

BIOSORPTION OF CHROMIUM (VI) BY *Citrus paradise* SHELL

Ismael Acosta Rodríguez

Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
iacosta@uaslp.mx

Juan F. Cárdenas González

Facultad de Ciencias
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
jfkardenas_08@hotmail.com

María de Guadalupe Moctezuma Zárate

Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
moctezum@uaslp.mx

Adriana S. Rodríguez Pérez

Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
asara128@hotmail.com

Erika Enríquez Domínguez

Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
Erika.e.domínguez@gmail.com

Juana Tovar Oviedo

Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
jtoviedo@uaslp.mx

Víctor M. Martínez Juárez

Área Académica de Medicina Veterinaria y
Zootecnia
Universidad Autónoma del Estado de Hidalgo
Hidalgo, México
victormj@uaeh.edu.mx

María Z. Acosta Nava

Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
zitaan2000@tahoo.com.mx

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 removal capacity of Chromium (VI) in solution by the grapefruit shell biomass, using the Diphenylcarbazide method to evaluate the metal concentration. Therefore, the highest biosorption of the metal (50 mg/L) occurs within 70 minutes, at pH of 1, and 28 °C. According to temperature, the highest removal was observed at 60°C, in 180 minutes, when the metal (1 g/L) is completely adsorbed. At the concentrations of Cr (VI) analyzed, the biomass showed excellent removal capacity, besides, removes efficiently the metal in situ (100% removal, 7 days of incubation, 5 g of biomass), and after of 1 hour 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, grapefruit Biomass, Detoxification

I. 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 use 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. The primary forms of chromium found in nature are chromium (III) and chromium (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 (CrO_4^{-2}) and dichromates ($\text{Cr}_2\text{O}_7^{-2}$) [3], which due to its high solubility are highly mobile in soil environments and water [4]. 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 [5, 6]. 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 dichromates, 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., [7], which in most cases are expensive or inefficient, especially when the concentration of these ions is very low [8]. 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 [9]. 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, 10]. 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 [11]. The objective of this study was to analyze in vitro biosorption of Cr (VI) by grapefruit shell biomass.

II. EXPERIMENTAL

A. Biosorbent used

The *Citrus paradise* shells, was obtained from the fruits harvested and offered in the market place Republic, between the months of June to September in 2015, of the capital city of San Luis Potosí, S.L.P. México. To obtain the biomasses, the shells and 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 and dust, and were 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 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 [12, 13], total Chromium was determine by electrothermal atomic absorption spectroscopy [12]. 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 for *C. paradise* was 70 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. In the literature [14], 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 [15, 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, 10].

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, 10, 15, 17, and 18] This was due to the dominant species (CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$) of Cr ions in solution, which were expect to interact more strongly with the ligands carrying positive charges [19].

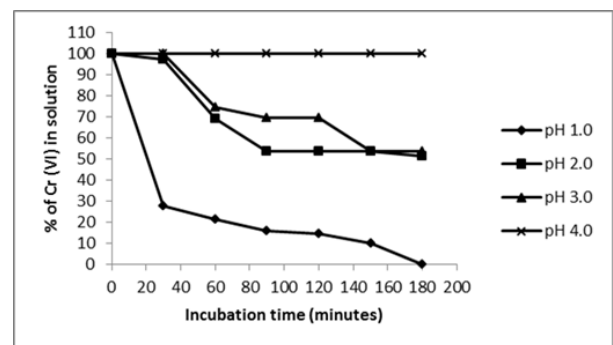


Figure 1. Effect of incubation time and pH on Chromium (VI) removal by the biomass of *C. paradise* shell. 50 mg/L Cr (VI), 100 rpm, 28°C.

B. Effect of the temperature

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 60 minutes of incubation. This results are coincident for tamarind shell with 95% of removal at 58°C and 3 hours [20], for the adsorption of cadmium (II) from aqueous solution on natural and oxidized corncob (40°C and 5 days) [21], but these are different for the mandarin waste [22], *Caladium bicolor* (wild cocoyam) biomass [23], and *Saccharomyces cerevisiae* [24]. 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 [20].

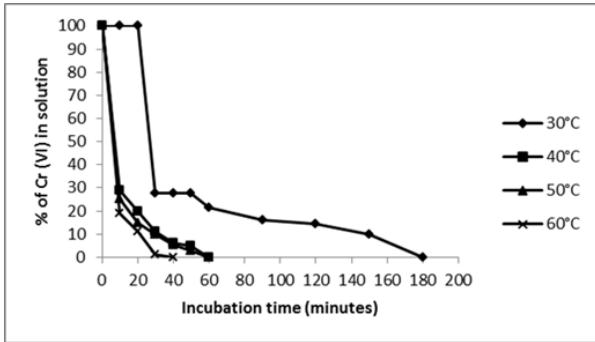
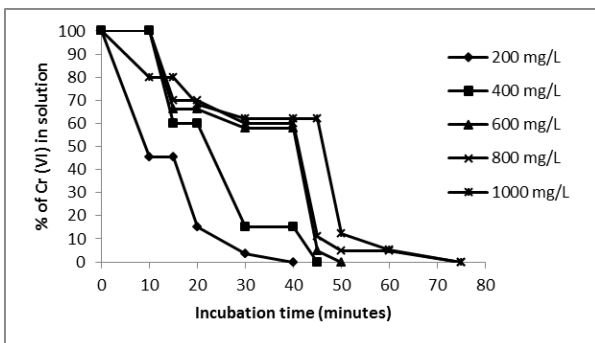


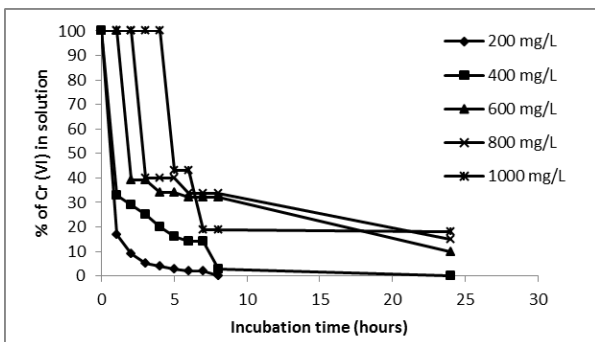
Figure 2. Effect of the temperature on Chromium (VI) removal by the biomass of *C. paradise* shell, 50 mg/L Cr (VI), pH 1.0, 100 rpm.

C. Effect of initial metal concentration

At low metal concentrations (200 mg/L), we observe the best results for removal, with the biomass analyzed, 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* and *Tamarindus indica* shell [15, 20]. With respect to other biomasses, most authors report lower removal efficiencies of metal, for example: 45 mg/L for eucalyptus bark [16], 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 [20].



a)



b)

Figure 3. Effect of initial metal concentration on Cr (VI) removal by biomass of *C. paradise* shell. pH 1.0, 100 rpm, a) 60°C, b) 28°C.

D. Effect of biosorbent dose

The influence of biomass concentration on the removal capacity of Cr (VI) is depicted in Figure 4. 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 [28]. Similar results have been reported for modified corn stalks [31], *C. reticulata* shell [15], and *Mucor hiemalis* and *Rhizopus nigricans*, although latter with 10 g of biomass [29, 30], but they are different from those reported for wastes biomass of mandarin (gabasse), with an optimal concentration of biomass of 100 mg/L [22].

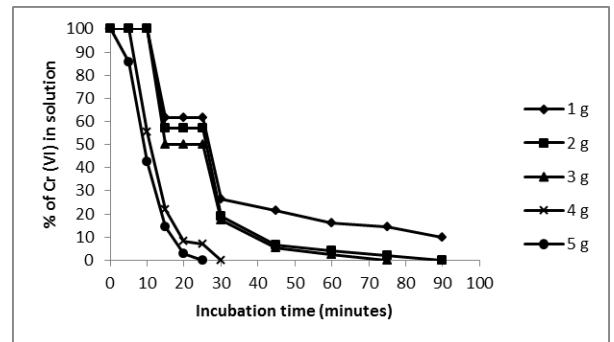


Figure 4. Effect of biomass concentration on the removal of 50 mg/L Cr (VI), 28°C, pH 1.0, 100 rpm.

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

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 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) [13]. Thus, at 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 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 [3, 15, 32, 33, and 34]. 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 study express 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 [3, 7, 8, 32, 35-38]. 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 [3, 7, 8, 32, 35-38].

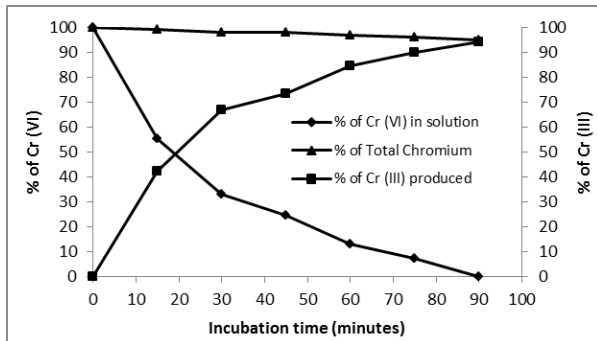


Figure 5. Time-course of Cr (VI) decrease and Cr (III) production in solution with 1.0 g/L Cr (VI). 28°C, pH 1.0, 100 rpm.

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

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 155 mg Cr(VI)/L, suspended in trideionized water. It was observe that in 7 days of incubation with the biomass, the Cr (VI) concentration of earth and water samples decrease fully (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 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.

The chromium removal abilities of this biomass, are equal or better than those of other reported, for example *C. reticulata* shell [15], *M. Americana* [17], and *Candida maltose* RR1 [38]. In particular, this biomass was superior to the other biomass because they 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) [39]. 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.

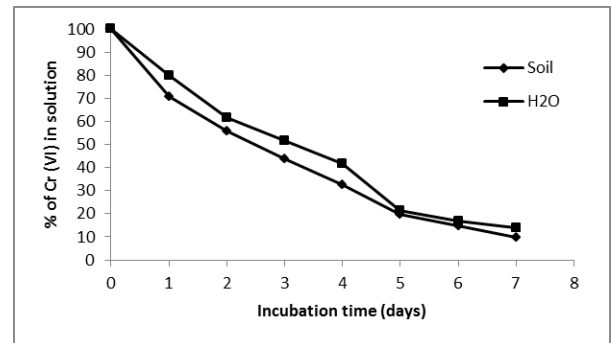


Figure 6. Removal of Cr (VI) in industrial wastes incubated with 5 g of biomass. 28°C, 100 rpm, 20 g and 100 mL of contaminated soil and water, (297 mg Cr (VI)/g soil, and 155 mg Cr (VI)/L).

IV. CONCLUSIONS

The biomass analyzed, showed complete capacity of biosorption of 1.0 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 (7 days of incubation, 5 g 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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