European Journal of Scientific Research
ISSN 1450-216X Vol.58 No.3 (2011), pp.392-400

http://www.eurojournals.com/ejsr.htm

Biosorption of Hexavalent Chromium Ions from Aqueous Solutions using Almond Green Hull as a Low-Cost Biosorbent

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Abstract

Raw agricultural wastes are affordable adsorbents for the removal of heavy metals from aqueous solutions. In this research, the use of almond green hull (as an eco-friendly and low-cost adsorbent) with no treatment having the ability to remove toxic hexavalent chromium (Cr (VI)) from aqueous solutions has been investigated. The influences of several main parameters such as pH value of solution, sorbent amount, initial metal-ion concentration, and contact time in batch experiments have been studied. The results revealed that almond green hull adsorbs over 94.14% of Cr (VI) from solutions containing 10 mg/L of Cr(VI) at sorbent amount of 4 g/L and pH=6 after 30 min of equilibration at room temperature. High removal efficiency of Cr (VI) occurred in the first 5 min of sorbent contact time for concentration of 10 mg/L solution. Adsorption isotherms were compared with both Langmuir and Freundlich adsorption models. The experimental data best fit with the Langmuir isotherm model with R^2=0.9989. The present study revealed that such a low-cost material could be used as an efficient sorbent for the removal of Cr(VI) from aqueous solutions.

Keywords: Almond green hull, Sorbent, Low- Cost, Chromium, Water Pollution.

1. Introduction

Heavy metals are major pollutants of environment in most parts of the world that may be generated during industrialization processes. In the last few decades, industrialization in many regions has increased the discharge of heavy metals in the environment and aquatic ecosystems (Mahvi et al. 2005 and Pehlivan et al. 2008). Toxic metals can seriously affect plants and animals and have been involved in causing a large number of afflictions (Sayadi et al. 2009). Therefore, eliminating heavy metals from environment is one of the most important issues.

Chromium exists in natural water in two main oxidation states, hexavalent chromium (Cr (VI)), and trivalent chromium (Cr(III)). Cr (VI) is more hazardous, carcinogenic, and mutagenic to living organisms (Demirbas et al. 2008). Cr (VI) is included in the CERCLA priority list of hazardous substances because it is threatening both human and environment (Moussavi et al. 2010).

Cr(VI) is widely used in manufacturing and processing plants, the main industrial sources of chromium pollution are tanneries, electroplating, metal processing, wood preservatives, paint and pigments, textile, dyeing, steel fabrication, canning industry and so on (Demirbas et al. 2008 and Moussavi et al. 2010). The tolerance limits for Cr (VI) based on the US EPA are 0.05 and 0.1 mg/L in drinking water and inland surface waters, respectively (Wang et al. 2009).

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 (Moussavi et al. 2010, Raji et al. 1998 and Ahmadpour et al. 2009). Most of these methods suffer from drawbacks such as high capital and operational costs and problems in the disposal of the residual metal sludges (Demirbas et al. 2008 and Gupta et al. 2010). The high cost of activated carbon sometimes limits its applicability for heavy metal removal (Dinesh 2006, Bansal et al. 2009 and Wahab et al. 2009). 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 (Jain et al. 2010, Levankumar et al. 2009, Gonzalez et al. 2008, Elangovan et al. 2008, Basha et al. 2008, Gao et al. 2008, Malkoc et al. 2007, Dakiky et al. 2002, Sharma 1994, Soner Altundogan et al. 2007, Kapoor et al. 1989, Selvi et al. 2001, Alaerts et al. 1989, Mohanty et al. 2005, Agarwal et al. 2006 and Basri Senturk et al. 2010).

Almond green hull as agricultural wastes is widely available and free of cost in most parts of Iran. In the present study, the locally available almond green hull without activation has been used to remove Cr(VI) from aqueous solutions. The equilibrium isotherm data were treated with two adsorption isotherm models, Langmuir and Freundlich, by utilizing both linear and non-linear optimization techniques.

2. Material and Methods

2.1. Preparation of Adsorbent

Almond green hull was obtained from a local fruit field in the eastern part of Iran. The sorbent was washed thoroughly several times with deionized water to remove many adhering and was dried in an oven at 105^0C for 24 h. The material was sieved in the mineral processing laboratory to obtain the particle size under 400µm. The sorbent was stored in a glass bottle and used for experiments as needed.

2.2. Reagents and Solutions

All solutions were prepared from analytical grade chemicals. One millimolar of Cr (VI) stock solution was prepared by dissolving 0.1471 g of $K_2Cr_2O_7$ (from Merck) (Standard Methods for the Examination of Water and Wastewater 2005). Distilled water was thoroughly employed as solvent. pH of the solution was adjusted by using either 0.1N NaOH or 0.1N H_2SO_4.

2.3. Adsorption Procedure

Hundred milliliters of Cr (VI) solution of known concentration (Co) at the initial pH was taken in a 500 mL Pyrex glass flask with a fixed dosage (4 g/L) of sorbent. The mixture was agitated at a speed of 45 rpm in a shaker bath at room temperature for a specified amount of time which was sufficient for the chromium uptake process to reach equilibrium.

Batch adsorption studies were performed at different pH (2, 4, 6, 8, and10), sorbent amount (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 g/L), initial metal-ion concentration (10, and 50 mg/L) and contact time (1, 3, 5, 10, 20, and 30 min) to obtain the equilibrium data. All experiments were performed in triplicate 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 (Kazemipour et al. 2008). Metal concentration in the solution was analyzed with 6405 UV–vis spectrophotometer in λ=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:

$$q_e = [V(C_o – C_e)] / W \qquad (1)$$

Where qe is adsorbed metal (mmol/g adsorbent) on the almond green hull, V is the solution volume (L), W is the amount of sorbent (g), and C_o 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:

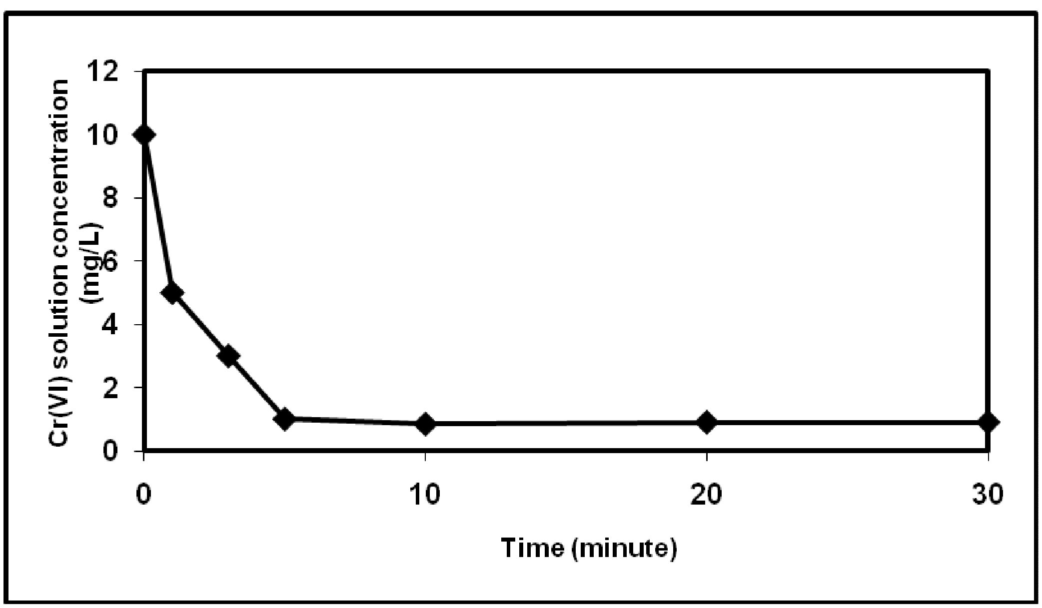
$$\text{Cr(VI) Removal}(\%) = [(C_o - C_e)\ C_o] / 100 \qquad (2)$$

3. Results and Discussion

3.1. The Effect of Contact Time

Fig. 1 illustrates the effect of contact time on adsorption efficiency of Cr (VI) for a fixed 4 g dose of adsorbent. The initial concentration was kept constant at 10 mg/L. The experimental data indicate that Cr (VI) ion adsorption increased by increasing time. This is due to higher contact between the sorbent surface and chromium ion. The results also indicate that there is not a significant difference among the amounts of Cr (VI) adsorbed after 5 minute from the start of reaction.

Figure 1: The effect of contact time on Cr (VI) removal (conditions: Cr (VI)=10 mg/L; pH=6; sorbent amount=4 g/L)

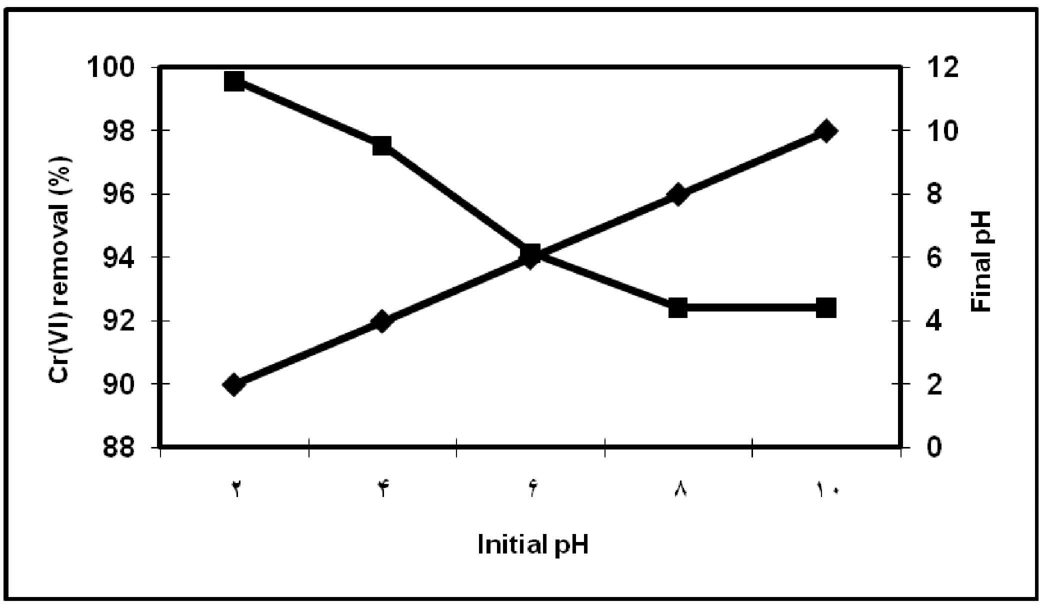


3.2. Effect of Initial pH on the Chromium (VI) Adsorption

Different studies have shown that pH of solution is an important parameter influencing the biosorption of metal ions. Fig. 2 shows the removal of Cr (VI) versus the pH at a constant Cr (VI) concentration of 10 mg/L, almond green hull concentration of 4 g/L, contact time of 30 min, and particle size of <400 µm. The final pH of solution at the end of each experiment was similar to that of initial value. The average Cr (VI) removal under selected conditions decreased from 99.6 to 92.4% when the pH of solution increased from 2 to 10.

The reduction of adsorption with the increase of pH may be ascribed to the decrease in electrostatic force of attraction between the sorbent and the sorbate ions. The raw almond green hull sample was analyzed using a Fourier transform infrared spectrometer (FTIR) and the result shows the presence of several functional groups (amine, carboxyl and hydroxyl groups) responsible for the binding of Cr (VI) onto the surface of this sorbent. These functional groups were positively charged when protonated and may electrostatically interact with the negatively charged metal complex. Similar results were obtained by many researchers (Pehlivan et al. 2008, Moussavi et al. 2010, Ahmadpour et al. 2009 and etc).

Figure 2: The effect of solution pH on Cr (VI) removal (conditions Cr (VI)=10 mg/L; sorbent amount = 4 g/L; and contact time= 3 min)

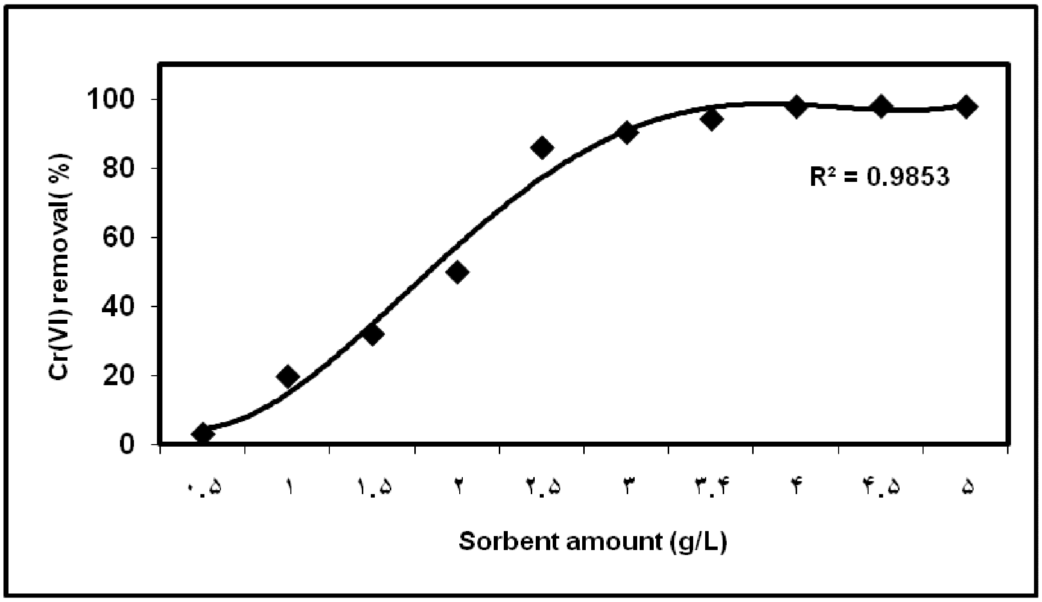


According to the previous studies and the results of present study, the maximum removal of Cr (VI) is obtained at pH=2, while pH= 6 was chosen in all other experiments for the following two reasons. The first reason was neutrality of solution at pH=6 that is considered as being more applicable. Secondly, adding acid to decrease pH of the solution produces sludge. This sludge should be removed due to the problems it may cause.

3.3. Effect of Sorbent Amount

The effect of sorbent variation on the removal of Cr(VI) ion by almond green hull is shown in Fig. 3. The amount of sorbent varied (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 g) and equilibrated for 30 min at an initial Cr (VI) ion concentration of 10 mg/L. It is apparent that the metal ion concentration in solution decreases with increasing sorbent amount up to 4 g for a given initial Cr (VI) concentration. Similar results are also reported by researchers for a variety of adsorbate–adsorbent systems (Pehlivan et al. 2008, Demirbas et al. 2008, Moussavi et al. 2010, Ahmadpoura et al. 2010, Tunali et al. 2005 and etc).

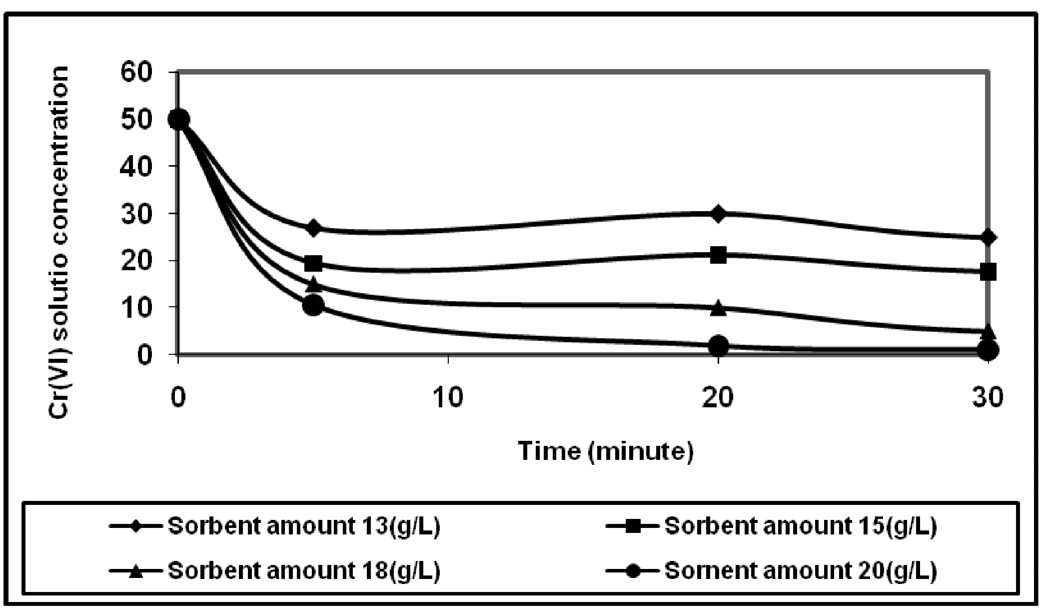
Figure 3: The effect of sorbent amount on Cr (VI) removal (conditions: Cr (VI)=10 mg/L; pH= 6; contact time=30 min)



3.4. Effect of Initial Cr (VI) Ion Concentration

The effect of initial Cr (VI) concentration on the sorption by almond green hull was investigated using concentration of 50 mg/L with different amounts of sorbent (13, 15, 18, and 20 g) at pH=6 after 40 min equilibrium and the result is shown in Fig. 4. The result reveals that the amount of Cr (VI) removal is highly affected by the sorbent amount. The Cr (VI) ion removal efficiency for almond green hull increased with increasing Cr (VI) ion concentration particularly at short time of 10 min, but the absolute amount of Cr (VI) adsorbed per unit weight of almond green hull was decreased. It could be related to higher initial concentrations and also the ratio of available adsorption sites to chromium molecules is less and binding sites can saturate more rapidly.

Figure 4: The effect of initial Cr (VI) concentration on Cr (VI) removal (conditions: Cr (VI) =50 mg/L; pH=6)



3.5. 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:

$$C_e/q_e = 1/(b\, q_{max}) + (C_e / q_{max}) \tag{3}$$

The Freundlich equation is:

$$\text{Log } q_e = \text{Log } K_f + (1/n) \text{ Log } C_e \tag{4}$$

Where q_e is the amount of adsorbed material at equilibrium (mg/g), C_e is the equilibrium metal concentration of the adsorbate (mg/L), q_{max} (mg/g) and b (L/mg) are the Langmuir constants, and K_f and n are Freundlich constants.

Results

3.6. Comparison of Almond Green Hull with other Adsorbents

The adsorption capacity of Cr (VI) onto almond green hull was compared with several low cost adsorbents and they are reported in Table 1. The adsorption capacity of Cr (VI) on almond green hull is calculated as 2.04 mg/g at pH=6 and room temperature. Almond green hull in this study possesses reasonable adsorption capacity in comparison with other sorbents.

Table 1: Comparison of maximum adsorption capacities of Cr (VI) in various adsorbents with and without activation.

Sorbent	q_{max} (mg/g)	Reference	Sorbent	q_{max} (mg/g)	Reference
Almond green hull	2.04	This study	Beech sawdust	16.1	Kapoor et al. 1989
Almond shell	3.40	Pehlivan et al. 2008	Cactus	7.08	Sharma et al. 1994
Almond shell	2.40	Mohan et al. 2005	Rice husks	0.6	Sumathi et al. 2005
Almond shell carbon	10.6	Dakiky et al. 2002	Rice straw	3.15	Gao et al. 2008
Walnut	2.28	Tunali et al. 2005	Sugarcane	0.28	Garg et al. 2007
Walnut shell	8.01	Pehlivan et al. 2008	Sugarcane bagasse	0.63	Garg et al. 2007
Ground nut shell	5.88	Pehlivan et al. 2008	Sugar cane bagasse	13.4	Soner Altundogan et al. 2007
Ground nut shell	2.3	Tunali et al. 2005	Maize corn cob	0.82	Garg et al. 2007
Hazelnut shell	8.28	Pehlivan et al. 2008	Maize cob	13.8	Soner Altundogan et al. 2007
Hazelnut shell activated carbon	17.7	Mohanty et al. 2005	Herb (leersia hexandra)	2.51	Li et al. 2009
Coconut tree sawdust	3.6	Selvi et al. 2001	Oil cake from Jatropha	0.63	Garg et al. 2007
Coconut shell carbon	20.0	Alaerts et al. 1989	Oak pine	0.47	Park et al. 2008
AC derived from coconut shells	1.38	Mohan et al. 2005	Coal	6.78	Gao et al. 2008
Palm pressed fibres	14.0	Mohanty et al. 2005	Spent activated clay	1.42	Weng et al. 2008
Sawdust	1.5	Arıca et al. 2005	River bed sand	0.15	Sharma et al. 2007

4. Conclusion

Almond green hull is a low-cost and efficient biosorbent. In the present work, almond green hull was considered for the removal of Cr (VI) from aqueous solutions so that it can replace the activated carbon which is a common and costly material. In the batch model of studies, increasing dose of adsorbent, initial concentration of Cr (VI), and contact time up to 30 min were found favorable for increasing the adsorption of Cr (VI). The adsorption data was satisfactorily explained by Langmuir isotherm.

Acknowledgement
The authors express their deepest thanks and gratitude to South Khorasan Water and Waste Water Company for providing necessary facilities. The authors are also thankful to Dr. M. H. Sayadi and Dr. M. Mobaraki from University of Birjand for their valuable suggestions and unflagging supports.

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