent Chromium were quantify by a spectrophotometric method employing diphenylcarbazide and chromazurol S, respectively [17,18], total Chromium was determine by electrothermal atomic absorption spectroscopy [17]. The information shown in the results section are the mean from three experiments carried out by triplicate.

III. RESULTS AND DISCUSSION

A. Effect of incubation time and pH

The optimum time and pH for Cr (VI) removal was 180 min, and pH 1.0, at constant values of biosorbent dosage (1 g/100 mL), with an initial metal concentration (50 mg/L), and 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. In the literature [19], report an optimum time of 60 min for the removal of lead by orange shell, 30 min and 2 hours for the removal of Cr (VI) by the *Citrus reticulata* shell and eucalyptus bark [20,21]. Changes in the 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.

Adsorption efficiency of Cr (VI) was observe a maximum at pH 1.0 with the biomass of *C. melo* shell. This was due to the dominant species (CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$) of Cr ions in solution, which were expect to interact more strongly with the ligands carrying positive charges [13].

B. Effect of the temperature

Temperature was found to be a critical parameter in the biosorption 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 40 min of incubation time. The results are coincident for tamarind shell with 95% of removal at 58°C and 3 hours [22], for the adsorption of cadmium (II) from aqueous solution on natural and oxidized corncob (40°C and 5 days) [23], but these are different for the mandarin waste [24], Caladium bicolor (wild cocoyam) biomass [25], and Saccharomyces cerevisiae [26]. 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 [22].

C. Effect of initial metal concentration

At low metal concentrations (200 mg/L) of biomass studied, we observe the best results for removal, adsorbing 100% in 40 min at 60°C while 1000 mg/mL of the metal are removed at 75 min and 24 h at 60°C and 28°C, respectively (Figures 3a, and 3b). 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* shell [20,22]. With respect to other biomasses, most authors report lower removal efficiencies of metal, for example: 45 mg/L for eucalyptus bark [21], 13.4 and 17.2 mg/L for bagasse and sugar cane pulp, 29 mg/L coconut fibers, 8.66 mg/L for wool [9], 25 and 250 mg/L of chitin and chitosan [27], and 1 mg/L for cellulose acetate [28]. 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 [22].

E. Time course of Cr (VI) decrease and Cr (III) production by sorption of Cr (VI) by different solutions

The ability of the biomass of C. melo shell to lower the initial Cr (VI) of 1.0 g/L and Cr (III) production in solution was analyzed. Figure 5 shows that the biomass exhibited a remarkable efficiency to diminish Cr (VI) level with the concomitant production of Cr (III) in the solution (indicated by the formation of a blue-green color and a white precipitate, and his determination for Cromazurol S, date not shown) [18]. Thus, after 90 min of incubation, the biomass analyzed, caused a drop in Cr (VI) from its initial concentration of 1.0 g/L to almost undetectable levels, and the decrease level occurred without change significant in total Chromium content. As expected, total Chromium concentration remained constant over time, in solution control. These observations indicate that this biomass is able to reduce Cr (VI) to Cr (III) in solution. Furthermore, as the C. melo shell contains vitamin C and some carbohydrates, we found that vitamin C and cystine reduce faster Cr (VI) to Cr (III), and could be very important part in the metal reduction, confirming some reports in the literature [2,3,20,32,33]. There are two mechanisms by which chromate could be reduced to a lower toxic metal. Oxidation state by an enzymatic reaction. Currently, we do not know whether the shell biomass used in this express study and Cr (VI) reducing enzyme(s). Further studies are necessary to extend our understanding of the effects of coexisting ions on the Cr (VI) reducing activity of the biomass reported in this study. In addition, Cr (VI) reducing capability has been described in some reports in the literature [2,3,8,34-38]. Biosorption is the second mechanism by which the chromate concentration could be reduced, because the biomass shell can be regarded as a mosaic of different groups that could form coordination complexes with metals, and our observations are like to the most of the reports in the literature [2,3,8,34-38].

D. Effect of biosorbent dose

The influence of biomass on the removal capacity of Cr (VI) is depict in Figure 4. If we increase, the amount of biomass also increases the removal of the metal in solution (100% of removal, with 5 g of biomass at 25 min), with more biosorption sites of the same, because the amount of added biosorbent determines the number of binding sites available for metal biosorption [29]. Similar results have been reported for modified corn stalks [30], C. reticulata shell [20], and Mucor hiemalis and Rhizopus nigricans, although latter with 10 g of biomass [31,1], but they are different from those reported for wastes biomass of mandarin (gabasse), with an optimal concentration of biomass of 100 mg/L [24].

F. Removal of Cr (VI) in industrial wastes with biomass of C. melo shell

We adapted a water-phase bioremediation assay to explore possible usefulness of biomass of C. melo shell, for eliminating Cr (VI) from industrial wastes, the biomass was incubate with non-sterilized contaminated soil and water containing 297 mg Cr (VI)/g, and 155 mg Cr(VI)/L, suspended in trideionized
water. It was observe that in seven days of incubation with the biomass, the Cr (VI) concentration of soil sample decrease 90.1%, and 86.1%, respectively, (Figure 6), 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 soil samples decreased by about of 18% (date not shown); this might be caused by indigenous microflora and (or) reducing components present in the soil. The chromium removal abilities of the biomass of *C. melo* shell, are equal or better than those of other reported, for example *C. reticulata* shell [20], *Mammea Americana* [39], and *Candida maltose* RR1 [37]. In particular, this biomass was superior to the other biomass because it has the capacity for efficient chromium reduction under acidic conditions. Many of the Cr (VI) reduction studies were carry out at neutral pH [40]. *Aspergillus niger* also has the ability to reduce and adsorb Cr (VI) [40]. When the initial concentration of Cr (VI) was 500 ppm, *A. niger* mycelium removed 8.9 mg of chromium/g dry weight of mycelium in 7 days.

**G. Desorption of Cr (VI) by different solutions**

Furthermore, we examined the ability of different solutions to desorb the metal biosorbed (250 mg/L) for the biomass of *C. melo* shell, obtaining high efficiency of biosorption with NaOH 0.1 N and 0.5 N (82.1% and 67.1%, respectively, figure 7), which are less than reported for desorption of Chromium (VI) with alkaline solutions (100%, pH = 9.5), 1.0 N NaOH (95%) and a hot solution of NaOH/Na$_2$CO$_3$ (90%), respectively, [41,42], higher than that reported (14.2%) using 0.2 M NaOH [43]. This indicates that binding of metal to biomass is not as strong and that it can be used up to 6-desorption cycles of removal, which further lower the metal removal process of niches contaminated with it.

## IV. CONCLUSIONS

The biomass of *C. melo* shell, showed complete capacity of biosorption of 1.0 g/L Cr (VI) in solution after 75 minutes of incubation, at 28°C, 100 rpm with 1 g of biomass, besides it removes the metal in situ (90.1%, and 86.1% removal, 7 days of incubation, 5 g of biomass), in soil and water contaminated, respectively. These results suggest the potential applicability of *C. melo* shell biomass for the remediation of Cr (VI) from polluted soils in the fields.

## V. REFERENCES


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