HEXAVALENT CHROMIUM REMOVAL BY Citrulus lanatus SHELL

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***Abstract*—Watermelon is a fruit highly valued for its flavor and water content, making it a highly sought-after product. However, some of the waste and rind produced by watermelon consumption are dumped in landfills and dumps, causing environmental problems. Therefore, the use of this waste is an option for reducing the pollution load and an opportunity to obtain biomass from this waste, for the elimination of heavy metals from contaminated environments. These metals are directly related to health risks for living beings, soil contamination, toxicity in plants, and negative effects on the quality of natural resources and the environment. These risks are related to the specific toxicity of each metal, bioaccumulation, persistence, and non-biodegradability, the greatest danger being their accumulation in plants and their transfer to humans and animals.**

On the other hand, watermelon (*Citrullus lanatus*) is a tropical, creeping herbaceous plant belonging to the Cucurbitaceae family, which propagates mainly by seeds and grows best in warm areas. While the fruit pulp is consumed, the peels and seeds are often discarded. The ever-growing global market for major tropical fruits is currently estimated at 85 million tons, of which approximately half is lost or wasted throughout the processing chain. Therefore, the development of novel processes for converting these by-products into value-added products could provide a viable way to manage this waste problem and try to use them in activities that benefit the world, for example, their use as biosorbents for the removal of hazardous and/or toxic contaminants from different contaminated sites.

Therefore, the objective of this work was to determine the removal capacity of Chromium (VI) by watermelon peel biomass, finding that 1 g of biomass eliminate 100 mg/L of the metal at 7 hours, pH 1.0, 28^{o}C and 100 rpm, and at higher temperatures the removal is greater, and if the metal concentration is increased, the removal capacity is reduced, since 37.1% is eliminated at 10 hours at 28°C, although at 60°C, 1 g/L is removed at 105 minutes. If the concentration of the bioadsorbent is increased, the metal removal also increases. Finally, 5 g of biomass eliminates 100% of Cr (VI) present in naturally contaminated soil (100 mg/g) and water (100 mg/L), in 105 hours at 28°C.

Keywords—Watermelon, Contamination, Chromium (VI), Elimination

I. INTRODUCTION

The Watermelon (*Citrulus lanatus*), belongs to the cucurbitaceae family, like pumpkins and squash. Due to its high water content (92%), the fruit's texture is soft and incredibly refreshing. The most common watermelon has red flesh, but there are also other types with orange, yellow, or white flesh. Uncut watermelon can remain at room temperature for two to three weeks, but once cut, it should be refrigerated [1]. Too, the watermelon It is an excellent source of vitamin C and is also a good source of vitamin A, as it contains beta carotene (the body converts beta carotene into vitamin A) [2]. Antioxidants free the body from free radicals, which, in normal amounts, help the body release toxins and keep it healthy, but in high amounts become toxic, damaging the body's cellular system and destroying cells and tissues. Watermelon is also a source of lycopene, as are tomatoes and mangoes. Lycopene has been widely studied for its anticancer and antioxidant properties [3]. Unlike other phytonutrients whose effects have only been studied in animals, lycopene's properties have been studied in humans, and it has been found that lycopene can prevent several types of cancer, including prostate, breast, endometrial, lung, and colon cancer [4].

Also, other properties have been described for watermelon and its compounds such as: the bacterial activities from *C. lanatus* seed oil [5], diabetes treatment [6, 7], antimicrobial activity on selected bacteria [8], and the removal of heavy metals by water melon [9].

On the other hand, the disproportionate industrial and demographic growth in most countries around the world has led to the contamination of surface and groundwater resources through the accumulation of various pollutants in different chemical forms. Because a large part of the population consumes untreated groundwater in developing and underdeveloped countries, contamination of both surface and groundwater represents a serious and direct threat to its consumers [10], and the chromium is a contaminant of different aquatic niches, has geogenic origins (chemical manipulation of minerals containing this metal), and anthropogenic origins (electroplating, production of dyes and colors, tanning), and presents a challenge for stakeholders involved in the management of groundwater resources [11]. This heavy metal has two oxidation states: trivalent chromium (Cr III) and hexavalent chromium (Cr VI), the latter being the most toxic due to its solubility in water and high reactivity, particularly at acidic pH, and therefore, it can enter cells. It has been reported that it can affect DNA causing several types of cancer, while Cr (III) is less toxic to the environment [11]. Therefore, different investigations have been carried out for the implementation of different efficient, economical and beneficial methods for the elimination of this and other heavy metals from contaminated waters.

Too, the great industrial growth has produced a progressive increase in wastewater discharges from the same and, heavy metals are the main contaminants of aquifers due to its high toxicity, persistence, and mobility. Not being biodegradable, can become toxic to vertebrates and invertebrates, and they are directly related to the risks to the health of living beings, soil contamination, plant toxicity, and negative effects on the quality of natural resources and the environment. These risks are related to the specific toxicity of each metal, bioaccumulation, persistence and non-biodegradability, the greatest danger being its accumulation in plants and its transfer to humans and animals [10]. Their distribution in the different environments is highly complex and involves different factors, among which are: redox potential, pH, organic matter content, cation exchange capacity, groundwater level and its fluctuations, among others [12], and there are different investigations for carry out to determine the contamination of heavy metals in the environment, such as: cobalt, lead, mercury, chromium (VI), cadmium, and others, like: heavy metals potentially dangerous for human and environmental health, contamination of water sources [13]. Others contaminants are of organic origin, such as hydrocarbons and pesticides, but, all are their importance and potential danger [14]. Some metals that are of great toxicological and ecotoxicological importance are: mercury, chromium, lead, cadmium, nickel and zinc, which, once released into the environment, accumulate and concentrate in the soil and sediments, where they can remain for hundreds of years affecting ecosystems. Therefore, it is more feasible to control the problem from the source and source of emission before they reach the environment [14]. In Mexico, agribusiness is one of the most important activities due to its growth in recent years, and it is the one that generates the most by-products that are not used [15], among which are: coffee bagasse, agave, maguey, sugar cane, straws from different crops, organic residues of fruits and vegetables [16]. In this regard, the use of different plant products with the ability to accumulate and/or bioadsorb heavy metals has been reported, which include watermelon biomass (*C. lanatus*), for example: the removal of different heavy metals [9], the removal of cadmium by the hust [17], trivalent chromium [18], copper and lead (19], and the metal ions removal from synthetic wastewater [20], so the objective of this work was to determine the removal capacity of Cr (VI) by watermelon rind biomass (*C. lanatus*).

II. EXPERIMENTAL

A. Biosorbent used

The *C. lanatus* peel biomass, was obtained from the marketplace Republic, in the months of July of 2025, of the capital city of San Luis Potosí, S.L.P., México. To obtain the biomass, the skin was washed with EDTA 10% (p/v) for 24 hours, and after with trideionized water during 7 days 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 72 hours in an oven, ground in blender and stored in amber vials until use.

B. Biosorption studies and determination of hexavalent chromium.

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 chromium ions. Hexavalent chromium was quantifying by a spectrophotometric method with Diphenylcarbazide [21]. 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

In this work, it was found that 1 g of the analyzed biomass removes 100 mg/L of the metal after 7 hours of incubation, pH 1.0, 28^{o}C and 100 rpm (See Fig. 1). These results are different to what was reported 150 minutes with different natural biomasses [22], 120 minutes for *Moringa stenopetala* seed powder [23], 24 hours for the biomass of palm leaf-derived biochar [24], 30 minutes for in natural and magnetic nanomodified hydroponic lettuce roots [25]. 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 [10]. Adsorption efficiency of Cr (VI) was observing a maximum at pH 1.0 and 7 hours with the biomass analyzed. The results showed with respect to the increase in pH resulted in decrease in the removal of the metal. It was reported an optimum pH 1.5 for adsorbents from agricultural waste material [22], a pH of 1.0 for in natural and magnetic nanomodified hydroponic lettuce roots [25]. Although other authors report an optimum pH 3.0 for adsorbents from agricultural waste material [20], pH of 2.0 for dry raw biomasses of *Dioscorea rotundata, Elaeis guineensis, Manihot esculenta, Theobroma cacao* and *Zea mays* [22], a pH value of 2.0 and 4.0, for the removal of this heavy metal from wastewater using *M. stenopetala* seed powder and banana peel powder [23], too, a pH value of 2.0 using palm leaf-derived biochar, tea stalk biochar, and waste of *Musa acuminata* residue [26, 27]. This was due to the dominant species (CrO_4^{2-} and $Cr_2O_7^{2-}$) of Chromium ions in solution, which were expected to interact more strongly with the ligands carrying positive charges [28].

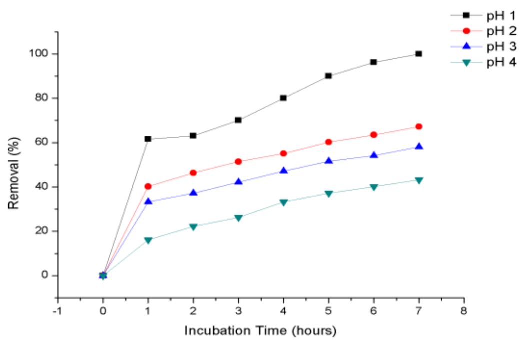

Figure 1. Effect of incubation time and pH on Chromium (VI) removal by watermelon skin biomass. 100 mg/L Cr (VI), 100 rpm, 28°C. 1.0 g of biomass.

B. Effect of temperature

On the other hand, the incubation temperature does not influence in the removal of the metal, since at temperatures of 40°C, 50°C and 60°C, the removal is complete after 120 minutes, while at 28°C, 100% of this contaminant is eliminated at 450 minutes (Figure 2). To maintain constant the temperature in all experiments, we use a shaking bath Yamato BT-25 model. These results are coincident for the biomass of palm leaf-derived biochar, with the same temperature of removal [26], by a reusable chitosan-modified multi-walled carbon nanotube composite [29], by dried twigs of *Melaleuca diosmifolia* [30], for the removal of Cr (VI). But they are different for removal of the same metal from wastewater using *M. stenopeta* seed powder and banana peel powder, if increase this parameter, decrease the removal capacity of this biomasses [23], and for different natural biomasses, which exhibit higher adsorption efficiency at intermediate and low temperature values [24]. The increase in temperature increases the rate of removal of Cr (VI) and decrease the contact time required for complete removal of the metal, to increase the redox reaction rate [31].

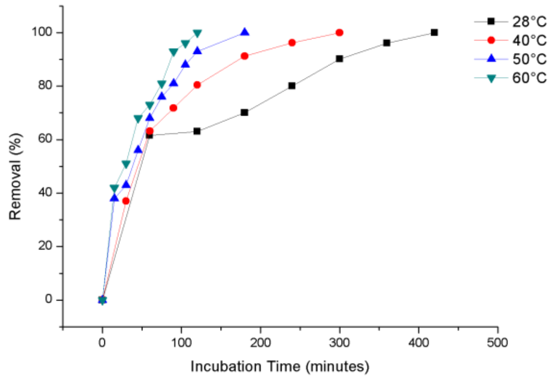

Figure 2. Effect of the temperature on Chromium (VI) removal by watermelon skin biomass. 100 mg/L Cr (VI), pH 1.0, 100 rpm. 1.0 g of biomass.

C. Effect of initial metal concentration

If the metal concentration is increased, the removal capacity is reduced, since 100% is eliminated after 8 hours at 28°C, although at 60°C, 1 g/L is removed after 140 minutes (See Fig. 3a, and 3b). These results are coincident for the removal of Cr (VI) by *Cucumis sativus* biomasses [29], but are different for the Cr (VI) removal using *M. stenopetala* seed powder and banana peel powder, in which if increase the heavy metal concentration decrease the efficiency of removal and palm leaf-derived biochar [23, 26]. 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 [28, 29].

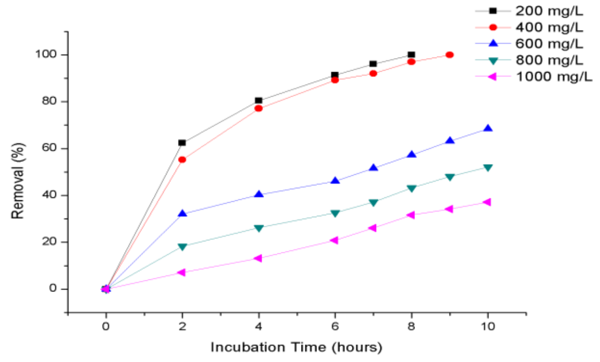

Figure 3a.- Effect of initial metal concentration on Chromium (VI) removal by 1 g of watermelon skin biomass. pH 1.0, 28°C. 100 rpm.

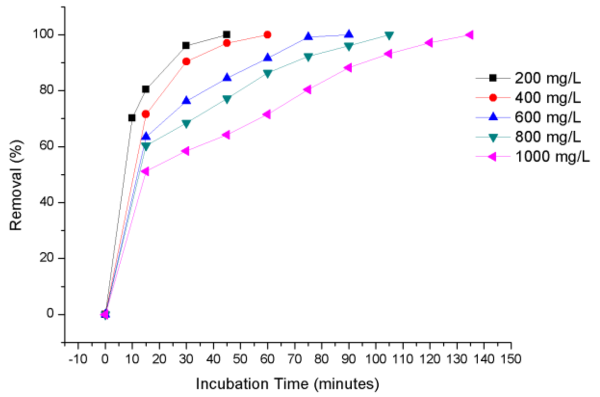

Figure 3b.- Effect of initial metal concentration on Chromium (VI) removal by 1 g of watermelon skin biomass. pH 1.0, 60°C. 100 rpm.

D. *Effect of biosorbent dose*

The influence of biomass concentration on the removal capacity of Cr (VI) is depict in Figure 4. If we increase the amount of biomass, the removal of the metal in solution increases significantly, because with 1 g of the analyzed biomass, 100% of the metal is removed after 420 minutes, while with 4 and 5 g, the removal is total after 120, and 100 minutes, respectively, although it has been reported what with more biosorption sites of the same, because the amount of added biosorbent determines the number of binding sites available for metal biosorption [32]. These results are similar for the removal of Cr (VI) from wastewater using *M. stenopetala* seed powder and banana peel powder, if increase the biomass concentration of 5 to 20 g/L [23], for palm leaf-derived biochar [28], and the removal of thw metal by *Cucumis sativus* biomass [33]. Too, was reported a efficient removal of the metal if the biomass concentration was increased using modified Russian knapweed flower powder to initial concentrations of the heavy metal of 2, 10 and 15 mg/L with pH 2.0 [34].

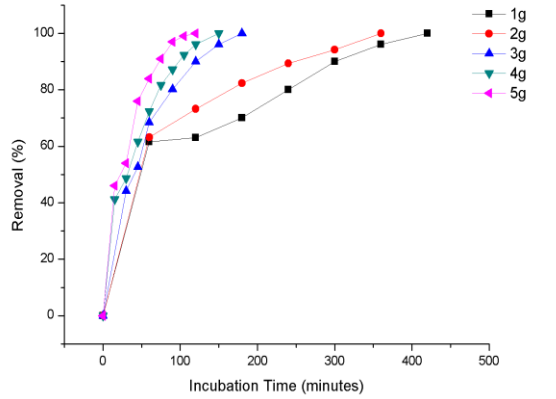

Figure 4. Effect of biomass concentration of watermelon skin biomass, on the removal of 100 mg/L Cr (VI), 28°C, pH 1.0, 100 rpm.

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

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 5 g of non-sterilized contaminated earth with 200 mg/g, suspended in trideionized water to a final volume of 200 mL, and 200 mL of wastewater containing 200 mg/L of Cr (VI) (adjusted). It was observing that in 105 hours of incubation, the Cr (VI) concentration of earth and water samples decrease completely in both samples (Figure 5), and the decrease level occurred without change significant in total chromium content during the experiments (date not shown). In the experiment carried out without 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 [11]. These results coincide with the literature reports for another natural biomass, such as for different natural biomasses [24, 35], for *Ginkgo biloba* leaves can effectively remove soil Cr (VI) and reduce this to Cr (III) via quercetin in soil (36), removal of this heavy metal from wastewater using *M. stenopetala* seed powder and banana peel powder [23], for the biomass of palm leaf-derived biochar [28], the removal of Chromium was found 95% from dilute tannery wastewater and 72% of the metal was extracted directly from raw tannery effluents by using different quantities of *Nicotiana tabacum* biomass (37), for the phytoremediation of chromium-polluted waters in cold region [38], for waste of *M. acuminata* residue [27], and is more efficient that *Avena sativa* L. biomass, in which a lower uptake of chromium from soil in the Cr(VI)-contaminated, was observed [39].

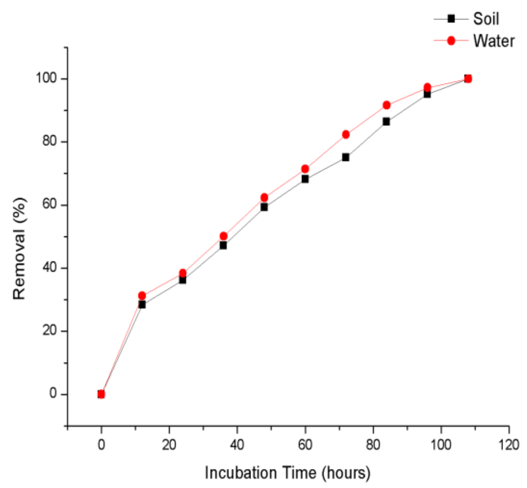

Figure 5. Removal of Cr (VI) in industrial wastes incubated with 5 g of watermelon skin biomass. 28°C, 100 rpm, 5 g of contaminated earth with 200 mg/g and 100 mL of contaminated water with 200 mg/L.

IV CONCLUSIONS

The biomass analyzed, showed complete capacity of biosorption of 1000 mg/L of Cr (VI) in solution at different time of incubation, at 28°C, 100 rpm with 1 g of natural biomass, besides this removal the metal *in situ* (105 hours of incubation, with 5 g of biomass), in both, earth and water contaminated, respectively. These results suggest their potential applicability for the remediation of this metal from polluted soils in the fields.

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