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REMOVAL OF CHROMIUM (VI) BY THE USE OF THE RESIDUE OF *Beta vulgaris* var. cycla BIOMASS

Martha E. Purata Díaz
Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
Martha_eugenia96@hotmail.com

Ana Sofia Reyes Barbosa
Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
Anasofiareyes436@hotmail.com

Paulina Olivo Fat
Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
Pau.olivo.f@outlook.com

Juan F. Cárdenas González
Unidad Académica Multidisciplinaria Zona Media
Universidad Autónoma de San Luis Potosí. Río
Verde, San Luis Potosí, México
jfkardenas_08@hotmail.com

Adriana S. Rodríguez Pérez
Unidad Académica Multidisciplinaria Zona Media
Universidad Autónoma de San Luis Potosí. Río
Verde, San Luis Potosí, México
asarai28@hotmail.com

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

María Eugenia Torre Bouscoulet
Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
metorre@uaslp.mx

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

***Abstract*—Chard is a leaf vegetable, which belongs to the family of the *Chenopodiaceae*. It is an herbaceous plant with long and succulent petioles, large and erect leaves, that are used for human consumption due to its culinary uses and nutritional content. Its production is exposed to contaminating factors such as toxic metals from irrigation water, so it can accumulate them, and when ingested by humans, they can be poisoned with these heavy metals, and this accumulation characteristic can be used to try to eliminate these contaminates from soil contaminated with them. So, the objective of this work was analyzing the Cr (VI) removal capacity in aqueous solution by the *Beta vulgaris* biomass, by the colorimetric method of Diphenylcarbazide, to evaluate the metal concentration. Biosorption at different pH was evaluated for 240 minutes. We too studied the effect of temperature in the range of 28 to 60°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 180 minutes, at pH of 1.0, 1.0 g of natural biomass, and 28°C. According to temperature, the highest removal was observed at 60°C, in 12 minutes, when the metal is completely adsorbed. It was observed that higher concentration of the metal, the removal is less, and if the biomass concentration increases, this does not affect the removal of the metal in solution. Besides its removal efficiently the metal *in situ* (100% in soil and water contaminated, after 24 hours of incubation, with 5 g of biomass and 28°C; so, it can be used to eliminate it from industrial wastewater.**

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

I. INTRODUCTION

There are edible species that stand out more for their culinary use than for their nutritional values. This is the case of chard (*Beta vulgaris* var. cycla), an intense green leaf, which despite having large amounts of vitamins and minerals, its celebrity lies more in its wide variety of uses in the kitchen. It has very low caloric intake and provides iron, calcium, phosphorus and magnesium. It is rich in A, B, and C vitamins. It also has other mineral salts that are very beneficial for our body. It is ideal to accompany brown rice or potatoes [1]. It is also used for the preparation of pies and fritters. Chard contains oxalic acid that causes an astringent sensation on the tongue, dry and bitter. For this reason, it is recommended to boil it in plenty of water and discard the cooking water or eat it raw when it is tender. Ideally, chop it raw. It is advisable to chew it well or process it when there are problems in the denture or in case of very sensitive intestines [2]. This is a biannual plant that does not form root or edible fruit. The leaves are the edible part. They can be wavy and/or wrinkled, depending on the crop; Petioles can be cream or white. For flowering to occur, it needs to go through a period of low temperatures. The floral stem reaches an average height of one meter and twenty centimeters. The inflorescence is composed of a long panicle, composed of small clusters. The flowers are sessile, that is, without a strong support to the stem, and hermaphrodites [3]. They can appear alone or in groups of two or three. Chard is a cold weather vegetable but tolerates frost and high temperatures. The temperature required for germination is 10 to 25°C. In Mexico it can be exploited all year. Generally, the direct sowing of the seeds in the earth is used, in single or double furrow. It is normal to place two to three seeds per stroke [3].

On the other hand, vegetables absorb minerals, which can be catalog in three groups. First, main elements, second instance secondary elements and finally microelements, and some of this, when absorbed by plants are usually considered as a potential source of pollution. The above is derived mainly from heavy metals and their toxicity in the environment and the health of consumers [4]. In this sense, phytoremediation has emerged as an alternative to solve this problem. In Mexico, plant species with metal accumulative capacity have been identified. These include *Scirpus americanus, Typha latifolia, Jatropha dioica, Eichhornia crassipes, Amaranthus hybridus*, and *B. vulgaris* var. cycla biomass [1, 2, and 4]. Thus, there is a need to develop or find innovative low-cost adsorbents with an affinity towards metal ions for the removal of different heavy metals from aqueous solution, which leads to high adsorption capacity [5, 6]. The objective of this study was to analyze in vitro biosorption of Cr (VI) by *B. vulgaris* var. cycla biomass.

II. EXPERIMENTAL

A. Biosorbent used

The *B. vulgaris* var. cycla biomass, was obtained from the fruits harvested and offered in the marketplace Republic, between the months of March to May in 2019, of the capital city of San Luis Potosí, S.L.P. México. To obtain the biomass, the leaves was washed with trideionized water during 3 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 24 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 employing Diphenylcarbazide [7, 8]. 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 by *B. vulgaris* biomass was 180 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 [9], report an optimum time of 8 h for the removal of Cr(VI) by porous carbon derived from corn straw, 150 and 180 minutes for Cr (VI) removal using oleaster (*Elaeagnus*) seed and cherry (*Prunus avium*) stone biochar [10], 10 hours by *Ananas comosus* biomass shell [11], and 120 minutes, 150 mg/L of the same metal and 2.5 g/L of natural biomass with *Macadamia* nutshell powder oxidized by hydrogen peroxide solutions [12]. 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 [4, 5, and 6]. Adsorption efficiency of Cr (VI) was observe a maximum at pH 1.0 and 180 minutes 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 the Cr (VI) removal using oleaster (*Elaeagnus*) seed and cherry (*P. avium*) stone biochar [10], a pH of 1-3, for the removal of the same metal by porous carbon derived from corn straw [9], an optimum pH of 1.0 by *A. comosus* biomass shell [11]. Although other authors report an optimum pH 2.0 for epicarpio of *Vitis vinifera* L. [13], a pH of 3.0 by hydrothermal carbon-sphere-Fe_3O_4 [14], pH of 2.0 by modified Russian knapweed flower powder [15]. 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 [6, 16].

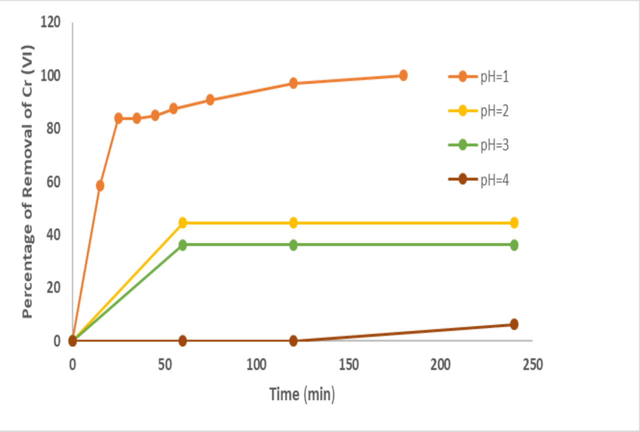

Figure 1. Effect of incubation time and pH on Chromium (VI) removal by *B. Vulgaris* biomass. 100 mg/L Cr (VI), 100 rpm, 28°C. 1.0 g of biomass.

B. *Effect of the temperature*

On the other hand, temperature was found to be a critical parameter in the bioadsorption of metal (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 12 and 180 minutes of incubation, for 60°C and 28^{o}C, respectively. This results are coincident for power of orange peel biosorbent for the removal of Pb (II) and Zn (II) [17], *A. comosus* biomass shell [11], and residue of the *Persea Americana* Shell [18], by a reusable chitosan-modified multi-walled carbon nanotube composite [19], by dried twigs of *Melaleuca diosmifolia* [20], for the tremoval of Cr (VI). 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 [21].

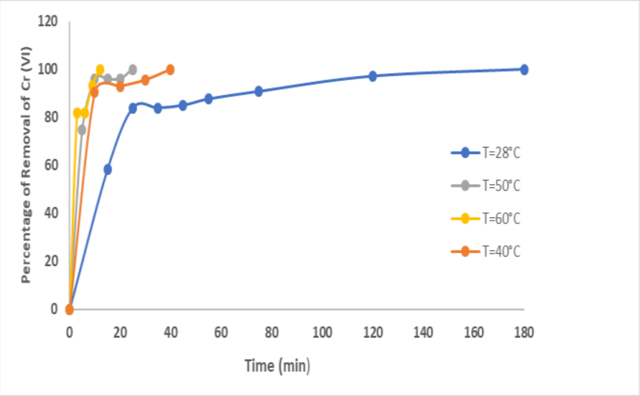

Figure 2. Effect of the temperature on Chromium (VI) removal by *B. vulgaris* biomass. 100 mg/L Cr (VI), pH 1.0, 100 rpm. 1.0 g of biomass.

C. *Effect of initial metal concentration*

We observe that the removal of metal was 100% at 5 and 24 hours, at 28°C, for 200 and 1000 mg/L, respectively (Figure 3). In addition, we observe the development of a blue-green and white precipitate, which changes more rapidly at higher temperatures (date not shown), and we determined this precipitate how Cr (III) [8]. The results are coincident for the removal of Pb (II) by dried green algae collected from Jeddah coast [22], the removal of Cr (VI) by residual biomass of eucalyptus leaves (*Globulus labill*) [23], and the removal of the same metal by coffee ground and mixed waste tea [16], and are different for the chromium removal using *Platanus hispánica* aquenium [24], in it was found that the increase in the initial concentration led to an increase in the removal of the contaminant [24]. 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 [6, 21].

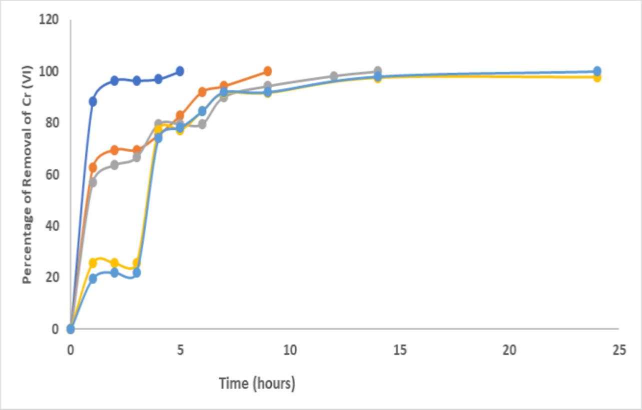

Figure 3. Effect of initial metal concentration on Cr (VI) removal by *B. Vulgaris* biomass. pH 1.0, 100 rpm, 28°C. ● 200 mg/L, ● 400 mg/L, ● 600 mg/L, ● 800 mg/L, ● 1000 mg/L.

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 decreased slightly, well the removal obtained was observed between 100%-96.2%, with 1-4 g of natural biomass, 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 [26]. Different results have been reported for almond green hull [27], 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 of 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 [10], using modified Russian knapweed flower powder to initial concentrations of Cr (VI) of 2, 10 and 15 mg/L with pH 2.0 [15], 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 [28], 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% [29].

Removal of Cr (VI) in industrial wastes with B. vulgaris 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 10 g of non-sterilized contaminated earth with 100 mg/g, and wastewater containing 100 mg/L of Cr (VI) (adjusted), suspended in trideionized water to a final volume of 100 mL. It was observing that in 24 hours of incubation, the Cr (VI) concentration of earth and water samples decrease fully 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 [5, 6, 11, and 18]. This results 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 Cu (II), Ni (II), and Cr (VI), with percentages of removal between 37-53%, 39-76%, and 11-33%, respectively [30], for a wastewater sample with Cr (III) (4 mg/L), Zn (II) (1 mg/L), Fe (II) (6 mg/L), Ni (II) (2 mg/L), and Cu (II) (31 mg/L) by *Macadamia* nutshell powder oxidized by hydrogen peroxide solutions [12], the Cr VI) biosorption, in aqueous solutions and in effluents industrial tannery, using biosorbent of eucalyptus tree waste leaves (*G. labill*), activated in acidic medium [23],

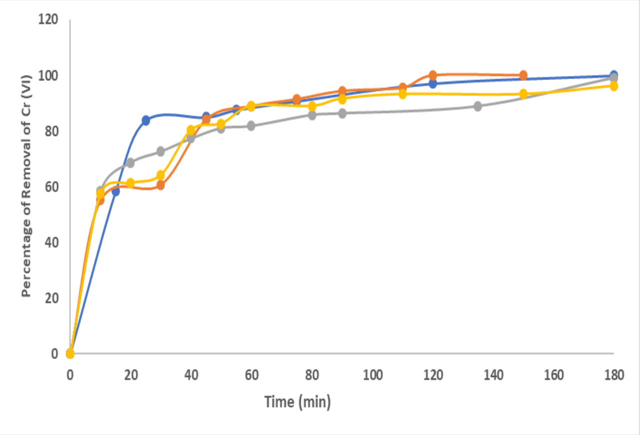

Figure 4. Effect of biomass concentration of *B. vulgaris* biomass, on the removal of 100 mg/L Cr (VI), 28°C, pH 1.0, 100 rpm.

●1 g, ●2 g, ●3 g, ●4 g.

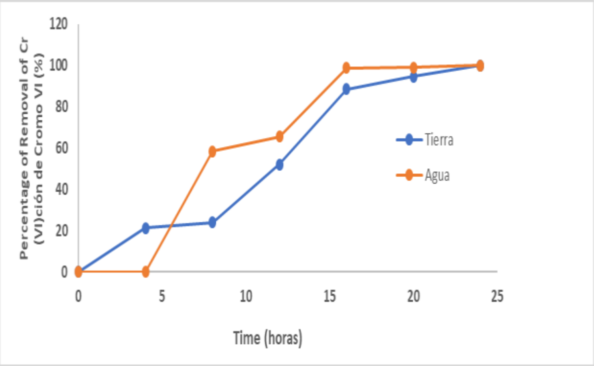

Figure 5. Removal of Cr (VI) in industrial wastes incubated with 5 g of *B. Vulgaris* biomass. 28°C, 100 rpm, 10 g of contaminated earth with 100 mg/g and 100 mL of contaminated water with 100 mg/L. contaminated water, (100 mg Cr (VI)/L (adjusted).

●Earth, ●Water

E. Conclusions

The biomass analyzed, showed complete capacity of biosorption of 100 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* (24 hours of incubation, with 5 g of biomass), in earth and water contaminated. These results suggest their potential applicability for the remediation of this metal from polluted soils in the fields.

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