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THE USE OF *Cucumis sativus* SHELL BIOMASS IN THE REMOVAL OF CHROMIUM (VI) IN AQUEOUS SOLUTION

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Abstract*— Heavy metals contamination constitutes currently one of the environmental problems most worrisome around the world, and the Chromium is one of the most important metals due to its wide industrial use. Contamination of soil and water is the result of an uncontrolled discharge of contaminants with this metal, because of an increasingly industrialized society, which increases the levels of the metal in the environment, representing a danger to health. Chromium can be generated by effluents from the industries of the tanning of leather, stainless steel, alloys, paints, cements, printer pigment and chrome plating, among others. The objective of this work was analyzing the Chromium (VI) removal capacity in aqueous solution by the *Cucumis sativus* shell biomass by 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°C, the removal at different initial concentrations of metal, and of biomass, and in contaminated niches. Therefore, the highest biosorption of the metal (100 mg/L) occurs within 4 hours and 25 minutes, at pH of 1.0, 1.0 g of natural biomass, and 28°C. According to temperature, the highest removal was observed 60°C, in 2 hours and 15 minutes, when the metal is completely adsorbed, and at higher metal concentration, 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 7 days of incubation, 5 g of biomass and 28°C; so, it can be used to eliminate it from industrial wastewater.

Keywords—Heavy metals, Chromium (VI), Removal, Cucumber, Shell Biomass.

I. INTRODUCTION

Cucumber (*Cucumis sativus*) is the sixth horticultural product of the highest global production, after potato (*Solanum tuberosum*), cassava (*Manihot esculenta*), tomato (*Solanum lycopersicum),* watermelon (*Citrullus lanatus*) and sweet potato (*Ipomea batatas*) [1], and is one of the horticultural crops most consumed at the level world for its nutritional value, with high economic potential for being a export product that is grown and consumed in

many regions of the world [2]. Among the 52 species of *Cucumis* sp., *C. sativus* has the highest value important due to the phytochemical and therapeutic potential [3]. For the economy agricultural sector in Mexico, the vegetable sector is particularly important due to its contribution to the generation of employment in the field. In east, Mexico cultivation is very important, since our country is the main world exporter of this vegetable and is relevant for national consumption [4]. Despite being not very nutritious due to its low dry matter content, it is rich in vitamin A and C; in addition, it contains sulfur, which is widely used in the cosmetic industry. Cucumber is very consumed for its good combination with salads. Of according to its composition, 100 g of the edible content of cucumber contains: calories 12, water 96.01 g, carbohydrates 2.50 g, fat 0.16 g, protein 0.57 g, fiber 0.7 g, ash 0.28 g, calcium 14 mg, phosphorus 21 mg, iron 0.16 mg, potassium 148 mg, thiamine 0.021 mg, riboflavin 0.011 mg, niacin 0.104 mg, ascorbic acid 2.8 mg. That is why the consumption of this vegetable is of great importance due to its nutritional value, health contributions, being used for the treatment of various diseases, mainly acne; it helps to weight loss and diabetes; without leaving behind their socioeconomic contribution, which has increased in recent years [5].

On the other hand, the increase in population, agriculture and industrial development are responsible for the increase in environmental pollution and toxic waste, and therefore, a wide variety of pollutants such as: industrial waste, pesticides and other chemicals used in the different anthropogenic activities pollute land and water from different sources, causing serious damage to the environment, which affects the quality of life and health of the population [6]. Among the main environmental pollutants are heavy metals, the presence of which must be considered very importantly in the different ecological niches. Of which, 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 [7], and can originate from different anthropogenic activities such as chromite mining, leather tanning, dyes and pigment synthesis, electroplating, metal finishing, explosives manufacturing, and metal alloy, [7]. The primary forms of metal found in nature are chromium (III) and chromium (VI) and these forms are converting to each other depending on environmental conditions [8].

Currently, the use of a wide variety of residual biomass for the removal of metal ions from polluted waters has been extensively investigated, including tree bark, wood waste, seeds and leaves of different trees, dried fruit shells, industrial and marine waste, as well as some biomaterials such as chitin and chitosan [9], dead microorganisms, clay minerals, industrial wastes and various other low cost materials [10]. The biomass of the cucumber peel has been used in the removal of different heavy metals and other pollutants in a natural or pretreated way to increase said removal capacity, for example: the removal of Cadmium (II) Ions from simulated wastewater by HCl modified *C. sativus* peel [11], the adsorption of crystal violet and rhodamine B by *C. sativus* activated with sulfuric acid [12], Lead, Arsenic, Nickel, Mercury and Iron uptake by *C. sativus* [13], the adsorptive treatment of methylene blue with *C. sativus* peel waste (14, 15], the lead (II) removal by *C. sativus* peel [16], and the phytoremediation of soils contaminated with chromium [17]. For the above, the objective of this study was to analyze *in vitro* biosorption of Cr (VI) by *Cucumis sativus* shell biomass.

II. Experimental

A. *Biosorbent used*

The *C. sativus shell* biomass, was obtained from the fruits harvested and offered in the marketplace Republic, between the months of August to September in 2019, of the capital city of San Luis Potosí, S.L.P. México. To obtain the biomass, the shells was washed with a 10% (p/v) of EDTA solution for 1 day, and 7 days with trideionized water at constant stirring, with water changes every 12 hours.

Subsequently, it was boiling 1 hour to removal traces of the color and dust and were dry at 80°C for 24 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 [18]. 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*

For the biomass studied in this work, it was observed that after 4 hours and 25 minutes, and pH 1.0, 92.2% of Cr (VI) is removed, while, at pH 2, 3 and 4, only a percentage less than 20% of the metal is removed, 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 [17], reported the phytoremediation of soils contaminated with Cr (VI), using a culture of the species *C. sativus* (gherkin), by means of phytostabilization and phytoimmobilization systems, reporting that after 80 days of cultivation in greenhouse conditions, the seedling reduced chromium levels by a 31% (250 mg Cr/kg of soil), an optimal incubation time of 4.5 and 5 hours, when

working with the biomass of *Persea americana* and hibiscus flower (*Hibiscus sabdariffa*) at a pH of 1.0, and a biomass concentration of 1 g/100 mL, with 50 and 100 mg/L of the metal [19, 20], 4.5 hours, 150 and 180 minutes to pH 1.5, for the Cr (VI) removal using oleaster (*Elaeagnus*) seed and cherry (*Prunus avium*) stone biochar [21]. 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 10].

Adsorption efficiency of Cr (VI) was observe a maximum at pH 1.0 and 4 h and 25 min with the biomass analyzed. It was reported a pH optimum of 1.0 by *P. americana* and hibiscus flower (*H. sabdariffa*) biomasses [19, 20], although other authors report an optimal pH of 2.0 for coffee pulp [22], for coffee ground and mixed waste tea [23]. This was due to the dominant species (CrO_4^{2-} and $Cr_2O_7^{2-}$) of Cr ions in solution, which were expected to interact more strongly with the ligands carrying positive charges [7 and 10].

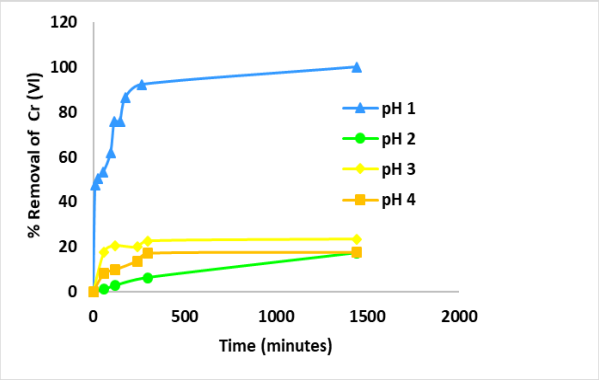

Figure 1. Effect of incubation time and pH on Chromium (VI) removal by the biomass of *C. sativus* shell. 100 mg/L Cr (VI), 100 rpm, 28°C. 1.0 g of biomass.

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 analyzed temperatures were 40°C, 50°C and 60°C, obtaining for the shell biomass at 60°C, at 2 hours and 15 minutes, 98.77% of the Cr (VI) in solution was removed, while, at the same time, at 40°C and 50°C, only 82.58% and 90.58% were removed respectively. This result is coincident for *P. americana* and hibiscus flower (*H. sabdariffa*) biomasses [19, 20], for the residue of *Spinacea Oleraceae* biomass [24], as well as newspaper, the temperature does not influence in the removal of the same metal [25]. The increase in temperature increases the rate of removal of the metal and decrease the contac time required for complete removal of this, to increase the redox reaction rate [26].

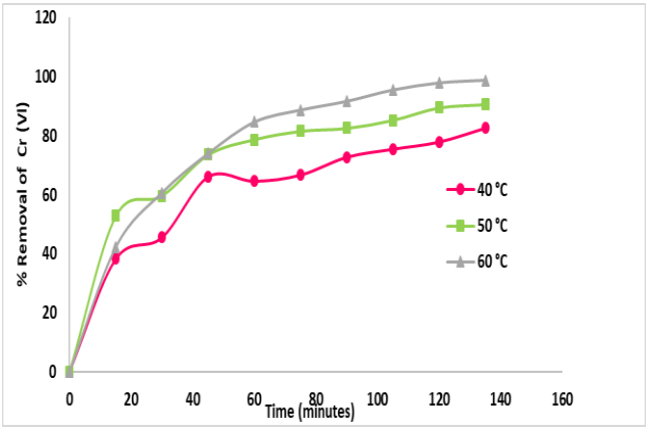

Figure 2. Effect of the temperature on Chromium (VI) removal by the biomass of *C. sativus* shell, 100 mg/L Cr (VI), pH 1.0, 100 rpm. 1.0 g of biomass.

C. *Effect of initial metal concentration*

Different concentrations of Cr (VI) (200, 400, 600, and 800 mg/L) were evaluated, in a solution at pH of 1 +/- 0.2, at 28°C and 60°C, at 100 rpm, using 1 g of *C. sativus* biomass. The results obtained for the removal at 60°C, indicate that, at a higher temperature, a greater removal of the metal is carried out in less time, obtaining that after 40 minutes a concentration of 800 mg/L is removal in solution (Figure 3), while at 28°C it is observed that the higher the concentration of Cr (VI) in solution, a longer time is required to remove the metal. (Figure 4). These results are coincident for *P. americana* and hibiscus flower (*H. sabdariffa*) biomasses [19, 20], coffee ground and mixed waste tea [23], *Tamarindus indica* shell [26], spent coffee grounds [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 [7,10].

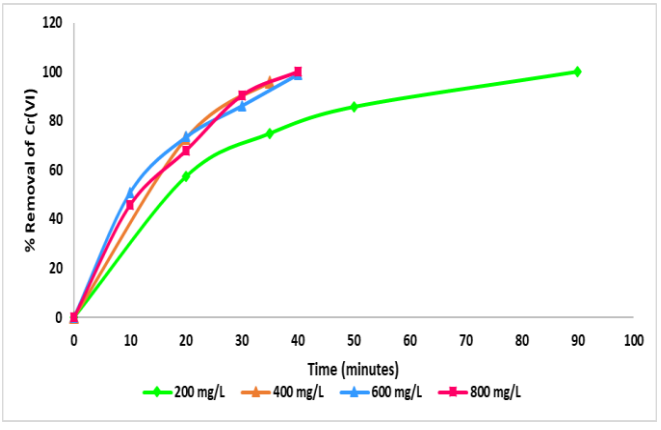

Figure 3. Effect of initial metal concentration on Cr (VI) removal by the biomass of *C. sativus* shell. pH 1.0, 100 rpm, 60°C. 1.0 g of biomass.

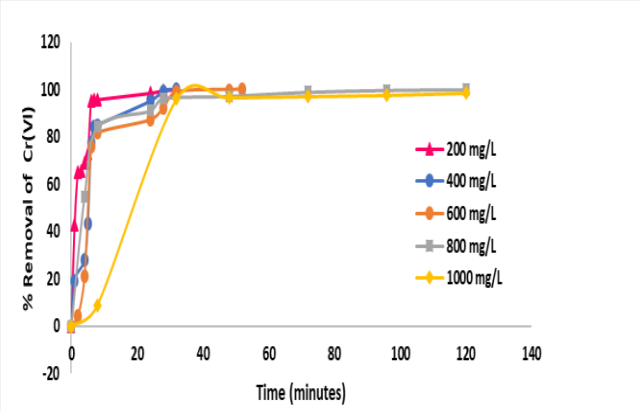

Figure 4. Effect of initial metal concentration on Cr (VI) removal by the biomass of *C. sativus* shell. pH 1.0, 100 rpm, 28°C. 1.0 g of biomass.

D. Effect of biosorbent dose

The removal of 100 mg/L of Cr (VI) was evaluated with different amounts of cucumber biomass (1, 2, 3, 4, and 5 g), at 28°C of incubation. It was found that the higher the concentration there is a greater removal of the metal, since with 5 g of biomass 100% of it was removed in a time of 3 hours, while with 2, 3 and 4 g of biomass in a time of 3 hours and 35 minutes, the removal of Cr (VI) was in a percentage lower than 95% (Figure 5), because there are 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 *P. americana*, with 50 mg/L of Cr (VI) and the same concentration of the biomass, in which, 5 g of the biomass removal fully the metal in 25 min, [19], for hibiscus flower biomass (*H. sabdariffa*), in the same conditions, getting a removal of 100% in 40 min [20]. With the increase in biosorbent dose from 0.01 to 1.0 g/50 mL, of waste human hair the percentage of Cr (VI) removal increased from 57.43 to 98.77% [29], too, the percentage of Cr (VI) removal are similar (~30%) when 0.5-2 g/L of coffee ground were applied. Then, the removal efficiency was gradually increased by increasing the coffee ground dose and seemed to be constant at the dosage between 5 and 6 g/L [23], and for modified corn stalks, the percentage of Cr (VI) removal from aqueous solution increased significantly from 74% to 99% when the adsorption concentration of this increased from 0.5 to 1.5 g/L. And after the critical dosage (1.5 g/L), the adsorption percentage remained constant [30], 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% [25].

E. Removal of Cr (VI) in industrial wastes with biomass of C. sativus biomass.

In order to analyze the possible use and capacity of *C. sativus* biomass to remove the metal from industrial waste, a removal test was set up in aqueous solution, in the presence of 5 g of cucumber peel, with non-sterile soil contaminated with approximately 200 mg of Cr (VI)/g of earth and 100 mL of water contaminated with approximately 200 mg of the same metal, by resuspending soil in tridesionized water at 28°C and 100 rpm, observing that at 7 days of incubation, 100% of the metal existing in the water contaminated with it, was removed, observing the same results in the soil contaminated (Figure 6). 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 [7,10,19 and 20], which coincides with the literature reports for other natural biomass, like for coffee pulp residues with a removal pf 59% [22], a removal of chromium (VI) between 82.6% and 90.2% of contaminated water from different sources by spent coffee grounds [27], 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 [31], the removal of 97.9% of chromium (VI) from electroplating wastewater by porous carbon derived from corn straw [32], and a removal of 90% of wastewater using materials derived from harmful algal bloom biomass [33].

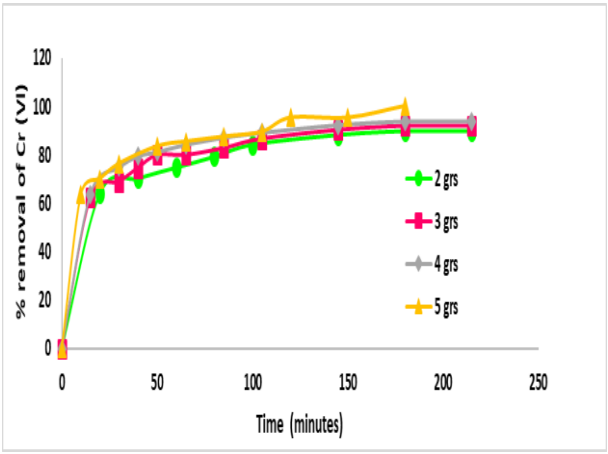

Figure 5. Effect of biomass concentration of *C. sativus* shell, on the removal of 100 mg/L Cr (VI), 28°C, pH 1.0, 100 rpm.

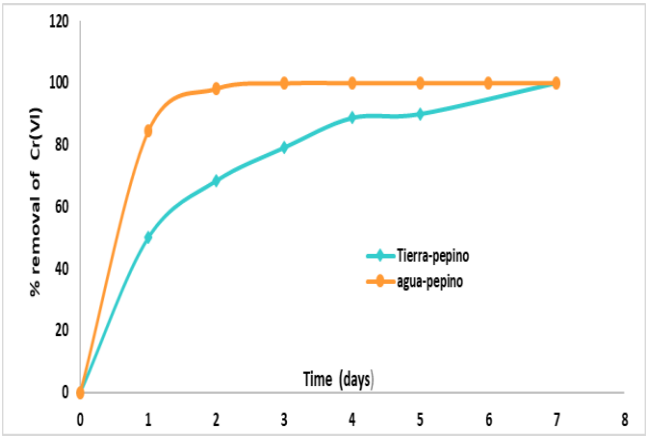

Figure 6. Removal of Cr (VI) in industrial wastes incubated with 5 g of *C. sativus* shell. 28°C, 100 rpm, 10 g of contaminated earth with 200 mg/g and 100 mL of contaminated water with 200 mg/L. contaminated water, (100 mg Cr (VI)/L (adjusted).

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* (7 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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