

CHROMIUM (VI) REMOVAL BY SAWDUST OF PINE TREE

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Abstract- Cr (VI) is a toxic metal on the list of priority pollutants due to its mutagenic and carcinogenic properties defined by the US EPA. Cr (VI) is mainly in discharges from electroplating, leather tanning, textile dyeing and metal finishing industries. The US EPA has the maximum allowable limit to Cr (VI) in drinking water and inland surface waters as 0.05 and 0.1 mg/L, respectively. Recently, a variety of low cost materials has been study for their ability to remove this metal from aqueous solution with promising results. We studied the Cr (VI) removal capacity in aqueous solution by sawdust biomass of pine tree. We use the diphenylcarbazide method to evaluate the metal concentration in solution and we obtain that the highest biosorption of the metal (50 mg/L) occurs within 9 hours, at pH of 1.0, and 28°C. The highest removal (100%), was observe at 50°C and 60°C, at 2 hours. At the analyzed concentrations of Cr (VI), sawdust showed good removal capacity of 1.0 g/L of the metal (100%, 40 min at 60°C, and 150 min at 28°C, respectively). If we increase the biosorbent concentration, increase the metal removal, with 100% at 60 min with 5 g of sawdust biomass. On the other hand, it removes efficiently the metal in situ (57.25%, and 72% of removal, 7 days of incubation, with 5 g of biomass, in soil and water contaminated, respectively). So, the biomass of pine tree can be used to eliminate the metal of contaminated sites.

Keywords – Chromium (VI); Removal; Sawdust biomass

I. INTRODUCTION

Chromium (Cr) is used in leather tanning, the manufacture of stainless steel, electroplating, textile dyeing and as a biocide in the cooling water of nuclear power plants. The discharges from these industries cause one of the major environmental pollution problems, due to the toxicity of this metal [1], which exists in nine valence states (from -2 to +6), but only the hexavalent (Cr (VI)) and trivalent (Cr (III)) forms have significance because they are the most stable oxidized ones [2]. The discharges are spill into water bodies and wastewaters, so we found the Cr (VI) as chromate (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$), depending of the pH of the solution [3]. These two divalent oxyanions are very water soluble and poorly adsorbed by soil and organic matter, making them mobile in soil and groundwater [2], which represent acute and chronic risks to animals and human health, because they are extremely toxic, mutagenic, carcinogenic and teratogenic [4]. While Cr (III) species: predominantly hydroxides, oxides or sulphates, are less water soluble, mobile, 100 times less toxic [5], and 1000 times less mutagenic [6]. The principal techniques for recovering or removing Cr (VI), from wastewater are chemical reduction and precipitation, adsorption on activated carbon, ion exchange and reverse osmosis in a basic medium [7]. However, these methods have certain disadvantages: high cost, low efficiency, generation of toxic sludge or other wastes that require disposal and imply operational complexity [8]. In recent years, several studies on the removal of Cr (VI), have been reported, using various low-cost adsorbents such as wool [9], used tires [10],

seaweed [11], fungal biomass [12], green algae [13], maple sawdust [14], sugar industry waste [15], etc. However, many of these naturally available adsorbents have low chromium adsorption capacity. So, it is necessary 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 [16]. The objective of this study was to analyze in vitro biosorption of Cr (VI) by biomass of sawdust.

II. MATERIAL AND METHODS

BIOSORBENT USED

Sawdust of pine tree was collect from different carpentry between the months of March to May in the 2014 year, in San Luis Potosí, S.L.P. México. To obtain the biomass, this was washed with water trideionized 72 hours under constant stirring, with water changes every 12 hours. Subsequently, boiled 1 hour to remove the dust and soluble impurities. The sawdust was dry at 80°C for 12 hours in the oven, ground in blender and stored in amber vials until use.

III. BIOSORPTION STUDIES AND DETERMINATION OF HEXAVALENT, TRIVALENT AND TOTAL CR

Were placed 1 g of dried sawdust/ 100 mL in contact with 50 mg/L of the metal-bearing solution in an Erlenmeyer flask at the desired temperature and pH. The flasks were agitated on a shaker at different times. Samples of 5 mL were taken in intervals and centrifuged at 3000 rpm for 5 minutes. The supernatant liquid was separate and analyzed for Cr (VI) ions.

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Hexavalent Chromium and trivalent Chromium were quantified by a spectrophotometric method employing diphenylcarbazide and chromazurol S, respectively [17;18], total Chromium was determined by electrothermal atomic absorption spectroscopy [17]. The values shown in the results section are the mean from three experiments carried out by triplicate.

IV. RESULTS AND DISCUSSION

V. EFFECT OF INCUBATION TIME AND PH

Figure 1 shows the effect of the incubation time and pH. The optimum time and pH for Cr (VI) removal was 9 h and pH 1.0, at constant values of biosorbent dosage (1 g/100 mL), with an initial metal concentration (50 mg/L), and temperature of 28°C. The literature [19], report an optimum time of 60 min for the removal of lead by orange shell, 30 min and 2 hours for the removal of Cr (VI) by the *Citrus reticulata* shell and eucalyptus bark [20; 21]. Changes in the permeability of unknown origin, could partly explain the differences found in the incubation time, providing greater or lesser exposure of the functional groups of the cell wall of biomass analyzed.

Adsorption efficiency of Cr (VI) was observed a maximum at pH 1.0 with sawdust biomass. The adsorption mechanism of Cr (VI) on sawdust biomass is due to electrostatic attraction and exchange. In acid solution, Cr (VI) exist mainly as HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, which have negative charges. Amido groups on sawdust biomass react with H^+ producing $-\text{NH}_3^+$, groups which adsorb Cr (VI) anion strongly through electrostatic attraction. When Cr (VI) anion reaches the surface of sawdust biomass, an ion exchange reaction occurred [13].

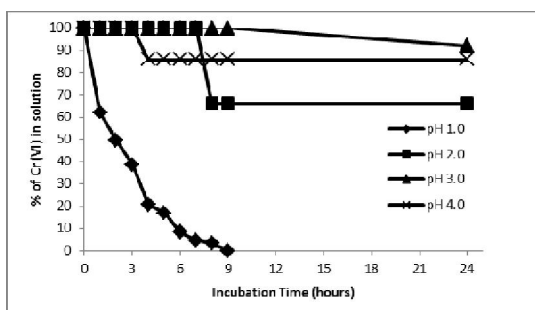


Fig. 1 Effect of incubation time and pH on Chromium (VI) removal by sawdust biomass. 50 mg/L Cr (VI), 100 rpm, 28°C.

VI. EFFECT OF THE TEMPERATURE

Temperature was found to be a critical parameter in the bioadsorption of Cr (VI) (Figure 2). The highest removal was observed at 50°C and 60°C, and 2 hours of incubation. At this point, the total removal of the metal is carried out. The results are coincident for tamarind shell with 95% of removal at 58°C and 3 hours [22], for the adsorption of cadmium(II) from aqueous solution on natural and oxidized corncob (40°C and 5 days) [23], but this are different for the mandarin waste [24], *Caladium bicolor* (wild cocoyam)

biomass [25], and *Saccharomyces cerevisiae* [26]. The increase in temperature increases the rate of removal of Chromium (VI) and decreases the contact time required for complete removal of the metal, to increase the redox reaction rate [22].

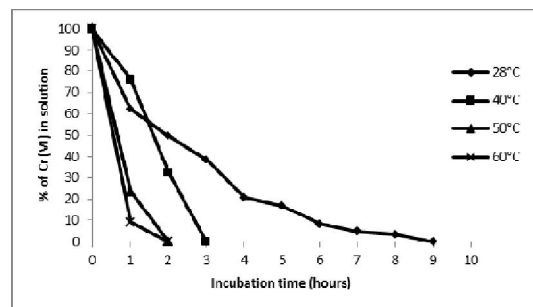
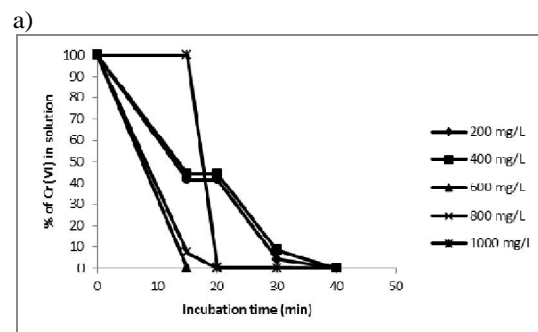


Fig. 2 Effect of temperature on Chromium (VI) removal by sawdust biomass. 50 mg/L Cr (VI), pH 1.0, 100 rpm.

VII. EFFECT OF INITIAL METAL CONCENTRATION

At all metal concentrations (200, 400, 600, 800, and 1000 mg/L) studied, the sawdust biomass, adsorbing 100% at 40 minutes at 60°C, while 800, and 1000 mg/mL of the metal are removed at 150 minutes and 28°C (Figures 3a, and 3b). In addition, we observed the development of a blue-green and a white precipitate, which changes more rapidly at higher temperatures (date not shown). The results are coincident for *C. reticulata* shell [20; 22]. With respect to other biomasses, most authors report lower removal efficiencies of metal, for example: 45 mg/L for eucalyptus bark [21], 13.4 and 17.2 mg/L for bagasse and sugar cane pulp, 29 mg/L coconut fibers, 8.66 mg/L for wool [9], 25 and 250 mg/L of chitin and chitosan [27], and 1.0 mg/L for cellulose acetate [28]. The increase in initial concentration of Cr (VI), results in the increased uptake capacity and decreased in the percentage of removal of Cr (VI). This was due to the increase in the number of ions competing for the available functional groups on the surface of biomass [22].



b)

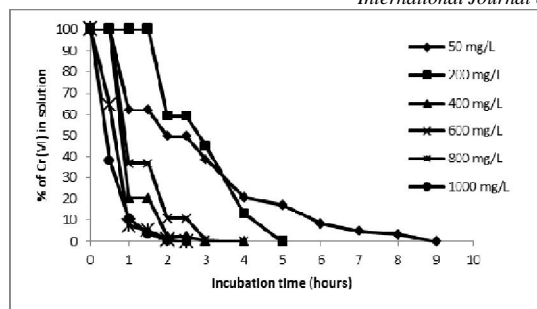


Fig. 3 Effect of initial metal concentration on Chromium (VI) removal by sawdust biomass. pH 1.0, 100 rpm. a) 60°C, b) 28°C.

VIII. EFFECT OF BIOSORBENT DOSE

The influence of biomass on the removal capacity of Cr (VI) is depicted in Figure 4. If we increase the amount of biomass so increases the removal of Cr (VI) in solution (100% of removal, with 5 g of biomass at 60 min, with more biosorption sites of the same, because the amount of added biosorbent determines the number of binding sites available for metal biosorption [29]. Similar results have been reported for modified corn stalks [30], *C. reticulata* shell [20], and *Mucor hiemalis* and *Rhizopus nigricans*, although latter with 10 g of biomass [31; 1], but they are different from those reported for biomass wastes from the mandarin (gabasse), with an optimal concentration of biomass of 100 mg/L [24].

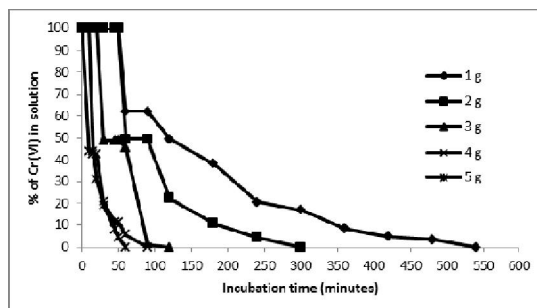


Fig. 4 Effect of biomass concentration on the removal of 50 mg/L Cr (VI). (28°C, pH= 1.0, 100 rpm).

IX. TIME COURSE OF CR (VI) DECREASE AND CR (III) PRODUCTION

The ability of the sawdust biomass to diminish the initial Cr (VI) of 1.0 g/L and Cr (III) production in solution was analyzed. Figure 5 shows that the biomass exhibited a remarkable efficiency to diminish Cr (VI) level with the concomitant production of Cr (III) in the solution (indicated by the formation of a blue-green color and a white precipitate, and his determination for Cromazurol S, date not shown) [18]. Thus, after 1 hour of incubation, the sawdust biomass caused a drop in Cr (VI) from its initial concentration of 1.0 g/L to almost undetectable levels, and the decrease level occurred without change significant in total Chromium content. As expected, total Chromium concentration remained constant over time, in solution control. These observations indicate that sawdust biomass is able to reduce Cr (VI) to Cr (III) in solution. In the literature,

exist other studies about different sawdust, and they report the reduction of Cr (VI) to Cr (III): with *Quercus crassipes shell* [32], with pepper tree bark [33]. [34] reported that Cr (VI) taken from the fine lateral roots of wetland plants was rapidly reduced to Cr (III). [35] reported that Cr (VI) could be bound to an oat by product, but easily reduced to Cr(III) by positively charged functional groups, and subsequently adsorbed by available carboxyl groups. For the reduction of Cr (VI) to Cr (III), not only protons, but also electrons are required. The electrons required for the reduction of Cr (VI) were possibly supply from the biomass, resulting in the oxidation of the organic compounds of the biomass, resulting in the partial release of soluble organics [7].

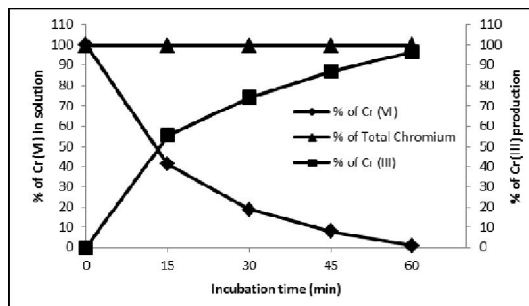


Fig. 5 Time-course of Cr (VI) decrease and Cr (III) production in solution with 1.0 g/L Cr (VI). 100 rpm, 28°C, pH 1.0.

X. REMOVAL OF CR (VI) IN INDUSTRIAL WASTES WITH SAWDUST OF PINE TREE

We adapted a water-phase biorremediation assay to explore possible usefulness of sawdust of pine tree for eliminating Cr (VI) from industrial wastes, the biomass was incubate with non-sterilized contaminated soil and water containing 297 mg Cr(VI)/g, and 155 mg Cr(VI)/L, suspended in trideionized water. It was observe that after six days of incubation with the biomass, the Cr (VI) concentration of soil sample decrease 57.25%, and 72%, respectively, (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 soil samples decreased by about of 18% (date not shown); this might be caused by indigenous microflora and (or) reducing components present in the soil.

The chromium removal abilities of sawdust of pine tree, are equal or better than those of other reported biomass, for example Citrus reticulata shell [20], *Mammea Americana* [36], and *Candida maltose* RR1, [37]. In particular, this biomass was superior to the other biomass because it has the capacity for efficient chromium reduction under acidic conditions. Many of the Cr (VI) reduction studies were carry out at neutral pH [38]. *Aspergillus niger* also has the ability to reduce and adsorb Cr (VI) [38]. When the initial concentration of Cr (VI) was 500 ppm, *A. niger* mycelium removed 8.9 mg of chromium/g dry weight of mycelium in 7 days.

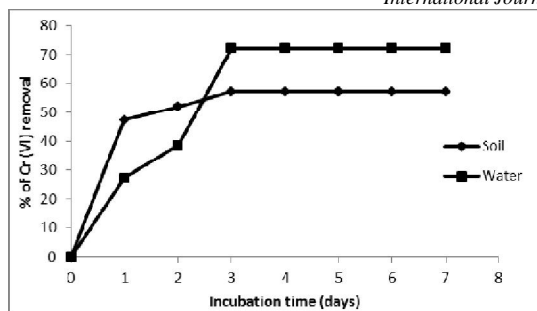


Fig. 6 Removal of Cr (VI) in industrial wastes incubated with 5 g of sawdust. 100 rpm, 28 °C. 20 g and 100 mL of contaminated soil water, (297 mg Cr (VI)/g soil, and 155 mg Cr (VI)/L)

XI. DESORPTION OF CHROMIUM (VI) BY DIFFERENT SOLUTIONS

Furthermore, we examined the ability of different solutions to desorb the metal biosorbed (250 mg/L) for the sawdust biomass, obtaining high efficiency with 0.1 N NaOH and 0.5 N (81% and 63%, respectively), which are less than reported for desorption of Chromium (VI) with alkaline solutions (100%, pH = 9.5), 1.0 N NaOH (95%) and a hot solution of NaOH/Na₂CO₃(90%), respectively, [39; 40], and are higher than reported (14.2%) using 0.2 M NaOH [Wang et. al., (2009)]. This indicates that binding of metal to biomass is not as strong and that it can be used up to 6-desorption cycles of removal, which further lowers the metal removal process of niches contaminated with it.

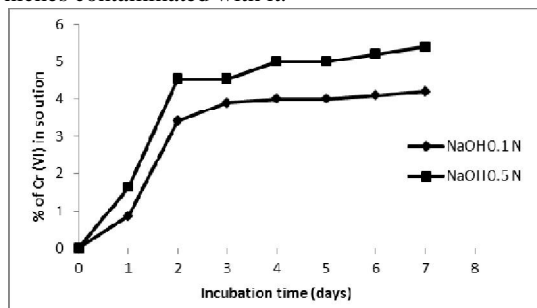


Fig. 7 Desorption of Chromium (VI) (250 mg/L) by different solutions (1 g of biomass. 28°C, 100 rpm).

XII. CONCLUSIONS

The sawdust of pine trees showed complete capacity of biosorption of 1.0 g/L Cr (VI) in solution after 150 minutes of incubation at 28°C, 100 rpm with 1 g of biomass, besides it removes the metal in situ (57.25%, and 72% removal, 7 days of incubation, 5 g of biomass), in earth and water contaminated, respectively. These results suggest the potential applicability of sawdust biomass for the remediation of Cr (VI) from polluted soils in the fields.

REFERENCES

[1] Bai, R.S. and Abraham, T.E., "Biosorption of Chromium (VI) from Aqueous Solution by *Rhizopus nigricans*," *Bioresour. Technol.*, pp. 73-81, vol. 79(1), 2001.

[2] Smith, W. A., Apel, W.A., Petersen, J.N., and Peyton, B.M., "Effect of Carbon and Energy Source on Bacterial Chromate Reduction," *Bioremediation J.*, pp. 205-215, vol. 6(3), 2002.

[3] Seng, H. and Wang, Y. T., "Biological Reduction of Chromium by *E. coli*," *J. Environ. Engin.*, pp. 560-572, vol. 120 (3), 1994.

[4] Marsh, T.L. and McInerney, M.J., "Relationship of Hydrogen Bioavailability to Chromate Reduction in Aquifer Sediments," *Appl. Environ. Microbiol.*, pp. 1517-1521, vol. 67(4), 2001.

[5] Beszedits, S., "Chromium Removal from Industrial Waste-waters," In: J. O. Nriagu and E. Nieboer, Eds., *Chromium in the Natural and Human Environments*, John Wiley, New York, pp. 232-263, 1988.

[6] Lofroth, G. and Ames, B.N., "Mutagenicity of Inorganic Compounds in *Salmonella typhimurium*: Arsenic, Chromium and Selenium," *Mutat. Res.*, pp. 65-66, vol. 53(1), 1978.

[7] Park, D., Yun, Y.S., Cho, H.Y. and Park, J.M., "Chromium Biosorption by Thermally Treated Biomass of the Brown Seaweed *Ecklonia* sp.," *Ind. Eng. Chem. Res.*, pp. 8226-8232, vol. 43(26), 2004.

[8] Sahin, Y. and Öztürk, A., "Biosorption of Chromium (VI) Ions from Aqueous Solution by the Bacterium *Bacillus thuriensis*," *Process Biochem.*, pp. 1895-1901, vol. 40(5), 2005.

[9] Dakiky, M., M. Khamis, M., Manassra, A. and Mereb, M., "Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents," *Adv. Environ. Res.*, pp. 533-540, vol. 6, 2002.

[10] Hamadi, N.K., Chen, X.D., Farid, M.M. and Lu, M.G.Q., "Adsorption kinetics for the removal of chromium (VI) from aqueous solution by adsorbents derived from used tires and sawdust," *Chem. Eng. J.*, pp. 95-105, vol. 84, 2001.

[11] Kratochvil, D., Pimentel, P., and Volesky, B., "Removal of trivalent and hexavalent chromium by seaweed biosorbent," *Environ. Sci. Technol.*, pp. 2693-2698, vol. 32, 1998.

[12] Park, D., Yun, Y.S., Jo, J.H., and Park, J.M., "Mechanism of hexavalent chromium removal by dead fungal biomass of *Aspergillus niger*," *Water Res.*, pp. 533-540, vol. 39, 2005.

[13] Gupta, V.K., Srivastava, A.K. and Jain, N., "Biosorption of chromium (VI) from aqueous solutions by green algae *Spirogyra* species," *Water Res.*, pp. 4079-4085, vol. 35, 2001.

[14] Yu, L.J., Shukla, S.S., Kenneth, L.D., Shukla, A., J.L. Margrave, J.L., "Adsorption of chromium from aqueous solutions by maple sawdust," *J. Hazard. Mat.*, pp. 53-63, vol. 53, 2004.

[15] Gupta, V.K., and Ali, I., "Removal of lead and chromium from wastewater using bagasse fly ash-a sugar industry waste," *J. Colloid Inter. Sci.*, pp. 321-328, vol. 271, 2004.

[16] Kumar, R., Bishnoi, N.R. and Bishnoi, G.K., "Biosorption of chromium (VI) from aqueous solution and electroplating wastewater using fungal biomass," *Chem. Eng. J.*, pp. 202-208, vol. 135, 2008.

[17] Greenberg, A.E., L. Clesceri, L.S. and Eaton, A.D., "Standard Methods for the Examination of Water and Wastewater," American Public Health Association, Washington, DC, USA, 18th edition, 1992.

[18] Pantaler, R.P. and Pulyaeva, I.V., "A spectrophotometric study of complexation between chromium and chromazurol S," *J. Anal. Chem. (Moscow)*, pp. 1634-1639, vol. 40, 1985.

[19] Pérez-Marín, A.B., Meseguer, V., Zapata, J.F., Ortuño, M., Aguilar, J., Sáez S., and Lloréns, M., "Removal of cadmium from aqueous solutions by adsorption onto orange waste," *J. Hazard. Mat.*, pp. 122-131, vol. 139, 2007.

[20] Acosta-Rodríguez, I., Coronado-Quintero, E., Cárdenas-González, J.F., Tovar-Oviedo, J. and Martínez-Juárez, V.M., "Hexavalent chromium removal by *Citrus reticulata* shell," *J. Natural Sci.*, pp. 29-39, vol. 1(1), 2013.

[21] Sarin, V. and Pant, K.K., "Removal of chromium from industrial waste by using eucalyptus bark," *Bioresour. Technol.*, pp. 15-20, vol. 97, 2006.

[22] Agarwal, G.S., Kumar, H., and Chaudari, S., "Biosorption of aqueous chromium (VI) by *Tamarindus indica* seeds," *Bioresour. Technol.*, pp. 949-956, vol. 97, 2006.

[23] Leyva-Ramos, R., Bernal-Jacome, L.A., and Acosta-Rodríguez, I., "Adsorption of cadmium (II) from aqueous solution on natural and oxidized corncob," *Separat. Purific. Technol.*, pp. 41-49, vol. 45, 2005.

- [24] Zubair, A., Bhatti, H.N., Hanif, M.A., and Shafqat, F., "Kinetic and equilibrium modeling for Cr (III) and Cr (VI) removal from aqueous solutions by *Citrus reticulata* waste biomass," Water Air Soil Pollut., pp. 305-318, vol. 191, 2008.
- [25] Jnr, M.H. and Spiff, A.I., "Effects of temperature on the sorption of Pb^{2+} and Cd^{2+} from aqueous solution by *Caladium bicolor* (wild cocoyam) biomass," Electron. J. Biotechnol., pp. 162-169, vol. 8(2), 2005.
- [26] Ozer, A. and Ozer, D., "Comparative study of the biosorption of Pb (II), Ni (II) and Cr (VI) ions onto *Saccharomyces cerevisiae*: Determination of biosorption heats," J. Hazard. Mater., pp. 219-229, vol. 100, 2003.
- [27] Sag, Y. and Aktay, Y., "Kinetic studies on sorption of Cr (VI) and Cu (II) ions by chitin, chitosan and *Rhizopus arrhizus*," Biochem. Engin. J., pp. 143-153, vol. 12, 2002.
- [28] Arthanareeswaran, G., Thanikaivelan, P., Jaya, N., Mohan, D., and Raajenthiren, M., "Removal of chromium from aqueous solution using cellulose acetate and sulfonated poly (ether ketone) blend ultrafiltration membranes," Biochem. Engin. J., pp. 43-153, vol. 12, 2002.
- [29] Cervantes, C., Campos-García, J., Devars, S., Gutiérrez-Corona, F., Loza-Tavera, H., Torres-Guzmán, J.C., and Moreno-Sánchez, R., "Interactions of chromium with microorganisms and plants," FEMS Microbiol. Rev. pp. 335-347, vol. 25, 2001.
- [30] Chen, S., Yue, Q., Gao, B., Li, Q., and Xu, X., "Removal of Cr (VI) from aqueous solution using modified corn stalks: Characteristic, equilibrium, kinetic and thermodynamic study," Chem. Engin. J., pp. 909-917, vol. 98, 2011.
- [31] Tewari, N., Vasudevan, P., and Guha, B., "Study on biosorption of Cr (VI) by *Mucor hiemalis*," Biochem. Engin. J., pp. 185-192, vol. 23, 2005.
- [32] Aranda García, E., "Biosorción de cromo y níquel por la cascara de la bellota de Encino *Quercus crassipes*," Humb&Bonpl. Tesis de Maestría en Ciencias Químico Biológicas. Escuela nacional de Ciencias Biológicas. IPN. México. 2010.
- [33] Netzahuatl-Muñoz, A. R., Cristiani-Urbina, M.C. and Cristiani-Urbina, E., "Estudio cinético de la remoción de cromo hexavalente y de cromo total por la corteza del árbol de pirul," Revista Cubana de Química, pp. 3-8, vol. 22(3), 2010.
- [34] Lytle, C. M., Lytle, F. W., Yang, N., Qian, J. H., Hansen, D., Zayed, A., Terry, N., "Reduction of Cr (VI) to Cr (III) by wetland plants: potential for in situ heavy metal detoxification," Environ. Sci. Technol., pp. 3087-3093, vol. 32, 1998.
- [35] Gardea-Torresdey, J. L., Tiemann, K. J., Armendariz, V., Bess-Oberto, L., Chianelli, R. R., Rios, J., Parsons, J. G., Gamez, G., "Characterization of Cr (VI) binding and reduction to Cr (III) by the agricultural by products of *Avena monida* (oat) biomass," J. Hazard. Mater., pp. 175-188, vol. 80, 2000.
- [36] Acosta, I., Sandoval, P., Bautista, D., Hernández, N., Cárdenas, J.F. y Martínez, V.M., "Bioadsorción de Cromo (VI) por la cáscara de Mamey (*Mammea americana L.*)," Avances en Ciencias e Ingeniería, pp. 1-9, vol. 3(2), 2012.
- [37] Ramírez-Ramírez, R., Calvo-Méndez, C., Avila-Rodríguez, M., Lappe, P., Ulloa, M., Vázquez-Juárez, R., and Gutiérrez-Corona, J.F., "Cr (VI) reduction in a Chromate-resistant strain of *Candida maltose* isolated from the leather industry," Antonie van Leeuwenhoek, pp. 63-68, vol. 85, 2004.
- [38] Fukuda, T., Ishino, Y., Ogawa, A., Tsutsumi, K., and Morita, H., "Cr (VI) reduction from contaminated soils by *Aspergillus* sp. N2 and *Penicillium* sp. N3 isolated from chromium deposits," J. Gener. Appl. Microbiol., pp. 295-303, vol. 54, 2008.
- [39] Singh, K.K., Hasan, S.H., Talat, M., Singh, V.K., and Gangwar, S.K., "Removal of Cr (VI) from aqueous solutions using wheat bran," Chem. Engin. J., pp. 113-121, vol. 151, 2009.
- [40] Gupta, S. and Babu, B.V., "Removal of toxic metal Cr (VI) from aqueous solutions using sawdust as adsorbent: Equilibrium, kinetics and regeneration studies," Chem. Engin. J., pp. 352-365, vol. 150, 2009.
- [41] Wang, X.S., Tang, Y.P. and Tao, S.R., "Kinetics, equilibrium and thermodynamic study on removal of Cr (VI) from aqueous solutions