REMOVAL OF CHROMIUM (VI) IN AQUEOUS SOLUTION BY *Hibiscus sabdariffa* FLOWER BIOMASS

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***Abstract*— Chromium (VI), is a very toxic and dangerous metal for human health, because at the industrial level, it is used in the tanning of skins, the production of pigments, preservatives of the textile and wood industry, alloys, antifouling paints, catalysts, anticorrosive agents, drilling muds, high temperature batteries, fungicides, metallic and electrogalvanized coatings, which are an important source of contamination by this metal, so currently, alternatives have been sought to try to eliminate it from the environment, and the objective of this work was analyze the Chromium (VI) removal capacity in aqueous solution by the *Hibiscus sabdariffa flower* biomass, using the colorimetric method of Diphenylcarbazide to evaluate the metal concentration. Biosorption at different pH was evaluated for 5 h. We too studied the effect of temperature in the range of 28 to 60^{o}C, the removal at different initial concentrations of Cr (VI) and of biomass, and in contaminated niches. Therefore, the highest biosorption of the metal (100 mg/L) occurs within 5 h, at pH of 1.0, 1,0 g of natural biomass, and 28°C. According to temperature, the highest removal was observed at 50^{o}C 60°C, in 40 minutes, when the metal is completely adsorbed. It was observed that the higher the concentration of the metal, the removal is less, and that, as the biomass concentration increases, the removal of the metal in solution is increased. Besides it removes efficiently the metal *in situ* (100% removal in soil and water contaminated, after 4 and 3 days of incubation, 5 g of biomass and 28^{o}C; so, it can be used to eliminate it from industrial wastewater.**

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

I. 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 [1].

Hexavalent chromium 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, and is usually associated with oxygen as chromates (CrO_4^{-2}) and dichromate ($Cr_2O_7^{-2}$) [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., [1, 4]. 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 [8, 9, and 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 [8]. The objective of this study was to analyze in vitro biosorption of Cr (VI) by *Hibiscus sabdariffa flower* biomass.

II. EXPERIMENTAL

A. Biosorbent used

The *H. sabdariffa flower* biomass, was obtained from the fruits harvested and offered in the market place Republic, between the months of August to September in 2018, of the capital city of San Luis Potosí, S.L.P. México. To obtain the biomass, the shells was washed with trideionized water during 7 days at constant stirring, with water changes every 12 hours.

Subsequently, it was boil 1 hour to removal traces of the color and dust, and were dry at 80°C for 12 hours in an oven, ground in blender and stored in amber vials until use.

B. Biosorption studies and determination of Cromium (VI)

For these studies, was used 1 g of dried biomass mixed with 100 mL of trideionized water containing 100 mg/L of the metal, in an Erlenmeyer flask at the desired temperature and pH. The flasks were agitated on a shaking bath Yamato BT-25 model. 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, which were quantifying by a Spectrophotometric method employing Diphenylcarbazide [11]. 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 *H. sabdariffa flower* biomass was 300 minutes and pH 1.0, at constant values of biosorbent dosage (1 g/100 mL), with an initial metal concentration of 100 mg/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 [12], report an optimum time of 8 h and pH of 1-3, for the removal of Cr(VI) by porous carbon derived from corn straw, 150 and 180 minutes to pH 1.5, for the Cr (VI) removal using oleaster (*Elaeagnus*) seed and cherry (*Prunus avium*) stone biochar [13], 10 hours by *Ananas comosus* biomass shell [9]. 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 [6, 7, and 8].

Adsorption efficiency of Cr (VI) was observe a maximum at pH 1.0 and 300 minutes with the biomass analyzed. It was reported a pH optimum of 1.0 by *A. comosus* biomass shell [9], and residue of the *Persea Americana* Shell [14], although other authors report an optimal pH of 2.0 for coffee pulp [15], for coffee ground and mixed waste tea [16]. This was due to the dominant species (CrO_4^{2-} and $Cr_2O_7^{2-}$) of Cr ions in solution, which were expect to interact more strongly with the ligands carrying positive charges [7 and 8].

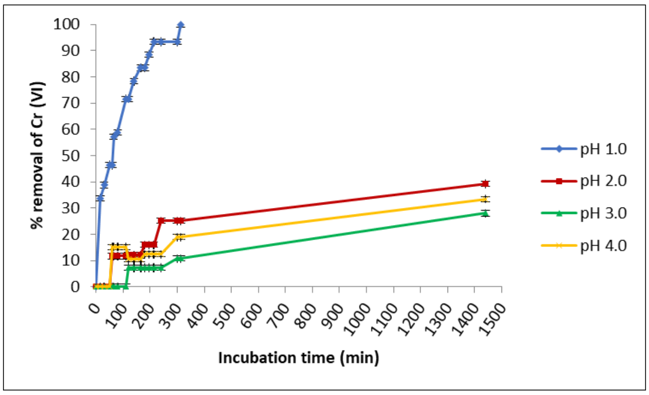

Figure 1. Effect of incubation time and pH on Chromium (VI) removal by the biomass of *H. sabdariffa* flower. 100 mg/L Cr (VI), 100 rpm, 28°C. 1.0 g of biomass.

B. *Effect of the temperature*

On the other hand, 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 50°C and 60°C with 40 minutes, and 28°C with 300 minutes of incubation. This results are coincident for *A. comosus* biomass shell [9], and residue of the *P. Americana* Shell [14], for spent coffee grounds [17], though for coffee ground and mixed waste tea, as well as newspaper, the temperature does not influence in the removal of the same metal [16, 18]. 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].

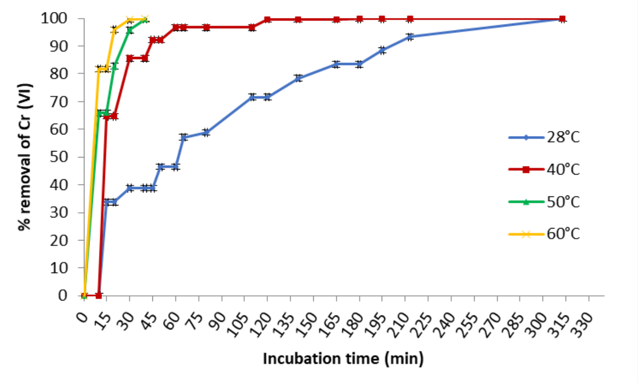

Figure 2. Effect of the temperature on Chromium (VI) removal by the biomass of *H. sabdariffa* flower, 100 mg/L Cr (VI), pH 1.0, 100 rpm. 1.0 g of biomass.

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 28°C, because the removal of the metal was 100% at 7 and 28 hours for 200 and 1000 mg/L, respectively (Figure 3). The results are coincident for *Tamarindus indica* shell [19] *Amarantus caudatus* [20], coffee ground and mixed waste tea [16], spent coffee grounds [17], *A. comosus* biomass shell [9], residue of the *P. Americana* Shell [14, and almond green hull [21]. 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 [8, 19]. On the other hand, at 60°C, 200 and 1000 mg/L, they are eliminated at 20 and 80 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 [6,7,8,9, 14, and 20].

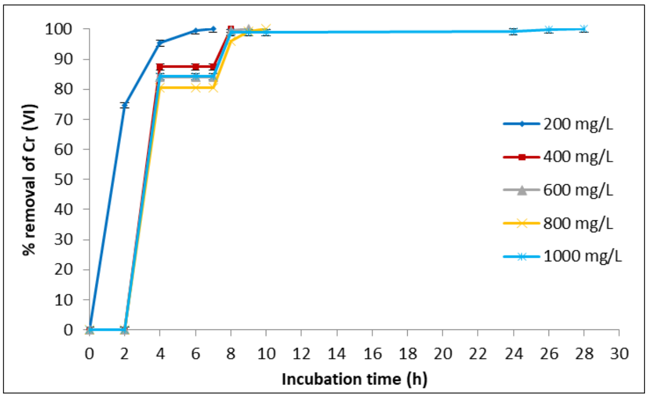

Figure 3. Effect of initial metal concentration on Cr (VI) removal by the biomass of *H. sabdariffa* flower. pH 1.0, 100 rpm, 28°C.

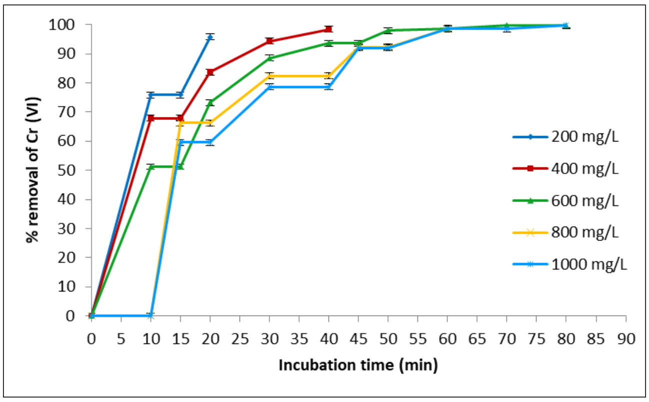

Figure 4. Effect of initial metal concentration on Cr (VI) removal by the biomass of *H. sabdariffa* flower. pH 1.0, 100 rpm, 60°C.

D. *Effect of biosorbent dose*

The influence of biomass concentration on the removal capacity of Cr (VI) is depict in Figure 5. If we increase, the amount of biomass also increases the removal of the metal in solution, well with 5 g of biomass the 100% of removal is to 40 minutes, with more biosorption sites of the same, because the amount of added biosorbent determines the number of binding sites available for metal biosorption [22]. Similar results have been reported for almond green hull [21], with a metal concentration of 10 mg/L, with 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, y 5 g de biomass. Too was reported a efficient removal of the metal if the biomass concentration was increased for oleaster (Elaeagnus) seed and cherry (*P. avium*) stone biochar [13], using modified Russian knapweed flower poder to initial concentrations of chromium (VI) of 2, 10 and 15 mg/L with pH 2.0 [23], with coffee grounds, where there is an increase in the removal of 39% to 97%, if the concentration of the bioadsorbent is increased of 0.05 to 0.3 g/100 mL [17], as well as for newspaper, where by increasing the concentration of 2 to 6 g/L, increase the removal efficiency of 43.4% to 98.3% [18].

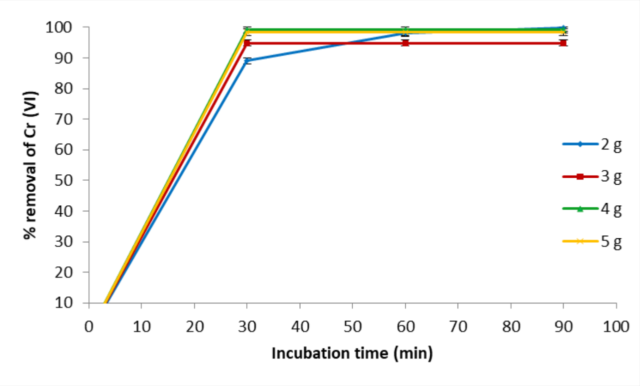

Figure 5. Effect of biomass concentration of *H. sabdariffa* flower, on the removal of 100 mg/L Cr (VI), 28°C, pH 1.0, 100 rpm.

E. *Removal of Cr (VI) in industrial wastes with biomass of* H. sabdariffa *flower.*

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 10 g of non-sterilized contaminated earth with 100 mg/g, and water containing 100 mg/L of Cr (VI) (adjusted), suspended in trideionized water to a final volume of 100 mL. It was observing that in 4 and 3 days of incubation with the biomass, the Cr (VI) concentration of earth and water samples decrease fully in both (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 [3, 6, 8, and 9]. Which coincides with the literature reports for other natural biomass, such as seeds of *Moringa oleifera* with 1 g of biomass and concentrations of 10 to 150 ppm of copper, nickel, and chromium (VI), with percentages of removal between 37-53%, 39-76%, and 11-33%, respectively [24], for coffee pulp residues with a removal pf 59% [15], the removal of 97.9% of chromium (VI) from electroplating wastewater by porous carbon derived from corn straw [12], a removal of chromium (VI) between 82.6% and 90.2% of contaminated water from different sources by spent coffee grounds [17], and a removal of 90% of wastewater using materials derived from harmful algal bloom biomass [25].

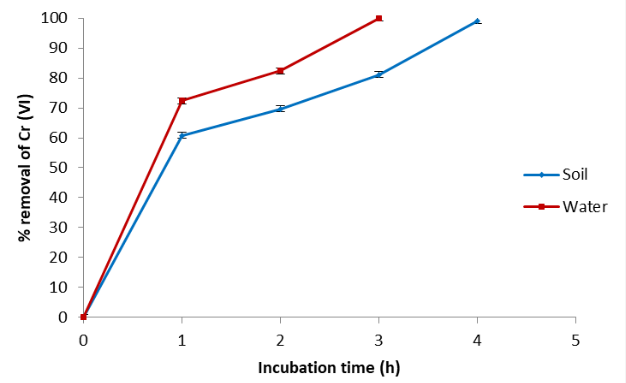

Figure 6. Removal of Cr (VI) in industrial wastes incubated with 5 g of *H. sabdariffa* flower. 28°C, 100 rpm, 10 g of contaminated earth with 100 mg/g and 100 mL of contaminated water with 100 mg/L. contaminated water, (100 mg Cr (VI)/L (adjusted).

IV. CONCLUSIONS

The biomass analyzed, showed complete capacity of biosorption of 100 mg/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* (4 and 3 days of incubation, with 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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