



EQUILIBRIUM AND THERMODYNAMIC ANALYSIS OF CHROMIUM(VI) BIOSORPTION BY OKRA POWDER

V. H. S. Ramos¹, J. C. Conceição¹, E. Jesus¹, Danilo Conceição¹, A. S. Silva²

1- Department of Chemical Engineering – Federal University of Sergipe.
Marechal Rondon Avenue, s/n – CEP: 491000-000 – São Cristóvão - SE – Brazil
Telephone: (079) 2105-6686 – Fax: (079) 2105-6676. Email: edilsonjs@ufs.br
2- Department of Mathematics – Federal University of Sergipe.
Marechal Rondon Avenue, s/n – CEP: 491000-000 – São Cristóvão - SE – Brazil
Telephone: (079) 2105-6676 – Fax: (079) 2105-6676. Email: ass@infonet.com.br

ABSTRACT: Was explored the removal Cr(VI) from aqueous solutions using okra powder after drying procedure. The experiments were performed at initial concentrations of Cr(VI) 1, 2, 4, 5 and 6 mg L⁻¹, amount of adsorbent 0.1, 0.2, 0.4 and 0.6 g, pH 2, 4, 5, 7, 8, contact time of 10-240 min and temperature of 25 ± 1°C. Adsorption of Cr(VI) in all cases was pH dependent, with greater removal at pH 2. The applicability of the Langmuir and Freundlich has been used for the equilibrium. The observed maximum biosorption capacity by Langmuir sorption model at pH 2 was 0.1266 mmol of Cr(VI)/g of okra powder. FTIR were used to prove the okra powder efficiency in the removal of Cr(VI) from aqueous solutions. The thermodynamic parameters such ΔG, ΔH and ΔS were calculated for predicting the nature of adsorption. According to the experimental results, okra powder seems to be an effective and alternative adsorbent precursor for the removal of Cr(VI).

KEYWORDS: biosorption, hexavalent chromium, okra powder, thermodynamic analysis, equilibrium study

1. INTRODUCTION

The problem of obtaining water for consumption and adequacy of effluents to the specifications make emerge new technologies that allow not only meeting the legal standards, but also the improvement in process efficiency. Several processes can be applied in the treatment of effluents containing heavy metals, such electrolysis, adsorption, reverse osmosis and caustic precipitation. The adsorption is shown to be effective in the treatment of liquid effluents contaminated by compounds of Cr(VI), this efficiency being mainly dependent on the adsorbent concentration, pH and temperature (Liu et al., 2007).

There are several sources of pollution that lead to contamination of these effluents; among these sources are included the burning of fossil fuels, production of ores, fertilizers and electroplating. Among the most common

contaminants are cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn).

Regarding the chromium, its chemical behavior in aqueous solution depends on various factors such as concentration, temperature, ionic strength, pH and solution potential. The pH is one of the parameters that most affect this metal species in solution (Pina, 2011). Chromium can occur in nature in various oxidation states, 2+, 3+ and 6+, there being much information available about the Cr³⁺ and Cr⁶⁺. The species derived from hydrolysis of Cr(VI) varies according to the solution pH, where the ionic form predominantly below pH 6.5 is HCrO₄⁻ (hydrogen-chromate ion) and the above pH 6.5 the CrO₄²⁻ (chromate). The neutral species, H₂CrO₄ (chromic acid), is predominant in pH below 1.0 (Sengupta and Clifford, 1986).

The biosorption is a process used to remove heavy metals involving a solid phase (biosorbent) and a liquid phase containing metal species. Due to



its biodegradability, natural products have been used in chemical processes. In the biosorption the capture of metal ions by the biomass is a passive process through physicochemical interactions between the ions and functional groups present on the biomass surface. The process is based on different mechanisms not affected by the constituents of biomass. It is a process that can be quick and reversible, and thus it is adequate for removal of heavy metal ions (Kuyucak and Volesky, 1988).

Biomass is any organic matter of plant and animal origin, including materials from its transformations and can be natural or artificial (Ozdemir et al, 2004). Among those of biological origin with ability to adsorb and/or absorb dissolved metal ions (Benvindo da Luz et al., 2002), there are the cactus (Dakiky et al., 2002), bagasse, (Gupta and Ali, 2004) *cyanobacterium* (Gupta and Rastogi, 2008a), green algae (Gupta and Rastogi, 2008b) *Oedogonium* sp. and *Nostoc* sp. (Gupta, and Rastogi, 2008c) Osage orange (Pehlivan et al., 2012), Brown Seaweeds (Lee and Park, 2012) and *Moringa Olefera* (Ndabigengesere et al., 1995; Rajeswari et al., 2013), powder okra (Ramos et al, 2013), okra powder modified (Conceição et al, 2013).

The plant *Albemoschus esculentus* (okra) finds excellent condition for cultivation in Brazil, especially with regard to climate, being popularly grown in the Northeast and Southeast of Brazil. In Sergipe, mainly due to the favorable weather, the plant has some desirable features like fast cycle, economically viable production cost, resistance to pests and high food and nutritional value (Mota et al., 2005). The mature seeds of okra tree are rich in oil, protein and polysaccharides.

The main goal of this work was to analyze the chemical balance parameters using okra powder by biosorption of Cr(VI) ion from aqueous solution. The amounts of equilibrium sorption isotherms were measured by using the Langmuir and Freundlich isotherms. The effects of contact time, solution pH and biosorbent concentration on biosorption were analyzed.

2. MATERIALS AND METHODS

2.1. Stock solution of ion Cr(VI)

The solution of Cr(VI) was prepared using $K_2Cr_2O_7$ (from Merck) dissolving 0.2838 g in 1000

mL deionized water, forming a solution with 100 mg L^{-1} of Cr(VI). From this solution by dilution were obtained solutions with concentrations of 1, 2, 4, 5 and 6 mg L^{-1} of Cr(VI).

2.2 Biosorbent preparation

The mature okra and those discarded in fairs were collected and washed with distilled water. They were then opened and placed in the greenhouse for 9 hours at $120 \text{ }^\circ\text{C}$ and soon after for 3.5 hours at $150 \text{ }^\circ\text{C}$, subsequently okras were crushed.

2.3 Titratable acidity determination

A sample containing 1.0 g biosorbent of 12-mesh particle size and 200 mL distilled water was stirred for 24 h under magnetic stirring. Subsequently, it was withdrawn an aliquot of 10 mL to a 100 mL flask and completed with distilled water. This solution was titrated with 0.01 M NaOH to the phenolphthalein end point (Morita and Assumpção, 2007; Instituto Adolfo Lutz, 1985). The experiments were performed in triplicate.

2.4 Elemental analysis

Elemental analysis was carried out with the Flash EA 1112 Séries da Thermo Finnigan. The biosorbent sample was added to tin capsules and analyzed for the composition of carbon, nitrogen and hydrogen at $900 \text{ }^\circ\text{C}$ under an O_2 (oxygen gas) and N_2 (nitrogen gas) atmosphere.

2.5 FTIR characterization of biosorbent

The FTIR spectra of okra powder were studied before and after Cr(VI) biosorption. A Nicolet model iS-10 FTIR Spectrometer was used in the region between 400 and 4000 cm^{-1} with 4 cm^{-1} resolution. Samples were analyzed as pellets with KBr.



2.6 Adsorption experiments: Chromium Estimation by Diphenylcarbazide Complex Method

Solutions at concentrations of 0.2, 0.4, 0.6, 0.8 and 1.0 mg L⁻¹ were obtained by dilution from the stock solution for constructing the calibration curve. A purple-violet-colored complex was developed in the reaction between hexavalent chromium and 1,5-diphenylcarbazide in acidic condition (Morita and Assumpção, 2007). Absorbance was measured at 540 nm wavelength. A standard graph of absorbance vs. concentration was obtained to determine chromium concentrations. A unknown concentration was determined by the samples absorbance value using UV-Vis spectrophotometer model Cary 60 Varian. The percentage of hexavalent chromium removal was determined by Equation 1.

$$\% \text{ Chromium removal} = \left[\frac{(C_i - C_e)}{C_i} \right] \times 100 \quad (1)$$

where C_i and C_e are the initial and equilibrium concentration of hexavalent chromium solution (in milligrams per liter), respectively.

Batch tests were used to study the influence of pH, initial conditions of Cr(VI) concentration 1, 2, 4, 5 and 6 mg L⁻¹, adsorbent amount 0.1, 0.2, 0.4 and 0.6 g, pH 2, 4, 7, 8, contact time 10-240 min and temperature of 25 ± 1°C.

3. RESULTS AND DISCUSSION

Carboxylic acid amounts have been calculated as 0.70 mmol/g de biosorbent. The elemental analysis indicated contents of C, H and N equal to 4.34 ± 0.2; 40.14 ± 0.2 and 0.99 ± 0.10%, respectively. The CHNS elemental analysis performed did not allow describing molecular formulas since okra powder is a natural compound made up of several substances (proteins, polysaccharides and organic acids). The okra fruit has high nutritional value and it is used as a complete source of fibers, calcium, minerals and vitamins (Auerswald et al.; 1999). The seeds account for 17% of the fruit and consist of oils (which can account for 40%) and proteins (Mota et al., 2005). For all cultivars of okra analyzed in

Mota et al., 2005), the starch levels ranged from 0.98 to 1.23% and the carbohydrate levels from 1.91 to 2.16% on fresh weight and moreover, the seeds contain polyphenolic compounds, mostly atequins derivatives and oligomeric flavonoids (Arapitsas, 2008).

Figure 1 shows the FTIR spectra of the okra powder before and after the sorption. Analyzing the two spectra, it is clear that some groups in the powder were involved in the biosorption of Cr(VI). The broad and strong band at 3400 cm⁻¹ was attributed to the -OH group of carboxylic acids (Pehlivan et al., 2012; Altun and Pehlivan, 2012). The peak at 2922 cm⁻¹ indicates the C-H vibration of CH₂ group (Pehlivan et al., 2012). The band at 1645 cm⁻¹ was attributed to the C = O vibration of carboxylic acids and N-substituted amide. The band at 1434 cm⁻¹ is attributed to symmetrical COO⁻ stretching motions of hemicellulose (Pehlivan et al., 2012). The analysis before and after adsorption showed change in the intensity of transmittance in the wavelength range studied (Shukla and Vankar, 2012). In 1434 and 1645 cm⁻¹ there was change in the intensity of bands, with the band appearing at 1645 cm⁻¹ becoming broader after absorption of chromium, and the band at 3400 cm⁻¹ assigned to the -OH group of carboxylic acids which may indicate that these groups were strongly involved in biosorption.

Chromium has different types of equilibrium depending on pH in aqueous solutions. As the pH is altered there is displacement of equilibrium. In the pH range 2-6, the ions HCrO₄⁻ and Cr₂O₇⁻² are in equilibrium. With the existence of several species of Cr(VI), the adsorption process of Cr(VI) is strongly affected by pH in the medium. The adsorption of Cr(VI) was more effective in acid medium, showing a removal of 63.8% at pH 2. The okra powder showed 10.3% removal at pH 7 and 8, indicating low removal capacity. It can also be said that the adsorption at high pH is not recommended because of the precipitation of the ion Cr(IV). Bind characteristics of chromium were observed through the peak of 913 cm attributed to the possible bond Cr=O (Santhana et al., 2012), characterizing the chemisorption process.

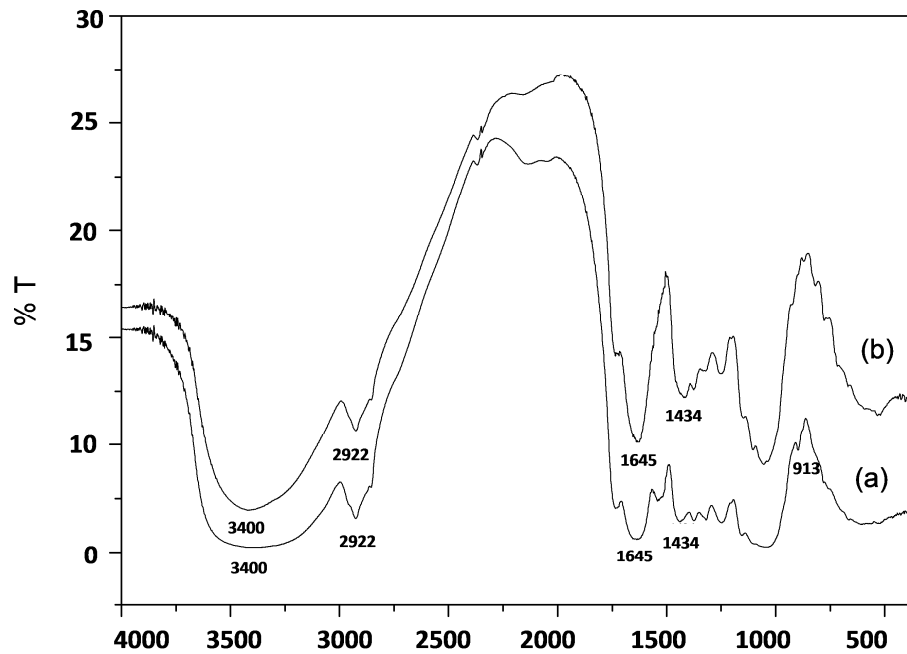


Figure 1. FTIR spectra of biosorbent (a) okra powder-Cr(VI) (b) okra powder

Figure 2 shows the mean removal of Cr(VI) depending on pH. The greatest removal occurred at pH 2, which favors the increased number of hydronium ions in the medium with possible protonation on the biosorbent surface. As the okra powder is rich in substances which have hydroxyl groups in their structures, these attract H⁺ ions which in turn interact with oxyanions of Cr(VI), in particular HCrO₄⁻ and Cr₂O₇²⁻, which are dominant at pH 2 (Altun and Pehlivan, 2012).

Figure 3 shows the removal behavior of Cr(VI) ion with the contact time. The contact time was varied from 10 to 240 minutes for adsorption of Cr(VI) with powdered okra. For okra powder the equilibrium time was 180 min. During adsorption, hexavalent chromium is impregnated on the adsorbent surface until the entire surface is covered with ions, at this point the concentration of Cr(VI) on the powder surface does not increase and remains in equilibrium with the adsorbent in solution.

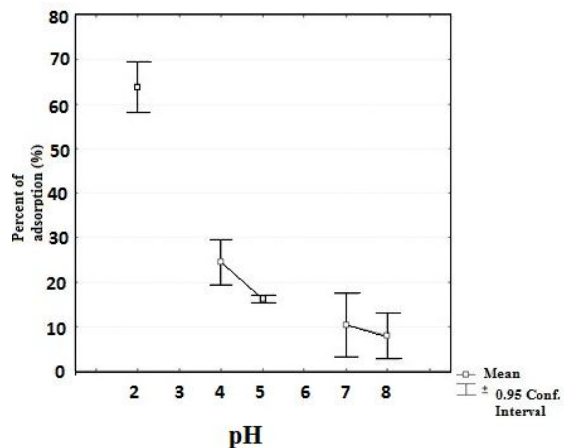


Figure 2. Effect of pH on the sorption of Cr(VI) by okra powder. (Conditions; initial concentration of Cr(VI), 5 mg L⁻¹ amount of biosorbent 0.1 g; 12-mesh particle size; volume of biosorption medium, 100 ml; temperature, 25 ± 1 °C; stirring time, 180 min).

The influence of biosorbent amount on the removal of Cr(VI) was analyzed. Figure 4 shows the behavior of the Cr(VI) removal percentage according to the biosorbent amount. The adsorption test was performed with initial concentration of Cr(VI) 5 mg L⁻¹ at pH 2 and equilibrium time of 180 min. The increase in the



metal ion removal by increasing the biosorbent mass was due to the presence of a greater amount of available active sites, which increases the surface area available for biosorption.

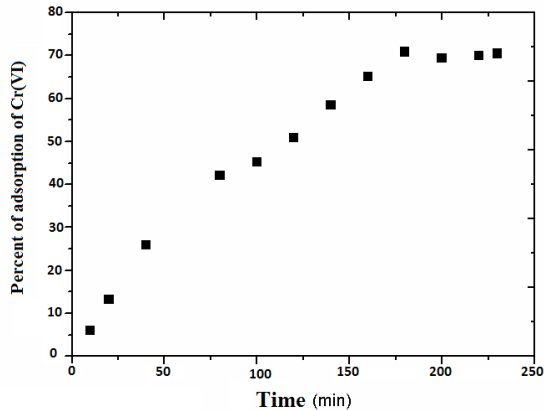


Figure 3. Effect of contact time on the sorption of Cr(VI) by Okra powder. (Conditions; initial concentration of Cr(VI), 5 mg L⁻¹; amount of biosorbent, 0.1 g; 12-mesh particle size; volume of biosorption medium, 100 ml; temperature 25 ± 1 °C; stirring rate 180 rpm; pH 2.

The adsorption of metal species in different biosorbents can be attributed to several mechanisms such as electrostatic attraction and repulsion, chemical interaction and ion exchange. The relationship between adsorbent and adsorbate in the equilibrium and maximum biosorption capacity of the biosorbent are studied using models of biosorption, such as the Langmuir and Freundlich isotherms Pehlivan et al., 2005). The isotherms behavior was analyzed according to the variation of the initial concentration of Cr(VI) and the optimum pH at the equilibrium time of 180 min.

Several isotherms are used to describe the relationship between the amount of adsorbate per unit of adsorbent and the concentration of unadsorbed adsorbate, the most important being the Freundlich and Langmuir (Pehlivan et al., 2012; Altun and Pehlivan, 2012; Shukla and Vankar, 2012; Bernardo, 2005).

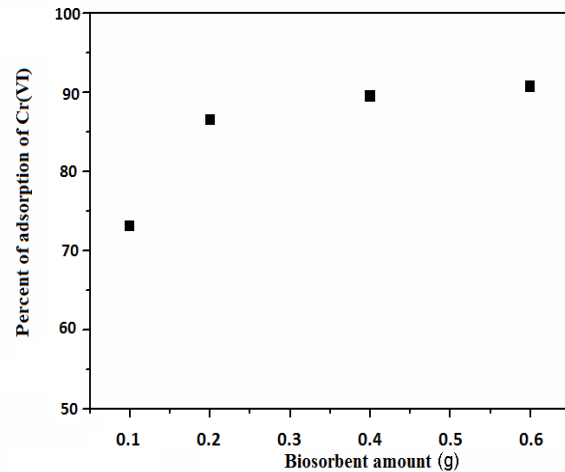


Figure 4. Effect of biosorbent amount on the sorption of Cr(VI) by Okra powder. (Conditions; initial concentration of Cr(VI), 5 mg L⁻¹ volume of biosorption medium, 100 ml; temperature, 25 ± 1 °C; stirring time, 180 min; pH 2).

Equation 2 represents the Freundlich isotherm, which is widely used to describe accurately the data on biosorption assay. Equation 2 represents the Freundlich isotherm in linear form.

$$Q_e = K_f C_e^{1/n} \quad (2)$$

where Q_e is the amount of adsorbate per unit of adsorbent (mmol of adsorbate per gram of adsorbent); C_e is the concentration of adsorbate in the equilibrium (mmol/L); K_f and n are coefficients to be determined experimentally. K_f corresponds to the Freundlich constant and it is related to the biosorption ability and n relates to biosorption intensity. Values of n in the range $1 < n < 10$ indicate favorable biosorption.

For fixed values of C_e and $1/n$, q_e will be as greater as K_{ad} and C_e , binding of biosorption will be stronger as smaller the value of $1/n$. The lower $1/n$, the biosorption capacity is independent of C_e and the biosorption isotherm (ratio between C_e and Q_e) is close to the horizontal. The higher the $1/n$ value the smaller the binding intensity on the biosorption.

The Langmuir isotherm (Equation 3) is given by

$$Q_e = \frac{q_{\max} C_e b}{1 + b C_e} \quad (3)$$



where b (L/mmol), q_{\max} (mmol/g) are coefficients to be determined experimentally.

The q_{\max} coefficient corresponds to the surface concentration in a single coating layer; the coefficient b is related to the adsorption energy and increases with increasing binding adsorption strengths. Values of b and q_{\max} can be determined experimentally by constructing the curve $1/Q_e$ versus $1/C_e$. Table 1 shows parameters determined by the isotherms used in this study.

Table 1. Parameters of the isotherm for the adsorbent okra powder

Isoterms	Parameters	Values
Langmuir	q_{\max}	0.1266 mmol g ⁻¹
	b	11.37 L mmol ⁻¹
	R^2	0.9525
Freundlich	K_f	2.0352
	n	1.2664
	R^2	0.9861

In order to fully understand the nature of adsorption the thermodynamic parameters such as free energy change (ΔG) and enthalpy change (ΔH) and entropy change (ΔS) could be calculated using the Equations 4-6. The values of ΔH and ΔS are determined from the slop and intercept of the linear plot of $\ln K_d$ vs. $1/T$ (Figure 5).

$$\Delta G = -RT \ln K_d \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

$$K_d = \frac{C_A}{C_e} \quad (7)$$

Here, the K_d value is the distribution coefficient, C_A is the amount of metal ion adsorbed at the solid interface at equilibrium, and C_e is the equilibrium concentration. R is the gas constant (8.314 J mol⁻¹ K⁻¹) and T is the absolute temperature (K).

The values of ΔH and ΔS are found to be -48.86 kJ mol⁻¹ and 0.1660 kJ/mol-K, respectively. The positive value of ΔH indicate and endothermic sorption reaction process. The positive value of ΔS shows the increasing randomness at the solid/liquid

interface during the sorption of Cr(VI) ions onto okra powder. The positive value of ΔH shows high probability that it is a chemisorption process and denotes an irreversible process (Lesmana, 2009). The value of ΔG using Equation 5 ($T=298,15$ K) is found to be -0.9148 kJmol⁻¹ that confirms the feasibility of the process and the spontaneous nature of sorption. Similar results were reported by Altun and Pehlivan (2012). Other experiments are being developed for further investigation of the potential of okra in the removal of other metals.

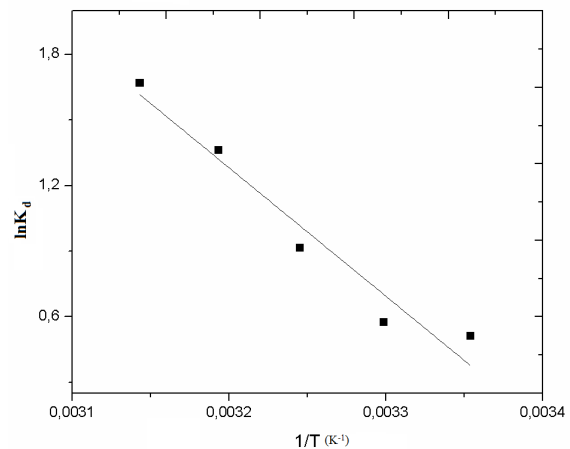


Figure 5. Effect of temperature (K) on the sorption of Cr(VI) by Okra powder. (Conditions; initial concentration of Cr(VI), 5 mg L⁻¹ volume of biosorption medium, 100 ml; temperature, stirring time, 180 min; pH 2). $R^2 = 0.94$.

The fundamental characteristics of the Langmuir isotherm can be expressed by the equilibrium parameter R_L using the Equation 8.

$$R_L = \frac{1}{1 + bC_i} \quad (8)$$

Here, C_i is the highest initial metal concentration (6 ppm or 0.1154 mmolL⁻¹) and b is the Langmuir isotherm coefficient (11.37 Lmol⁻¹). The value of R_L found (0,43) is between 0 and 1, which indicates spontaneous adsorption (Santos, 2009). Using the Freundlich isotherm, the value of n found 1.2664 denotes spontaneous adsorption. Values of n in the range $1 < n < 10$ indicate favorable biosorption (spontaneous adsorption) (Sulak, 2012).



4. CONCLUSIONS

The biosorption of Cr(VI) ions on okra powder was analyzed and it showed good sorption ability for Cr(VI) ion. The biosorption of Cr(VI) ions increased with increasing contact time and attained an optimum at about 180 min. The Cr(VI) ion removal depended on the initial Cr(VI) ion concentration and pH of the Cr(VI) ion solution. The experimental values were adjusted with either Freundlich model as the Langmuir, the later had led to a lower chi square, which may indicate a monolayer adsorption. However, the occurrence of biosorption in monolayer and heterogeneous conditions on the surfaces of adsorbents can coexist under the experimental conditions. Once it is a material found in nature that does not require chemical modification, cost/benefit relationship should be investigated for its application in wastewater treatment. The positive values of ΔH and ΔS showed that adsorption process was endothermic in nature. The negative ΔG value indicated the feasibility and spontaneous nature of the adsorption process of Cr(VI) onto okra powder.

Acknowledgement The authors would like to thank the Federal University of Sergipe and FAPITEC-SE for scientific and technological development and Laboratory of Environmental Chemistry.

5. REFERENCES

- ALTUN, T.; PEHLIVAN, E. Removal of Cr(VI) from aqueous solutions by modified walnut shells. *Food Chem.* v.132 p.693-700, 2012.
- ARAPITSAS, P. Identification and Quantification of Polyphenolic Compounds from Okra Seeds and Skins., *Food Chem.*, v.110. p.1041-1045, 2008.
- AUERSWALD, H.; SCHWARZ, D.; KORNELSON, C.; KRUMBEIN, A.
- BENVINDO DA LUZ, A.; SAMPAIO, J. A.; ALMEIDA, S. L. M. Tratamento de minérios, rev. e ampliada, p. 23. Rio de Janeiro: CETEM/MCT, 2002.
- BERNARDO, L.D. and DANTAS, A.D.B. Métodos e técnicas de tratamento de água. 2. ed São Carlos, SP: Rima. , 2005.
- CONCEIÇÃO, J. C.; RAMOS, V.H.S.; JESUS, E.; MARQUES, J. J.; SILVA, A. S.; SILVA, D. C. Biossorção de Cr(VI) de soluções aquosas com pó de quiabo quimicamente modificado. In: Congresso Brasileiro de Sistemas particulados (ENEMP), Maceió, 2012.
- DAKIKY, M.; KHAMIS, M.; MANASSRA, A; MER'EB, M. Selective adsorption of chromium VI in industrial wastewater using low-cost abundantly available adsorbents, *Adv. Environ. Res.* v. 6. p.533-540, 2002.
- GUPTA, V.K; RASTOGI, A. Sorption and desorption studies of chromium(VI) from nonviable cyanobacterium *Nostoc muscorum* biomass, *J. Hazard. Mater.*, v.154. p.347-354, 2008a.
- GUPTA, V.K; RASTOGI, A. Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: kinetics and equilibrium studies. *J. Hazard. Mater.*, v.1. p.407-414, 2008b.
- GUPTA, V.K.; ALI, L. Removal of lead and chromium from wastewater using bagasse fly ash-a sugar industry waste, *J. Colloid. Interf. Sci.*, v.2. p.321-328, 2004.
- GUPTA, V.K.; RASTOGI, A. Biosorption of lead(II) from aqueous solutions by non-living algal biomass *Oedogonium sp.* and *Nostoc sp.*—a comparative study, *J. Hazard. Mater.*, v.152 p.407-414, 2008c.
- INSTITUTO ADOLFO LUTZ, Normas Analíticas do Instituto Adolfo Lutz. v. 1: Métodos químicos e físicos para análise de alimentos. Sao Paulo: IMESP 13-14, 1985.
- KUYUCAK, N.; VOLESKY, B. Biosorbents for recovery of metals from industrial solutions. *Biotechnol. Lett.*, v. 10 p. 137-142, 1988.
- LEE, S.H.; PARK, C. Biosorption of Heavy Metal Ions by Brown Seaweeds from Southern Coast of Korea, *Biotechnol. Bioprocess Eng.*, v.17 p.853-861, 2012.



LESMANA, S. O; FEBRIANA, N.; SOETAREDO, F. E.; SUNARSO AND J.; ISMADJI, S. Studies on potential applications of biomass for the separation of heavy metals from water and wastewater. *Biochemical Engineering Journal*, v. 44 p. 19–41, 2009.

LIU, S.X.; CHEN, X. Y.; LIU, Z. F.; WANG, H. L. Activated carbon with excellent chromium(VI) adsorption performance prepared by acid–base surface modification, *J. Hazard. Mater.*, v. 141, 315–319, 2007.

MORITA, T.; ASSUMPCÃO, R.M. *Manual de Soluções, Reagentes e Solventes*. 2 ed., São Paulo: Edgard Blucher, 2007.

MOTA, W.F.; FINGER, F. L.; SILVA, D. J. H.; CORRÊA, P. C.; FIRME, L. P.; NEVES, L. L. M. Caracterização físico-química de frutos de quatro cultivares de quiabo. *Hortic. bras.*, v.23. p.722-725, 2005.

NDABIGENGESERE, A.; NARASIAH, and G. B. TALBOT, K. S. Active agents and mechanism of coagulation of turbid waters using *Moringa oleifera*. *Wat. Res.*, v.29 p.703-710, 1995.

OZDEMIR, G; CEYHAN, N; OZTURK, T; AKIRMAK, F and COSAR, T. Biosorption of chromium(VI), cadmium(II) and copper(II) by *Pantoea sp.* TEM18, *Chem. Eng. J.*, v.3. p 249–253, 2004.

PEHLIVAN, E.; PEHLIVAN, E. and KAHRAMAN, H. T. Hexavalent chromium removal by Osage Orange, *Food. Chem.*, v.133 p.1478–1484, 2012.

PINA, F. D. S. Tratamento de águas contaminadas com crômio(VI) por bioadsorção em algas marinhas. Faculdade de Engenharia da Universidade do Porto, Porto, Portugal, 2011.

RAJESWARI, M.; AGRAWAL, P.; PRIYA, S. P.; PRIYA, G. R.; SANDHYA, G. R. and PAVITHRA, G. M. Continuous Biosorption of Cadmium by *Moringa oleifera* in a Packed Column. *Biotechnol.*, *Bioprocess Eng.*, v.18 p.321-325, 2013.

RAMOS, V.H.S; CONCEIÇÃO, J. C.; JESUS, E. J.; MARQUES, J.J.; SILVA, A.C.; SILVA, D. C. Remoção de cromo hexavalente por bioadsorção usando pó de quiabo. In: Congresso Brasileiro de Sistemas Particulados (ENEMP), Maceió, 2012.

SANTOS, E. B.; VIEIRA, E.F.S.; CESTARI, A.R.; BARRETO, L.S. Caracterização de escamas do peixe piau (*Leporinus elongatus*) e sua aplicação na remoção de Cu(II) de meio aquoso. *Química Nova*, v.32, nº1, p.134-138, 2009.

SANTHANA, A.; KUMAR, K.; KALIDHASAN, S.; RAJESH, V. and RAJESH, N. Application of Cellulose-Clay Composite Biosorbent toward the Effective Adsorption and Removal of Chromium from Industrial Wastewater. *Ind. Eng. Chem. Res.*, v.51. p.58–69, 2012.

SENGUPTA, A. K.; CLIFFORD, D. Important Process Variables in Chromate Ion Exchange, *Environ. Sci. Technol.*, v. 20 p. 149-155, 1986.

SHUKLA, D.; VANKAR, S. Efficient biosorption of chromium(VI) ion by dry *Araucaria* leaves. *Environ. Sci. Pollut. Res.*, v.19. p. 2321-2328, 2012.

SULAK, M. T; YATMAZ, H. C. Removal of textile dyes from aqueous solutions with eco-friendly biosorbent. *Desalination and Water Treatment*, v. 37. p. 169-177, 2012.