Efficiency of Pomegranate Peels Powder on Adsorption of Hexavalent Chromium [Cr (VI)] from Industrial Wastewater

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Abstract

The research is focusing on the use of pomegranate peels powder to reduce hexavalent chromium concentration in the industrial wastewater by batch processing adsorption. Estimated amount of potassium dichromate was dissolved in distilled water to get synthetic solution containing hexavalent chromium ions at a concentration of 40 mg/L. The effect of different parameters such as pH, mixing time, pomegranate peels powder dose, initial metal concentration on hexavalent chromium removal efficiency was investigated. Furthermore, Langmuir, Freundlich and Brunauer, Emett and Teller (BET) isotherm models were evaluated. The results indicate that the maximum hexavalent chromium removal was achieved at pH 2.5; equilibrium was attained at 150 minute with 96.7% Cr (VI) percentage removal, and the experimental results were in agreement with BET model.

Keywords: Pomegranate Peels; Adsorption; Removal Efficiency and Adsorption Isotherm.

كفاءة مسحوق قشور الرمان في امتزاز الكروم السداسي من مياه المطلقات الصناعية

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الخلاصة

يركز البحث على استخدام مسحوق قشور الرمان لتقليل تركيز الكروم السداسي من مياه المطلقات الصناعية بالامتزاز وبنظام الوجبات باستخدام ماء ملوث صناعيا بالكروم السداسي عن طريق اذابة كمية محسوبة من مادة داي كرومات البوتاسيوم بالماء المقطر للحصول على ماء ملوث بالكروم السداسي بتركيز 40ملغم / لتر. درس تأثير الدالة الحامضية، زمن المزج، التركيز الابتدائي وكمية مسحوق قشور الرمان المضافة على نسبة الازالة فضلا عن تقويم موديلات لانكمير، فروندلج و بي اي تي للامتزاز. بينت النتائج ان اعلى نسبة ازالة للكروم السداسي هي 96.7% بدالة حامضية 2.5 وبزمن تماس 150 دقيقة وهو زمن الوصول الى حالة التوازن وكذلك بينت النتائج العملية التطابق مع معادلة براونر ايميت تيلر (بي اي تي) ايزوثيرم الامتزاز.

الكلمات المفتاحية: قشور الرمان ، الامتزاز ، كفاءة الازالة و ايزوثيرم الامتزاز

Introduction

Chromium is a heavy metal that releases into the environment through different industrial activities such as, electroplating, metal cleaning and dyeing processes (Belay and Ravindhranath, , 2010).

Chromium is present in drinking water at low level (Ahmed *et al*., 2012; Devaprasath *et al*., 2007), it is considered as one of the top 16th toxic pollutants (Nameni, *et al.*, 2008). There are two forms of chromium which are presented in the industrial wastewater, hexavalent (Strong Oxidizing Agent) and trivalent which is less toxic (Ahmed *et al.*, 2012; Abdulwanees *et al.*, 2012; Bera *et al*., 2012: Kaakani, 2012).

The exposure to high concentrations of chromium is toxic, mutagenic, carcinogenic and teratogenic (Belay and Ravindhranath, 2010). Hexavalent chromium is considered to be the hazardous form of chromium due to its carcinogenic and corrosive effect on tissue, in addition to that, it causes nausea, ulceration, skin sensitization and kidney damage(Park, *et al*., 2004; Ahmed *et al*, 2005; Devaprasath *et al*., 2007), and has a major problem when inhaled (Kulkarni *et al.*, 2013).

Environment is polluted with hexavalent through the discharge of electroplating, leather tanning, glass ceramic and paint industry (Devaprasath *et al*., 2007), and the two forms of hexavalent chromium that usually exists in wastewater were chromate $(CrO_4)^{-2}$ and $(Cr_2O_7)^{-2}$ (Abdulwanees *et al*., 2012; Yuan *et al*., 2010).

The allowable concentration of hexavalent chromium discharge into the surface water is 0.1 mg/L and 0.05 mg/L in potable water (Attia *et al*., 2010; Madhavi *et al*., 2012)

Different technologies have been used to reduce hexavalent chromium concentration from wastewater like, precipitation, ion exchange, electro-lysis , reverse osmosis, solvent extraction, electrodialysis, photo-catalysis and adsorption, (Kulkarni *et al*., 2013; Ahmed *et al*., 2012; Malkoc *et a*l., 2006; Baral *et al*., 2006). Adsorption has been considered to be the favorable method, because of its simplicity, economy process and selectivity towards metal ions removal (Abdelwanees *et al*., 2012).

Aim of the Research

The aim of this research is to study the ability of pomegranate peels powder to reduce hexavalent chromium concentration from water by adsorption, and investigating the effect of different parameters on the removal efficiency.

Materials and Methods

Adsorbate (Hexavalent Chromium Solution)

2.828 gram of analytical grade of potassium dichromate ($K_2Cr_2O_7$) (imported from Fluka Company), Hexavalent chromium [Cr (VI)] was dissolved in 1000 milliliter of distilled water to get a stock solution of 1000 mg/L Cr (VI) concentration.This solution was then diluted with distilled water to get desired concentration of hexavalent chromium solution for adsorption experiments (Malkoc *et a*l., 2006).

Adsorbent (Pomegranate Peels Powder)

Pomegranate peels powder (purchased from local food market as a powder) were washed several times with hot water and filtered with whatman-31 filter paper with a pore size of 1.4μm to remove dust and colored materials. These processes were repeated until the filtrate becomes nearly colorless, at this stage the cake was washed with distilled water and dried using oven at 90^0C

Hexavalent Chromium Concentration Measurement

The concentration of hexavalent chromium was measured through 210/211 VGP flame atomic absorption spectrophotometer (Konstantinos *et al*., 2011).

Experimental Procedure

To investigate the effect of pH, mixing time, initial Cr (VI) concentration and pomegranate peels powder dose on hexavalent chromium removal, a batch adsorption unit (Plate 1) was used at temperature of 25^0C (Nameni, *et al.*, 2008). The effect of pH on Cr (VI) concentration reduction was investigated by a set of 5 samples of 50 milliliter with 40 mg/L hexavalent chromium solution, the pH of the samples was in the following range 2.5, 4, 5, 6 to 8 and were adjusted using 0.1N concentrated sulphuric acid and 0.1N sodium hydroxide solution (Ahmed *et al.*, 2012), each 50 ml sample was mixed with 1 gram (arbitrary) of pomegranate peels powder and was shaken at 210 rpm for 60 minutes. After that the solution was filtered using Whatman-31 filter paper with a pore size of 1.4µm, and the filtrate was analyzed to estimate the Cr (VI) concentration in solution after adsorption by flame atomic absorption spectrophotometer.

Different pomegranate peels powder at doses of 0.3, 0.5, 0.7, 0.9 and 1 gram respectively was used, each dose was added to 50 ml of 40 mg/L hexavalent chromium solution at pH of 2.5, and these samples were shaken for 60 minutes at 210 rpm. The filtrate was then separated using Whatman-31 filter paper and analyzed to evaluate Cr (VI) concentration remaining in solution by flame atomic absorption spectrophotometer.

The effect of mixing time was investigated using the best pH that gave the maximum Cr (VI) reduction which was 2.5, 5 samples of 50 ml solution at a pH of 2.5 with 40 mg/L Cr (VI) concentration was mixed with 1 gram of pomegranate peels powder, these samples were shaken at 210 rpm for stirring time 30, 60, 120, 150 and 180 min. respectively, after that the samples were filtered with whatman-31 filter paper and the filtrate was analyzed to evaluate the concentration of Cr (VI) in solution after adsorption by flame atomic absorption spectrophotometer.

To study the effect of initial hexavalent chromium concentration on percentage removal, 4 samples of 50 ml with Cr (VI) concentration of 20, 40, 60 and 80 mg/l respectively were prepared at a pH of 2.5. Each sample was mixed with 1 gram of pomegranate peels powder which was shaken at 210 rpm for 60 minutes. The solution was then filtered using whatman-31 filter paper and the hexavalent chromium concentration in filtrate was computed by flame atomic absorption spectrophotometer.

Plate (1) Laboratory Batch Adsorption Unit

Different pomegranate peels powder at dose of 0.4, 0.5, 0.8, 0.9, 1, and 1.2 gram respectively was used to obtain the equilibrium data by batch studies. These doses were added to 6 beakers contain 50 ml solution of 40 mg/L hexavalent chromium concentration. These beakers were placed in the laboratory adsorption unit (Plate 1) and agitated for a period of equilibrium time which was estimated from the relationship between mixing time and percentage removal of hexavalent chromium, after that the solution was filtered with whatman-31 filter paper to obtain the hexavalent chromium concentration remaining in solution at equilibrium status for different adsorbent dosage.

Adsorption isotherm curves were obtained by plotting adsorbent capacity at equilibrium q_e (mg/g) against the equilibrium concentration of hexavalent chromium concentration in the solution, qe was calculated according to the following equation (Ahmad *et al*., 2005)

$$qe = \frac{V_l(C_o - C_e)}{M}$$

Where:
qe =Adsorbent capacity (mg/g)
V_l =Volume of sample (l)
Co = initial concentration of hexavalent chromium in sample (mg/l)
Ce = Concentration of hexavalent chromium in sample after adsorption (mg/l)
M = Mass of adsorbent (g)

The experimental data were compared using Langmuir, Freundlich and BET isotherm models.

Langmuir offered the following equation (Mondai and Lalvani, 2000)

$$qe = \frac{abc_e}{1+ac_e} \quad (1)$$

Where:
qe is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/gm)
C_e is the equilibrium concentration of adsorbate in water (mg/l)
a and b are constants

Taking the reciprocal of both sides of the Langmuir equation yields:

$$\frac{1}{qe} = \frac{1}{b} + \frac{1}{abce} \quad (2)$$

Freundlich offered the following equation (Zwani *et al.*, 2009)

$$qe = Kf \cdot C_e^{\frac{1}{n}} \quad (3)$$

Where:
K_f is a constant related to overall adsorption capacity (mg/gm)
1/n is the constant related to surface hetrogenityBET isotherm model can be expressed as follows (Volesky, 2003)

$$qe = \frac{BC_e x_m}{(C_s - C_e)\left[1 + \left((B-1)\frac{C_e}{C_s}\right)\right]} \quad (4)$$

Equation (4) can be arranged to be:

$$\frac{C_e}{(Cs-Ce)qe} = \frac{1}{Bx_m} + \frac{(B-1)}{Bx_m}\frac{C_e}{C_s} \quad (5)$$

Where:
B is a constant relating to the energy of interaction with the surface
Xm is the amount of adsorbate adsorbed per unit weight of adsorbent for mono layer adsorption (mg/gm)

Results and Discussion

Effect of Solution pH on Hexavalent Chromium Reduction

pH is considered to be the most critical parameter that affect the adsorption process (Dave *et al*., 2009), because of its impact on the surface charge of the adsorbent (Rahmani *et al.*,2011).

Figure (1) shows the relationship between pH and hexavalent chromium percentage removal. It is evident from this Figure that the increasement of the pH from 2.5 to 5 leads to reduction in percentage of removal of hexavalent chromium which decreased from 95% to 65%; this is due to the fact that under acidic condition, the adsorbed surface becomes highly protonated, this protonation is capable to attract the Cr (VI) in the anionic form. This surface protonation reduces gradually with the increases of pH, and that is clear from the decreasing of hexavalent chromium removal from 65% to 30% when pH was increased from 5 to 8. The mentioned decrease is due to completion between OH^- and chromate ions (Kulkarni *et al*., 2013).

It was clear from Figure 1 that maximum hexavalent chromium removal was achieved at pH 2.5. Comparing with results showed in literature by using wheat bran as adsorbent, (Nameni, *et al.*, 2008) stated that hexavalent chromium

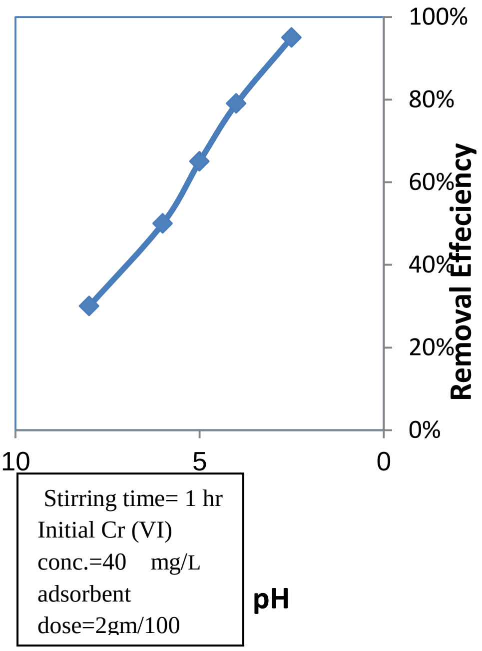

Figure (1) Effect of Solution pH on the Hexavalent Chromium Reduction

removal efficiency decreased with the increasing of pH and maximum hexavalent chromium efficiency was achieved at

Effect of Stirring Time

Stirring time is an important factor in the adsorption process (Nameni, *et al.*, 2008),

Figure (2) illustrates the effect of mixing time on the hexavalent chromium removal efficiency, that the

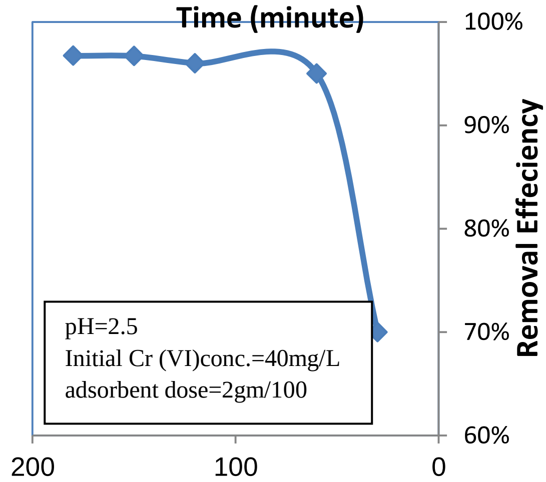

Figure (2) Effect of Stirring Time on the Removal of Hexavalent Chromium from Solution

percentage of adsorption increased from 70% to 95% with increasing of mixing time from 30 minutes to 60 minutes, this is due to maintaining the pomegranate peels powder in suspension offering enough time for hexavalent chromium removal (Bouquerra *et al*., 2008), after that the rate of hexavalent chromium removal was gradually increased from 95% to 96.7% when mixing time was increased from 60 minutes to 150 minutes and became constant after 150 minutes, because the adsorption phase reached to equilibrium. This equilibrium was attained at 150 minutes (equilibrium time).

The increase of hexavalent chromium removal with the increasing of mixing time is similar to another investigation which showed in the literature by using pinus roxburghii as adsorbent (Ahmed *et al*, 2005).

Effect of Pomegranate Peels Powder Dosage

The effect of pomegranate peels powder dosage on hexavalent chromium percentage removal was shown in Figure (3). The results showed that with the increase of the pomegranate peels powder from 0.3 gram to 1 gram, the percentage of hexavalent chromium removal was increased from 75% to 95%, due to the availability of more adsorption sites for hexavalent chromium ions (Bouquerra *et al*., 2009; Nameni, *et al*., 2008), when the pomegranate peels powder was increased.

The increase of hexavalent chromium removal with the increasing of pomegranate peels powder dosage is conform with that showed in literature by using wheat bran as adsorbent for hexavalent chromium (Nameni, *et al*., 2008).

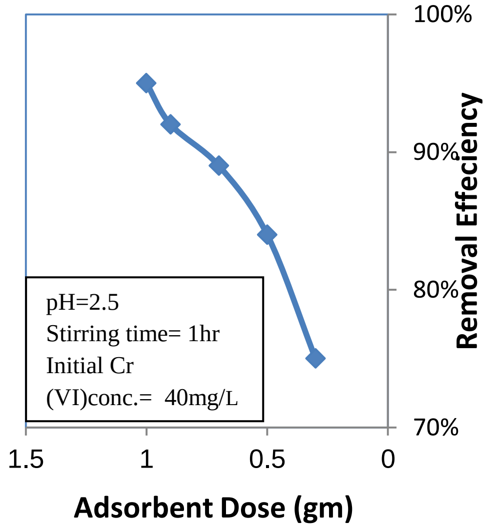

Figure (3) Effect of Powdered Pomegranate Peels on the Removal of Hexavalent Chromium from Solution

Effect of Hexavalent Chromium Initial Concentration

Figure (4) shows the effect of hexavalent chromium concentration on its percentage removal.

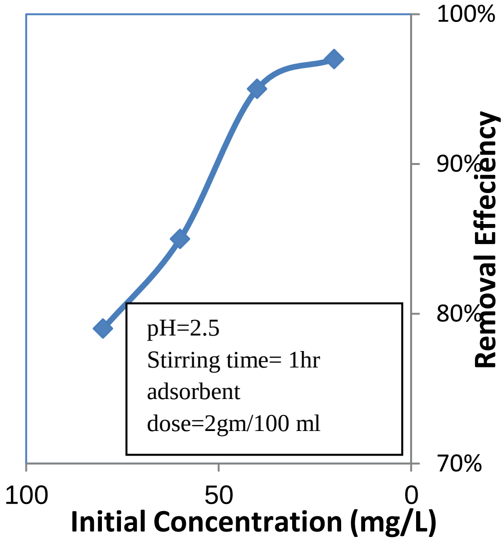

Figure (4) Effect of Initial Concentration of Hexavalent on its Removal from Solution

The percentage removal of hexavalent chromium was decreased from 96.7% to 79% when the hexavalent chromium concentration in water was increased from 20 mg/L to 80 mg/L. This decrease in the percentage of removal is due to the fact that, the pomegranate peels powder has a limited number of active sites, these sites become saturated with hexavalent chromium ions and there is no vacant sites for remainder ions of hexavalent ions to adsorb(Ajouyed *et al*., 2011).

The decrease in percentage of removal of hexavalent chromium with the increasing of hexavalent chromium concentration in water is happened in accordance with the work of (Abdulwanees *et al*., 2012) that used activated carbon and bentonite as adsorbent for hexavalent chromium.

Adsorption Isotherm

Adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid, with which it is in contact (Cengeloglu *et al*., 2007). It is also an equation relating the amount of metal ions adsorbed on the adsorbent surface, and the equilibrium concentration of the metal ions in solution (Watts, 1998).

Several models were found to describe and predict the equilibrium distribution of metal ions between liquid phase and solid phase, three types of these models were evaluated and these were Langmuir, Freundlich and BET isotherm models

Figures 5 to 7 describe the use of the Langmuir, Freundlich and BET models for adsorption of hexavalent chromium at initial concentration of 40mg/L, pH 2.5, stirring time 150 minutes and adsorbent dose from 0.4 to 2.4 gm per 100 ml.

Langmuir isotherm was achieved by plotting 1/Ce versus 1/qe (equation 2) to give a straight line with a correlation coefficient (R^2) equal to 0.9656. The constant (a) which represents adsorption capacity, (b) which is related to the energy of adsorption were estimated to be 1.359 and 3.4036 respectively from the slope and intercept of the linear plot.

Freundlich isotherm was achieved by plotting Ce versus qe (equation 3) to give a nearly straight line with a correlation coefficient (R^2) equal to 0.9958. The values of kf and n which were an indicative of adsorption capacity and intensity for adsorption were calculated to be 1.9951 and 4.15 respectively from the slope and intercept of straight line.

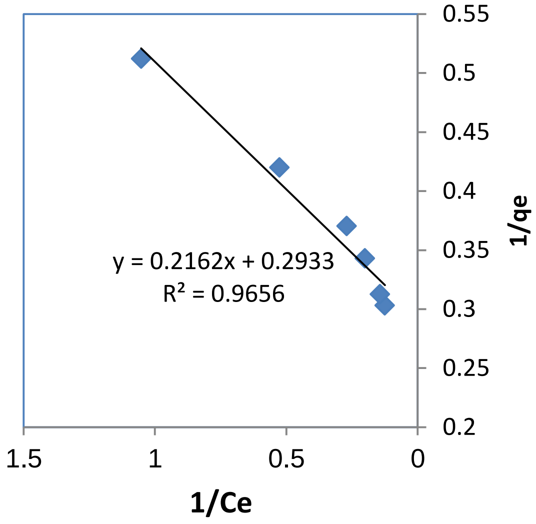

Figure (5) Langmuir Isotherm Model

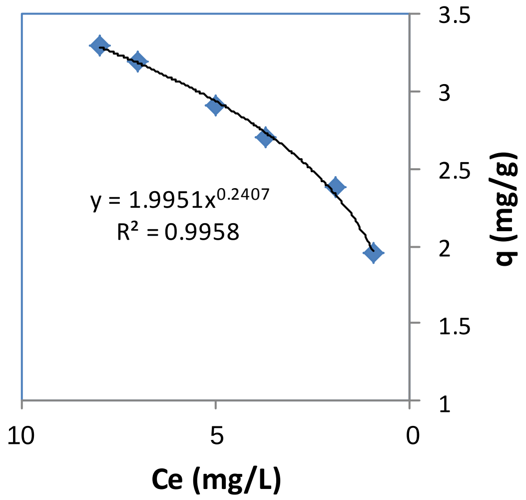

Figure (6) Freundlich Isotherm Model

BET isotherm was achieved by plotting $\frac{C_e}{(C_s - C_e)q_e}$ versus $\frac{C_e}{C_s}$ (equation 5) to give straight line with a correlation coefficient (R^2) equal to 0.9998. The values of B which was related to the energy of interaction with the surface and X_m which was related to the amount of a Cr (VI) adsorbed per unit weight of adsorbent for mono layer adsorption (mg/gm) were calculated to be 88.21 and 2.77 respectively from the slope and intercept of straight line.

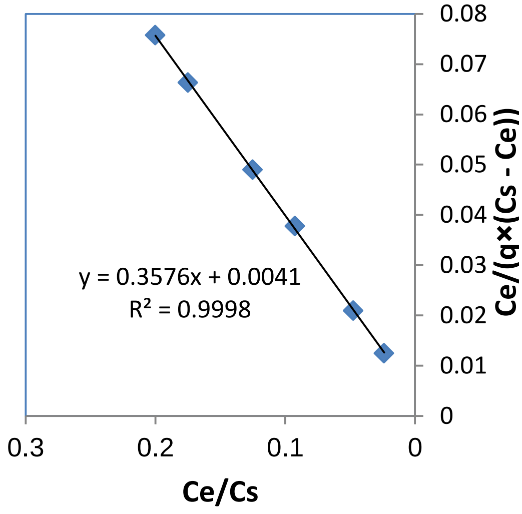

Figure (7) BET Isotherm Model

From the values of correlation coefficient of these three models, BET isotherm is in agreement with the experimental data.

Table (1) Correlation Coefficient and Constants for Langmuir, Freundlich and BET Models

	Langmuir	Freundlich	BET
R^2	0.9656	0.9958	0.9998
a	1.359		
b	3.4036		
k_f		1.9951	
n		4.15	
B			88.21
X_m			2.77

It is clear from Table (1) that the correlation coefficient of BET model which was 0.9998 higher than those for Langmuir and Freundlich models which were 0.9656 and 0.9958 respectively, this means that BET model was in agreement with the experimental data that the adsorption of hexavalent chromium by pomegranate peels powder was multilayer adsorption, and the amount of hexavalent chromium adsorbed per unit weight of pomegranate peels powder at equilibrium (X_m) and it was equal to 2.77 mg/gm.

In comparison of pomegranate peels powder with other adsorbent materials based on their maximum adsorption capacity for hexavalent chromium, the pomegranate peels powder has higher adsorption capacity (X_m) of 2.77 mg/gm compared with those stated in literature ((Nameni, *et al.*, 2008).

Conclusions

It is evident from the results that pomegranate peels powder has a higher adsorption power towards hexavalent chromium ions; it has a removal efficiency of 96.7% for Cr (VI) ions. This indicates that pomegranate peels powder was capable to receive and settled down the heavy metal ions, so pomegranate peels powder was an efficient adsorbent for hexavalent ions because of its higher adsorption power, abundant, cheap and eco-friendly however, for these reasons the world want to use plant wastes as adsorbent for pollutants.

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