

Optimization of operating parameters affecting the removal of chromium from aqueous solution using bio absorption Jujube fruit powder, Jujube fruit charcoal and compression with Granular Activated Carbon (GAC)

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Abstract

Introduction: Heavy metals in water resource are one of the most important environmental problems of countries. Chromium is considered as one of the important environmental pollutants due to its toxicity considered as water contaminant that may disturb metabolic activity. This research aims to study the potential of Jujube fruit powder for low cost adsorption of Cr (VI) in compression with Granular Activated Carbon (GAC).

Methods and Materials: In the present study, adsorption of dissolved Chromium (VI) onto Jujube fruit powder Jujube fruit charcoal and standard granular activated carbon (GAC) has been investigated and compared. The effect of contact time, pH value, initial concentration of dissolved Chromium and amount of adsorbent on the adsorption of Cr by the mentioned adsorbents was investigated.

Results: Results showed that the adsorption process was highly dependent on pH. Maximum Cr removal was achieved when the pH of the mixture fell within 2. The amounts of Cr (VI) adsorbed increased with the increase in dose of three adsorbents. Adsorption test results revealed that Cr adsorption on the studied adsorbents could be better described by Longmuir isotherm.

Conclusions: Maximum Cr removal efficiencies were obtained by Jujube fruit powder, Jujube fruit charcoal and GAC 66, 35 and 62 mg/g. Experimental results show low cost biosorbent was effective for the removal of hexavalent Chromium from aqueous solution.

Keywords: Adsorption, Chromium Removal (VI), Jujube fruit powder, Jujube fruit charcoal, Granular Activated Carbon.

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Introduction

Heavy metals are major pollutants of environment in most parts of the world that may be generated during industrialization processes. The use of metals and chemicals in process industries has resulted in the generation of large quantities of effluent that contain high levels of toxic heavy metals. It is well known that the presence of heavy metals such as cadmium, chromium, copper, nickel and manganese have harmful effects on human physiology and other biological systems because of their bioaccumulation, non-biodegradable properties and toxicities, even at low concentrations. Among the different heavy metals, chromium is a common and very toxic pollutant introduced into natural waters from a variety of industrial wastewaters [1]. Thus, the removal of heavy metals, such as hexavalent chromium from water has attracted considerable attention. Chromium exists in either +3 or +6 oxidation states, as all other oxidation states are not stable in aqueous systems. Chromium (VI) is 100-1000 times more toxic to organisms than Cr (III) and more readily transported in soils [2]. Chromium (VI) is carcinogenic to both humans and animals [3]. Strong exposure of chromium (VI) causes cancer in the digestive tract and lungs and may cause gastric pain, nausea, vomiting, severe diarrhea, and hemorrhage [4, 5, 6]. Cr (III) is essential for human nutrition (especially in glucose metabolism) and it is relatively innocuous and immobile. Cr (VI) is widely used in manufacturing and processing plants, the main industrial sources of Chromium pollution is tanneries, electroplating, metal processing, wood preservatives, paint and pigments, textile, dyeing, steel fabrication, canning industry and so on [7, 8]. According to the United States Environmental Protection Agency (USEPA) the maximum permissible limits in wastewater and potable water is 1 mg/l

and 0.05 mg/l for chromium (VI) [9]. Several methods utilized to remove Cr(VI) from aqueous solutions/wastewater include: reduction followed by electrochemical precipitation, chemical precipitation, chemical oxidation– reduction, ultrafiltration, ion exchange, reverse osmosis, solvent extraction, electrodialysis, electrochemical, coagulation, evaporation and adsorption [7,10,11,12]. Most of these methods suffer from drawbacks such as high capital and operational costs and problems in the disposal of the residual metal sludges [7, 13]. Therefore, there is a need to search an effective low cost adsorbent for economical wastewater treatment. Among these methods adsorption is one of the most economically favorable, as well as being a technically easy method [14]. The high cost of activated carbon sometimes limits its applicability for heavy metal removal [15-17]. Therefore, the interest of researchers is increasing using alternative materials, which are quite low cost, easily available and extremely effective adsorbents. Many studies have been conducted on the agricultural wastes as cheap and environmentally friendly natural materials, as well as certain waste from agricultural operations that are available in large quantities [18- 23]. Considerable attention has been devoted to the study of removal of heavy metal ions from solution by adsorption using agricultural materials such as waste wool, nut wastes, tree bark, modified cotton, sawdust, sunflower, Almond and apricot shells, groundnut shell, corn cob powder, almond green hull, coir pith and peanut husks carbon [24-35]. In the present work, we describe the use of Jujube fruit powder, and Jujube fruit charcoal and compression with granular activated carbon (GAC). Bio adsorbent without activation has been used to remove hexavalent chromium from aqueous solution. The effects of

adsorbent dose, pH, contact time and initial metal ion concentration on the adsorption capacity were investigated. The equilibrium of adsorption was modeled by using the Langmuir and Freundlich isotherms.

Methods and Materials

This study is an experimental study that is performed in a batch system. Jujube fruits were collected from agricultural wastes as adsorbents (agricultural wastes of Birjand) and rinsed by distilled water to eliminate possible contamination of meat remaining on it. The fruits were oven dried at a temperature of 700 ° and burned for 1 hour and then was powdered porcelain mortar [36]. Powder particle size of 50 mesh sieve was used in all experimental procedures. Some of the drying oven and milled powders were used as the adsorbent. A granular activated carbon with quality laboratory (GAC) was purchased from Merck Germany Company. The stock solution was prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$) in de-ionized water. One mill molar of Cr (VI) stock solution was prepared by dissolving 0.1471 g of $K_2Cr_2O_7$ (from Merck) with 99% purity, by dissolving in distilled water was used. The pH of the solution was adjusted by using either 0.1N NaOH or 0.1N HNO_3 . The samples were agitated in a reciprocating shaker to reach equilibrium. Batch adsorption studies performed the effect of pH on adsorption of Cr (VI) onto the biosorbent and was investigated by varying the solution pH from 1.0 to 10.0, and adsorbent amount (0.3, 0.5, 1, 1.5, 2, 2.5 and 3 g/L), initial metal-ion concentration (0.1, 0.5, 1, 1.5, 2, 4 and 6 mg/L) and contact time (10, 30, 60, 90, 120, 150, 180, 210 and 240 min) to obtain the equilibrium data. All experiments were conducted with three

replications and the results average was reported. Cr (VI) concentrations in the solutions were determined by the standard colorimetric method with 1, 5-diphenylcarbazide in an acid medium [37]. Metal concentration in the solution was analyzed with 6405 UV-vis spectrophotometer in $\lambda=540$ nm and also the concentration of Cr (VI) ions were calculated from the change in metal concentration in the aqueous solution before and after equilibrium sorption by using the following equation:

$$q_e = \frac{[V(C_0 - C_e)]}{W} \quad (1)$$

Where q_e is adsorbed metal (mmol/g adsorbent) on the almond green hull, V is the solution

E volume (L), W is the amount of sorbent (g), and C_0 and C_e (mg/L) are the initial and equilibrium Cr (VI) concentrations of the solution, respectively. The Cr (VI) percent removal (%) was calculated using the following equation:

$$\text{Cr (VI) Removal (\%)} = \frac{[(C_0 - C_e) / C_0] \times 100}{100} \quad (2)$$

Adsorption Isotherms

Equilibrium data are usually described by various adsorption isotherms. Two isotherm equations were used in the present study, Langmuir and Freundlich.

The Langmuir equation is:

$$Q = \frac{(q_m \cdot k_1 \cdot c)}{1 + k_1 \cdot c} \quad (3)$$

$$C/Q = 1/(K_1 \cdot Q_m) + \left(\frac{c}{Q_m}\right) \quad (4)$$

The Freundlich equation is:

$$Q = K_f \cdot C^{1/n} \quad (5)$$

$$\log q \cdot \log Kf + \left(\frac{1}{n}\right) \cdot \log C$$

(6)

Where q_m is the amount of adsorbed material at equilibrium (mg/g), C is the equilibrium metal

Concentration of the adsorbate (mg/L), q_{max} (mg/g) and b (L/mg) are the Langmuir constants, and K and n are Freundlich constants [38, 39].

Results

Effect of contact time Fig. 1 shows the adsorption of Cr (VI) by Jujube fruit powder, Jujube fruit charcoal and activated carbon as a function of time. Effect of contact time on the removal efficiency in systems studied by varying the exposure time from 10 minutes to 240 minutes in pH = 3, amount of adsorbent 1.5g/l and the initial concentration of hexavalent chromium 1.5 mg/l were evaluated. Contact the optimum time to measure the Jujube fruit powder, Jujube fruit charcoal, and granular activated carbon (GAC), respectively, 180, 210 and 150 minutes. Fig. 1 shows rapid adsorption in the initial min for all adsorbent [40].

Effect of PH

The pH of the aqueous solution is an important controlling parameter in the adsorption process and anion adsorption is strongly pH-dependent. Different studies have shown that pH of solution is an important parameter influencing the biosorption of metal ions [16-20]. Fig. 2 shows the removal of Cr (VI) versus the pH at a constant Cr (VI) concentration of 1/5 mg/L, adsorbent concentration of 1/5 g/L, contact time of 210, 180 and 150 min. It was observed that the adsorption capacity of the

prepared adsorbent was highly dependent on the pH of the solution. As results show, the optimum initial pH was observed at pH 2.0. The results indicate that the adsorption capacity of the prepared adsorbent increases with decreasing the pH of the solution.

Effect of adsorbent dose

The effect of sorbent variation on the removal of Cr (VI) ion by Jujube fruit powder, Jujube fruit charcoal and granular activated carbon (GAC) is shown in Fig. 3. The effect of adsorbent dose on Cr (VI) uptake was investigated by varying the adsorbent dose (0.3, 0.5, 1, 1.5, 2, 2.5 and 3 g/l) for an optimum time for any adsorbent. Experimental results showed that the percentage removal Cr (VI) rises with the increasing amount of adsorbent up to 1.5 g/l for granular activated carbon (GAC), Jujube fruit powder, and 2.5 g/l for Jujube fruit charcoal. After this dose of adsorbent no significant change was observed but for bioadsorbent percentage removal Cr (VI) increases with the increasing amount of adsorbent.

Effect of initial Cr (VI) concentration

The effect of Cr (VI) concentration on the sorbent by varying the initial Cr (VI) concentration (0.1, 0.5, 1, 1.5, 2, 4 and 6 mg/L) for optimum value of time for any adsorbent interval is shown in Fig. 4. Experimental results showed that the percentage removal Cr (VI) decreases with the increasing of initial Cr (VI). In changing the initial concentration from 0.1 to 6 mg/l, the percentage removal decreased from 94 to 79 percentages for granular activated carbon, 89 to 77 percentages for Jujube fruit charcoal and 99 to 67 percentages for Jujube fruit powder.

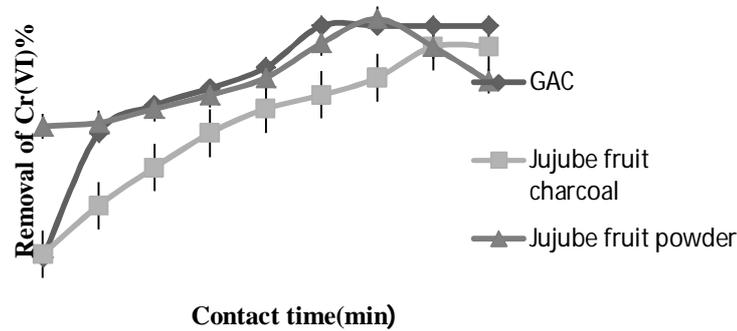


Figure 1: Effect of contact time on the removal of Cr (VI) (initial Cr (VI) concentration=1.5 mg/l, adsorbent dose =1.5g/l, pH = 3)

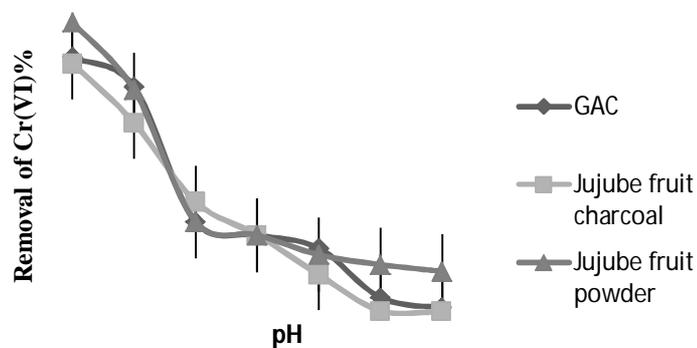


Figure 2: Effect of pH on the removal of Cr (VI) (initial Cr (VI) concentration=1.5 mg/l, adsorbent dose=1.5 g/l contact time= optimum contact time for any adsorbent)

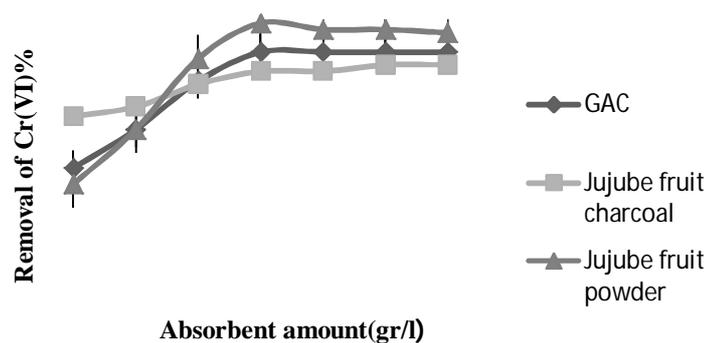


Figure 3: Effect of amount of adsorbent on the removal of Cr (VI) (initial Cr (VI) concentration=1.5 mg/l, contact time= optimum contact time for any adsorbent, pH = 2)

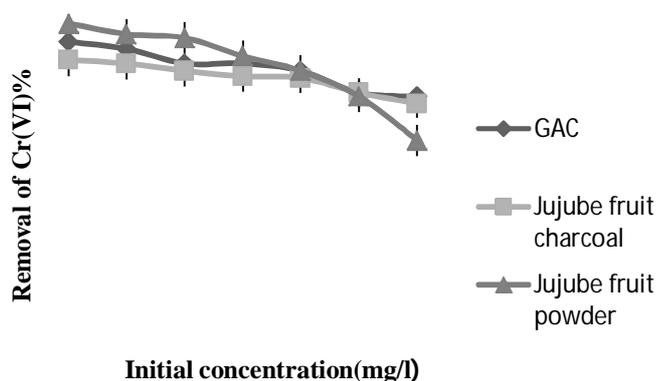


Figure 4. Effect of initial Cr (VI) concentration on the removal of Cr (VI) (adsorbent dose=1.5 g/l, pH = 2, contact time= optimum contact time for any adsorbent)

Discussion

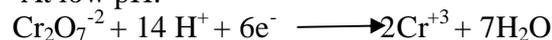
Effect of contact time Contact the optimum time to measure the Jujube fruit powder, Jujube fruit charcoal, and granular activated carbon (GAC), respectively, 180, 210 and 150 minutes. Fig. 1 shows rapid adsorption in the initial min for all adsorbent. The removal of Cr (VI) is rapid, but it gradually decreases with time until it reaches equilibrium. Further increase in contact time did not show an increase in biosorption. The fast adsorption at the initial stage was probably due to the initial concentration gradient between the adsorbate in solution and the number of vacant sites available on the adsorbent surface at the beginning [30,41].

Effect of pH

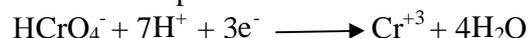
Chromium (VI) removal was investigated as a function of solution pH and the result is indicated in Fig. 2. It was observed that the adsorption capacity of the prepared adsorbent was highly dependent on the pH of the solution. As results show, the optimum initial pH was observed at pH 2.0. The results indicate that the adsorption capacity of the prepared adsorbent increases with decreasing the pH of the solution. The reduction of adsorption with the increase of pH may be ascribed to the decrease in electrostatic force of attraction between the

adsorbent and the sorbate ions. Cr (VI) ions mostly exist as $\text{H}_2\text{Cr}_2\text{O}_4$ form at high acidic medium (pH =1). At pH 2-6 there is equilibrium between $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- species, if the Cr (VI) concentration is less than 0.02 M, HCrO_4^- is predominant form, when Cr (VI) concentration is greater than 0.02 M the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) is the predominant species and under alkaline condition (pH>8) it exists as chromate CrO_4^{2-} anion [42]. The improved removal of Cr at low pH is probably due to reduction of hexavalent Cr to trivalent Cr.

At low pH:



At moderate pH:



At low pH, there is presence of a large number of H^+ ions, which in turn neutralizes the negatively charged adsorbent surface thereby reducing hindrance to diffusion of dichromate ion. It is anticipated that the effect of pH on adsorption is also governed by the development of an electrical double layer on the adsorbent. The polarity of the double layer at the adsorbent surface may be changed from positive to negative as the H^+ -ion concentration changes from acidic to basic with the increase of pH. It was found that at lower pH the system attained

equilibrium faster and the percentage of chromium adsorbed increased [8,12]. Similar results are also reported by other researchers for a variety of pH systems [30-33, 35].

Effect of adsorbent dose

Experimental results showed that the percentage removal Cr (VI) rises with the increasing amount of adsorbent up to 1.5 g/l for granular activated carbon (GAC), Jujube fruit powder, and 2.5 g/l for Jujube fruit charcoal. After this dose of adsorbent no significant change was observed but for bioadsorbent percentage removal Cr (VI) increases with the increasing amount of adsorbent. The phenomenon of an increase in percent chromium removal with increase in adsorbent dose is due to the availability of more and more adsorbent surfaces for the solutes to adsorb. Never the less, very slow increase in removal beyond an optimum dose may be attributed to the attainment of equilibrium between adsorbate and adsorbent at the operating conditions [33]. The results showed that the removal will be effective until the following optimum increases and the effective absorption are minimal. Similar results are also reported by some researchers for a variety of adsorbate-adsorbent systems [18, 30, 32, 35].

Effect of initial Cr (VI) concentration

The percentage removal was decreased with the increase in Cr (VI) concentration. At low concentrations the ratio of available surface to the initial Cr (VI) concentration is larger, so the removal becomes independent of

initial concentrations. However, in the case of higher concentrations this ratio is low; the percentage removal then depends on the initial concentration. The results indicate that within a certain range of initial metal concentration, the percentage of metal adsorption on adsorbent is determined by the sorption capacity of the adsorbent [35]. Similar results are also reported by researchers for a variety of adsorbate-adsorbent systems [10,16,43].

Equilibrium adsorption isotherms

Several models had been used in literatures to describe the experimental data of adsorption isotherms. The Langmuir [38] and Freundlich [39] models are the most frequently employed models that also were used in this study. Langmuir isotherm is based on the monolayer adsorption of chromium ions on the surface of adsorbent sites [10]. Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption sites. Equilibrium data obtained were fitted to the Langmuir and Freundlich isotherms. The following expressions of straight line were found by means of mathematical transformation of isotherms equation. The estimated model parameters with correlation coefficient (R^2) for the two models are shown in fig 5 to fig 10. It was observed that results fitted better in the Langmuir model in terms of R^2 value, recording 0.9984 for granular activated carbon, 0.9949 for Jujube fruit charcoal and 0.9988 for Jujube fruit powder.

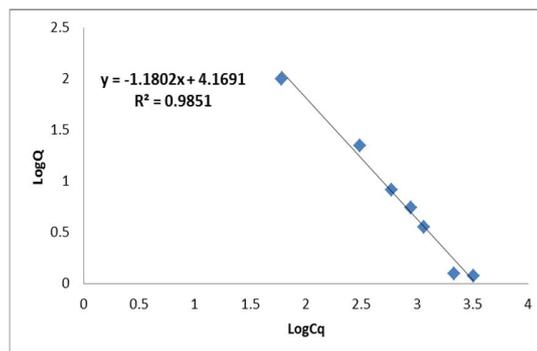
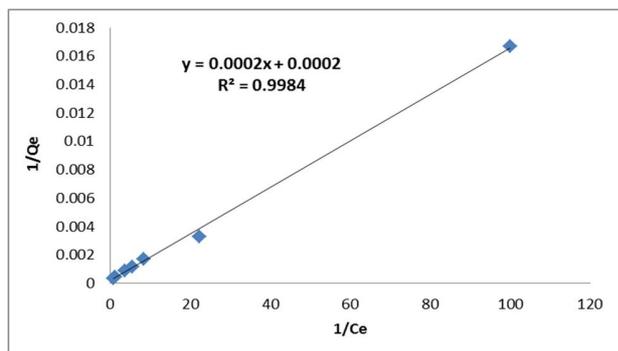


Figure5: Langmuir isotherm for Adsorption Cr by GAC

Figure6: Freundlich isotherm for Adsorption Cr by GAC

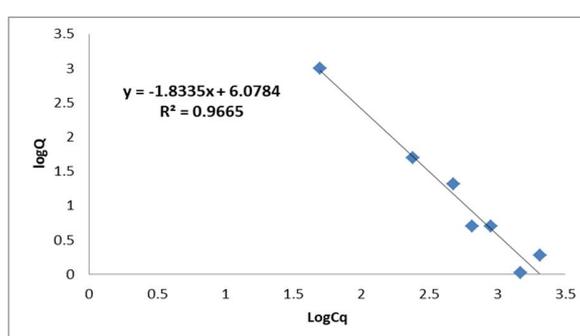
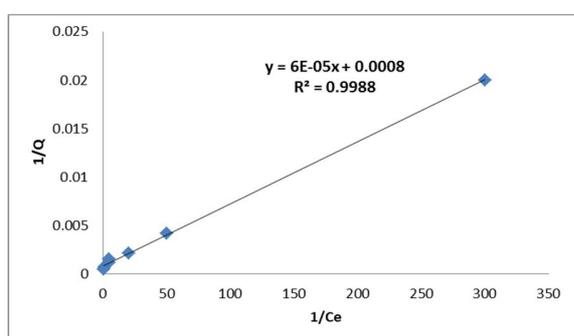


Figure7: Langmuir isotherm for Adsorption Cr by Jujube Fruit powder

Figure8: Freundlich isotherm for Adsorption Cr by Jujube fruit powder

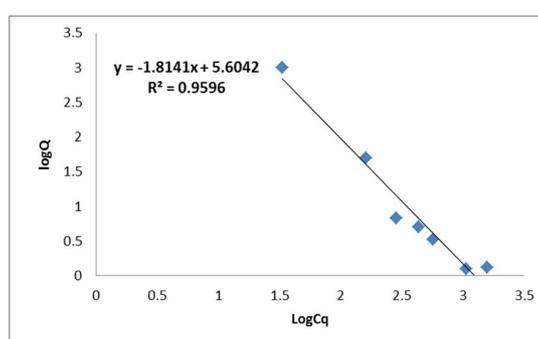
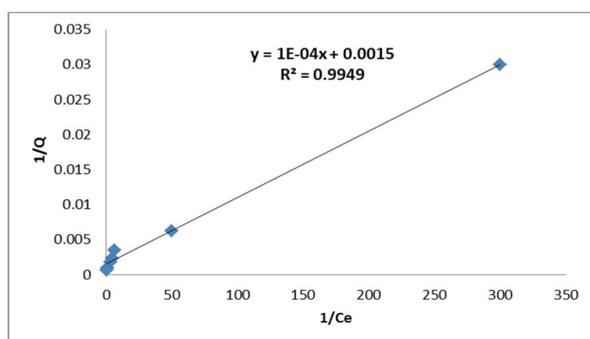


Figure9: Langmuir isotherm for Adsorption Cr by Jujube Fruit charcoal

Figure10: Freundlich isotherm for Adsorption Cr by Jujube fruit charcoal

Conclusions

The biosorbent evaluated can remove hexavalent chromium from aqueous solution. The adsorption process is a function of the contact time, initial concentration, pH and adsorbent dose. The amounts of Cr (VI) adsorbed increased with increase in dose of three adsorbents and their contact time. The contact time of 150

min for GAC, 180 min for Jujube fruit powder and 210 min for Jujube fruit charcoal was found to be optimum. Adsorption of Cr (VI) is found to be effective in the lower pH and found to be maximum at pH 2.0. Removal of Cr (VI) rised as adsorbent dose increased. The Langmuir isotherm was fitted better than the

Freundlich isotherms. Maximum Cr removal efficiencies were obtained by Jujube fruit powder, Jujube fruit charcoal and GAC 66, 35 and 62 mg/g. Jujube fruit powder and Jujube fruit charcoal is a low-cost and efficient biosorbent for the removal of Cr (VI) from aqueous solution and it will be an alternative to more costly adsorbents such as granular activated carbon.

References

- 1-Donmez G, Aksu Z. Removal of chromium (VI) from saline wastewaters by *Dunaliella* species. *Process Biochem* 2002;38 (5):751–62.
- 2-Low KS, Lee CK, Ng AY. Column study on the sorption of Cr (VI) using quaternized rice hulls. *Bioresour Technol* 1999;68:205-8.
- 3-Mungasavalli DP, Viraraghavan T, Jin YC. Biosorption of chromium from aqueous solutions by pretreated *Aspergillus niger*. *Colloid Surface A* 2007; 301(3):214-23.
- 4-Mohanty K, Jha M, Biswas MN, Meikap BC, Biswas MN. Removal of chromium (VI) from dilute aqueous solutions by activated carbon developed from *Terminalia arjuna* nuts activated with zinc chloride. *Chem Eng Sci* 2005; 60(11):3049-59.
- 5-El-Sikaily A, El Nemr A, Khaled A, Abdelwehab O. Removal of toxic chromium from wastewater using green alga *Ulva lactuca* and its activated carbon. *J Hazard Mater* 2007; 148(1-2):216-28.
- 6-Li H, Li Z, Liu T, Xiao X, Peng Z, Deng L. A novel technology for biosorption and recovery hexavalent chromium in wastewater by bio-functional magnetic beads. *Bioresour Technol* 2008; 99(14):6271–9.
- 7-Demirbas E, Kobya M, Konukman AE. Error analysis of equilibrium studies for the almond shell activated carbon adsorption of Cr (VI) from aqueous solutions. *J Hazard Mater* 2008; 154(1-3):787–94.
- 8-Moussavi G, Barikbin B. Biosorption of chromium (VI) from industrial wastewater onto pistachio hull waste biomass. *Chem Eng* 2010; 162(3):893–900.
- 9-Park D, Yun YS, Park JM. Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia* sp. *Chemosphere* 2005;60(10):1356-64.
- 10-Aliabadi M, Morshedzadeh K, Soheyli H. Removal of hexavalent chromium from aqueous solution by lignocellulosic solid wastes. *Int J Environ Sci Te* 2006;3:321-5.
- 11-Raji C, Anirudhan TS. Batch Cr (VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics. *Water Res* 1998; 32(12):3772–80.
- 12-Ahmadpour A, Tahmasbi M, Rohani Bastami T, Besharati JA. Rapid removal of cobalt ion from aqueous solutions by almond green hull. *J Hazard Mater* 2009;166(2-3):925–30.
- 13-Gupta VK, Rastogi A, Nayak A. Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material. *J Colloid Interface Sci* 2010; 342(1):135–41.
- 14-Chen JP, Wang XY. Removing copper, zinc, and lead ion by granular activated carbon in pretreated fixed-bed columns. *Sep Purif Technol* 2000;19(3):157–67.
- 15-Mohan D, Pittman CU Jr. Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. *J Hazard Mater* 2006;137(2):762–811.
- 16-Bansal M, Singh D, Garg VK. A comparative study for the removal of hexavalent chromium from aqueous solution by agriculture wastes' carbons. *J Hazard Mater* 2009; 171(1-3):83–92.
- 17-Wahab MA, Jellali S, Jedidi N. Ammonium biosorption onto sawdust: FTIR analysis, kinetics and adsorption isotherms modeling. *Bioresour Technol* 2010;101(14):5070–5.
- 18-Jain M, Garg VK, Kadirvelu K. Equilibrium and kinetic studies for sequestration of Cr (VI) from simulated wastewater using sunflower waste biomass. *J Hazard Mater* 2009; 171(1-3):328–34.
- 19- Levankumar L, Muthukumaran V, Gobinath MB. Batch adsorption and kinetics of chromium (VI) removal from aqueous solutions by *Ocimum americanum* L. seed pods. *J Hazard Mater* 2009;161(2-3):709–13.
- 20-Gonzalez MH, Araújo GC, Pelizaro CB, Menezes EA, Lemos SG, de Sousa GB. et al. Coconut coir as biosorbent for Cr(VI) removal from laboratory wastewater. *J Hazard Mater* 2008;159(2-3):252–6.
- 21-Elangovan R, Philip L, Chandraraj K. Biosorption of hexavalent and trivalent chromium by palm flower (*Borassus aethiopicum*). *Chem Eng* 2008;141(1-3):99–111.
- 22-Basha S, Murthy ZVP, Jha B. Biosorption of hexavalent chromium by chemically modified seaweed, *Cystoseira indica*. *Chem Eng* 2008;137(3):480–8.
- 23-Gao H, Liu Y, Zeng G, Xu W, Li T, Xia W. Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste--rice straw. *J Hazard Mater* 2008;150(2):446–52.

- 24-Kadirvelu K, Thamaraiselvi K, Namasivayam C. Adsorption of nickel (II) from aqueous solution onto activated carbon prepared from coirpith. *Sep Purif Technol* 2001;24(3):497-505.
- 25-Ricordel S, Taha S, Cisse I, Dorange G. Heavy metals removal by adsorption onto peanut husks carbon: characterization, kinetic study and modeling. *Sep Purif Technol* 2001;24(4):389-401.
- 26-Jeme EA. Controls of manganese, iron, cobalt, nickel, copper and zinc concentrations in soils and water. *Adv Chem Ser* 1968;7(1):33-7.
- 27-Thomas MJ, Theis TL. Effects of selected ions on the removal of chrome hydroxide. *Water Pollut* 1976;48(8):20-32.
- 28-Dean JG, Bosqui FL, Lanouette KL. Removing heavy metals from waste water. *Environ Sci Technol* 1972; 3(13):6-18.
- 29-Inove Y, Munemori M. Co-precipitation of Hg (II) with Fe (III) hydroxide. *Environ Sci Technol* 1968:34-43.
- 30-Jain M, Garg VK, Kadirvelu K. Chromium removal from aqueous system and industrial wastewater by agricultural wastes. *Biomed* 2013;17(1):30-9.
- 31-Sallau AB, Aliyu S, Ukuwa S. Biosorption of chromium(VI) from aqueous solution by corn cob powder. *Int J Environ Bioenergy* 2012;4(3):131-40.
- 32-Choundhury TR, Pathen KM, Amin MdN, Ali M, Quraishi SB, Mustafa AI. Adsorption of Cr (III) from aqueous solution by groundnut shell. *J Environ Sci Water Res* 2012;1(6):144-50.
- 33-Khazaei I, Aliabadi M, Mosavian HT. Use of agricultural waste for removal of Cr(VI) from aqueous solution. *Iran J Chem Eng* 2011;8(4):11-23.
- 34-Sahranavard M, Ahmadpour A, Doosti MR. Biosorption of hexavalent chromium ions from aqueous solutions using almond green hull as a low-cost biosorbent. *Eur J Sci Res* 2011;58(3):392-400.
- 35-Qaiser S, Saleemi AR, Umar M. Biosorption of lead (II) and chromium (VI) on groundnut hull: Equilibrium, kinetics and thermodynamics study, *Electronic. J BioTechnol* 2009;12(4):1-17
- 36-El-Hendway ANA, Samra SE, Girgis BS. Adsorption characteristics of activated carbons obtained from corncobs. *J Colloid Interface Sci* 2001;180(3):209-21.
- 37-Eaton AD, Clesceri LS, Greenberg AE. Standard methods for the examination of water and wastewater. Washington: American public health association; 1995. P. 225-7.
- 38-Langmuir I. The constitution and fundamental properties of solids and liquids. *JAm Chem Soc* 1916;38:2221-95
- 39-Freundlich H, Hatfield HS. *Colloid and Capillary Chemistry*. London: Methuen; 1926.
- 40-Ajmal M, Rao RA, Ahmad R, Ahmad J, Rao LA. Removal and recovery of heavy metals from electroplating wastewater by using kyanite as an adsorbent. *J Hazard Mater* 2001;87(1-3):127-37.
- 41-Gueu S, Yao B, Adouby K, Ado G. Kinetics and thermodynamics study of lead adsorption on to activated carbons from coconut and seed hull of the palm tree. *Int J Environ Sci Te* 2007;4(1):11-7.
- 42-Agrawal A, Pal C, Sahu KK. Extractive removal of chromium (VI) from industrial waste solution. *J Hazard Mater* 2008;159(2-3):458-64.
- 43-Wong SX, Li ZZ, Tao SR. Removal of chromium (VI) from aqueous solution using walnut hull. *J Environ Manage* 2009; 90(2):721-9.