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REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTION BY Opuntia Ficus-indica BIOMASS

Juan F. Cárdenas-González¹, Itzel Alcaraz-Vázquez¹, María de Guadalupe Moctezuma-Zarate¹, Adriana Rodríguez-Pérez¹, Víctor M. Martínez-Juárez² e Ismael Acosta Rodríguez¹

¹Laboratorio de Micología Experimental. Facultad de Ciencias Químicas. Universidad Autónoma de San Luis Potosí, ²Área Académica de Medicina Veterinaria y Zootecnia. Instituto de Ciencias Agropecuarias. Universidad Autónoma del Estado de Hidalgo, México

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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 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 removal this metal from aqueous solution with promising results. We studied the removal capacity of Cr (VI) in solution by the Opuntia ficus-indica biomass, using the Diphenylcarbazide method to evaluate the metal concentration. Therefore, the highest biosorption of the metal (50 mg/L) occurs within 30 minutes, at pH 1.0, and 28°C. According to temperature, the highest removal was observed at 60°C, in 9 minutes, when the metal (50 mg/L) is completely adsorbed. At the concentrations of Cr (VI) and biomass analyzed, we observe an excellent removal capacity, besides, it removal efficiently the metal in situ (100% removal, at 6 and 7 days of incubation, 5 g of biomass, for water and earth contaminated), and after of 80 minutes of incubation, the studied biomass reduces 1.0 g of Cr (VI) with the simultaneous production of Cr (III), so it can be used to eliminate it from industrial wastewater.

KEYWORDS: Chromium (VI), Removal, Biomass, Opuntia Ficus-indica

INTRODUCTION

Chromium is regarded as an environmental pollutant due to its wide use in various industrial activities, such as electrolytic plating, leather tanning, explosives manufacturing etc. The stable forms of chromium in the environment are trivalent (Cr (III)) and hexavalent chromium (Cr (VI)). Further, Cr (VI) is highly soluble, making it mobile in soil and aquatic environments, with consequent toxicity ecosystems. Chromium in their different forms can be different in the production of steel alloys and other metals chromed, for dyes and pigments, and the preservation of leather and wood. It can also be find naturally in the soil [1]. The primary forms of chromium found in nature are Cr (III) and Cr (VI) and these forms are converted to each other depending on environmental conditions [2]. Cr (VI) is consider the most toxic form of chromium, and is usually associated with oxygen as chromates (CrO₄²⁻) and dichromate (Cr₂O₇²⁻) [3], which due to its high solubility are highly mobile in soil environments and water [2]. Moreover, Cr (III) is in the form of oxides, hydroxides or poorly soluble sulfates, by which it is much less mobile, and there joined organic matter in the soil and aquatic environments [4,5]. Cr (VI) is a strong oxidizing agent, and in the presence of organic matter is reduced to Cr (III); this transformation is faster in acidic environments [3]. However, high levels of Cr (VI) may exceed the reducing capacity of the environment and thus can persist as a contaminant. 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. [1,5].

There are studies of many methods for removal of chromium ion present in water industrial waste, 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 [6]. 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 [6]. Recently, varieties of low cost materials have been studied 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 [1, 7]. 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 [6-9]. The objective of this study was to analyze in vitro biosorption of Cr (VI) by *Opuntia ficus-indica* biomass.

**MATERIALS AND METHODS**

**Biosorbent used**

The *Opuntia ficus-indica* biomass was obtained from the store offered in the market place Republic, in February 2016, of the capital city of San Luis Potosi, S.L.P. México. To obtain the biomass, the product was washed with trideionized water 72 hours under constant stirring, with water changes every 12 hours. Subsequently, boiled 1 hour to remove traces of dust, and were dry at 80°C for 12 hours in the oven, ground in blender and stored in amber vials until use.

**Biosorption studies and determination of hexavalent chromium**

In these studies, 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 [10, 11], total Chromium was determine by electrothermal atomic absorption spectroscopy [10]. The information shown in the results section are the mean from three experiments carried out by triplicate. The information shown in the results section are the mean from three experiments carried out by triplicate.

**RESULTS AND DISCUSSION**

The optimum time and pH for Cr (VI) removal for *Opuntia ficus-indica* biomass was 30 minutes 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. Adsorption efficiency of Cr (VI) was observe a maximum at pH 1.0 with the biomass analyzed. As the initial pH values increased from 1.0 to 4.0, the removal efficiencies of Cr (VI) with the biomass decreased from 100% to 42.9%, respectively (Figure 1). It has been reported, an optimum time of 48 h for the removal of Cr (VI) by the fruiting body of *Auricularia polytricha*, which is one of the most common edible mushrooms in China and other places in the world [12], 48 min for the removal of Cr(VI) from aqueous solutions using powder of potato peelings [13], 30 minutes for the removal of Cr (VI) by the *Citrus reticulata* shell [14], 70 minutes for *Citrus paradise* shell [15], and 24 h for modified Russian knapweed flower powder [16]. 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 [1,6]. Adsorption efficiency of Cr (VI) was observe a maximum at pH 1.0 with the biomass analyzed, and this is like to some reports: *C. reticulata*, *C. Paradise*, *Mammea americana* L. and *Litchi chinensis* shells [7,8,12,13], and for the fruiting body of *A. polytricha*, [12], but are different for the removal of the same metal with powder of potato peelings [13], who report an optimum pH of 2.5, a pH of 2.0 for modified Russian knapweed flower powder [16], a pH of 4.0 using chitosan [17], for the removal of lead (II) in solution with african palm bagasse [18], and a pH of 2.0 with granular activated charcoal prepared of *Cordia macleodii* tree bark [9]. This was due to the dominant species (CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) of Cr ions in solution, which were expect to interact more strongly with the ligands carrying positive charges [1].

Temperature was found to be a critical parameter in the bioadsorption 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 with 9 minutes of incubation, and our results are coincident for tamarind shell with 95% of removal at 58°C and 3 h [19], for the adsorption of the same metal with *C. reticulata*, *C. Paradise*, *M. americana* L., shells [7,8,12, and 15], and for the granular activated charcoal prepared of *C. macleodii* tree bark [9], but, are different for the mandarin waste [20], *Caladium bicolor* (wild cocoyam) biomass [21], and *Saccharomyces cerevisiae* [22]. 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 [19].
Figure 1. Effect of incubation time and pH on Chromium (VI) removal by the biomass of Opuntia ficus-indica. 50 mg/L Cr (VI), 100 rpm, 28°C, 1 g of biomass.

Figure 2. Effect of the temperature on Chromium (VI) removal by the biomass of Opuntia ficus-indica. 50 mg/L Cr (VI), 100 rpm, pH 1.0, 1 g of biomass.

It was found that the concentration of the metal does not influence in the removal of the same, since the analyzed concentrations (200-1000 mg/L) are eliminated at 70 minutes (Figure 3). This results are like for sawdust pine tree [8], and different natural biomasses [23], but are different for the granular activated charcoal prepared of C. macleodii tree bark [9], for C. reticulate, [14], Tamarindus indica shell [19], the fruiting body of A. polytricha [12], for modified Acroptilon repens (Russian knapweed) flower powder [16], for the removal of Cr (VI) from aqueous solutions using powder of potato peelings [15], and chitosan [17]. With respect to other biomasses, most authors report lower removal efficiencies of metal, for example: 45 mg/L for eucalyptus bark [24], 13.4 and 17.2 mg/L for bagasse and sugar cane pulp, 29 mg/L coconut fibers, 8.66 mg/L for wool [25], 25 and 250 mg/L of chitin and chitosan [26], and 1 mg/L for cellulose acetate [27]. 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 [19]. In addition, we observe the development of a blue-green and white precipitate, which changes more rapidly at higher concentration, and indicate the production of Cr (III) (Figure 4), which are similar for the adsorption of the same metal with C. reticulata, C. Paradise, M. americana L., shells [7,8,12, and 15].
On the other hand, 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 biosorbent determines the number of binding sites available for metal biosorption [29]. Similar results have been reported for modified corn stalks [29], C. reticulata, C. Paradise M. americana L. and L. chinensis shell [7,8,14,23], which, removal efficiency increased from 88% to 100%, 56.1% to 91.7% and 45% to 79.2% at concentrations of 2, 10 and 15 mg/L, respectively, and for the removal of Cr(VI) from aqueous solutions using powder of potato peelings [13], which a complete removal is attained after only 48 minutes with a dosage of 4 g/L, whilst a dosage of 0.5 g/L requires 120 minutes to attain 96 ± 2% removal. But they are different from those reported for the fruiting body of A. polytricha, for modified A. repens (Russian knapweed) flower powder [16], with a removal amount of Cr (VI) reached the highest at the dosage of 4 g/L and then declined with the dosage, and with wastes biomass of mandarin (gabasse), with an optimal concentration of biomass of 100 mg/L [20].

Figure 3. Effect of the initial concentration of metal on Chromium (VI) removal by the biomass of Opuntia ficus-indica, 100 rpm, 28°C, pH 1.0, 1 g of biomass.

Figure 4. Formation of green color by different concentration of Chromium (VI) by the biomass of Opuntia ficus-indica, 100 rpm, 28°C, pH 1.0, 1 g of biomass.
Figure 5. Effect of the initial biomass concentration on the removal of 200 mg/L of Chromium (VI), by the biomass of Opuntia ficus-indica, 100 rpm, 28°C, pH 1.0.

The ability of this biomass of to lower the initial Cr (VI) of 1.0 g/L and Cr (III) production in solution was analyzed. Figure 6 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). Thus, at 80 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 this biomass 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 (date not shown), confirming some reports in the literature [14,31,32, and 33].

Figure 6. Time-course of Cr (VI) decrease and Cr (III) production in solution with 1.0 g/L Cr (VI). 28°C, pH 1.0, 100 rpm.

Finally, we adapted a water-phase bioremediation assay to explore possible usefulness of this biomass for eliminating Cr (VI) from industrial wastes, the biomass (5 g), was incubate with non-sterilized contaminated earth and water containing 297 mg Cr (VI)/g, and 200 mg Cr(VI)/L, suspended in trideionized water. It was observe that in 6 and 7 days of incubation with the biomass, the Cr (VI) concentration of water and earth samples decrease totally (Figure 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 of 18% (date not shown); this might be caused by indigenous microflora and or reducing components present in the soil. In the literature, was reported the ability of the yeast Candida tropicalis to remove Cr was tested in artificially contaminated soils in a microcosm system.
to simulate natural environmental conditions, showing reduction of 72.2% of 40 mg/L Cr (VI) [34]. An A. niger strain isolated from a tannery was used in an airlift reactor for the treatment of tanning wastewater, leading to maximum removal efficiency by adsorption of 88% of an initial Cr (III) concentration of 1300 mg/L [35]. These results are even better than those obtained (removal efficiency of 72%) with the same organism using a stirred tank reactor [36]. The use of a consortium of Cr-resistant fungi immobilized in a support material in a stirred tank bioreactor filled with wastewater from a tannery achieved an overall removal efficiency of 99.9% of the total Cr present.

CONCLUSION
The biomass analyzed, showed complete capacity of biosorption of 50 g/L Cr (VI) in solution at different time of incubation, at 28°C, 100 rpm with 1 g of biomass, besides this removal the metal in situ (6 and days of incubation, 5 g of biomass), in water and earth contaminated. These results suggest their potential applicability for the remediation of Cr (VI) from polluted soils in the fields.

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