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Removal of Chromium (VI) from Polluted Water using Barberry Leaf as a Cheap Absorbent

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Abstract

It is now well recognized that heavy metals in the environment cause pollution that can be harmful to living organisms. Without control, heavy metals that are transferred to the environment may undergo significant changes and have a serious impact on aquatic environments, public health and economics. In view of the serious detrimental effect to the environment and health of wastewater containing Cr (VI), there is an urgent need for regulation. The objective of the present study was to investigate Cr (VI) removal from aqueous solutions using barberry leaves. The effects of parameters such as acidity, contact time, sorbent dose and initial concentration were evaluated for batch mode. Results showed maximum adsorption in an acidic medium at pH level 2; initial Cr(VI) concentration of 80 mg L−1 and temperature of 25◦C with a contact time of 10 min at 200 rpm stirring speed. Test results were analysed by adsorption isotherms and kinetics modelling and the best adaptation was made by the Langmuir isotherm and the second best by the para-stage synthetic model.

Key words: chromium removal, aqueous solutions, barberry leaves, Isotherm.

حذف کروم شش ظرفیتی از آب های آلوده بوسیله برگ زرشک بعنوان جاذبی ارزان قیمت

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چکیده

آلودگی محیط زیست توسط فلزات سنگین به خوبی به رسمیت شناخته شده است و می تواند برای موجودات زنده مضر باشد. فلزات انتقال یافته به محیط زیست ممکن است دستخوش تحولات شده و بر محیط‌های آبی، سلامت عمومی و اقتصاد تاثیر بزرگی داشته باشند و با توجه به اثرات جدی زیست محیطی و بهداشتی فاضلاب حاوی کروم (VI) باید با آن قانونمند برخورد شود. در این مقاله هدف بررسی حذف کروم شش ظرفیتی از محلول های آبی توسط برگ زرشک می باشد. اثر پارامترهای مختلفی نظیر اسیدیته، زمان تماس، مقدار جاذب و غلظت اولیه در حالت ناپیوسته مورد بررسی قرار گرفته است. یافته های این بررسی نشان می دهد حداکثر فرایند جذب در اسیدیته برابر ۲، غلظت اولیه ۸۰ میلی گرم بر لیتر و دمای ۲۵ درجه سانتیگراد با زمان تماس ۱۰دقیقه و سرعت ۲۰۰دور بر دقیقه صورت می گیرد. ارزیابی نتایج تجربی با مدل های ایزوترم وسینتیک نشان می‌دهد که فرایند جذب با ایزوترم لانگمویر و مدل سنتیکی شبه مرتبه دوم بهترین تطابق را دارد.

کلمات کلیدی: محلول های آبی، حذف کروم، برگ زرشک، ایزوترم.

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1. Introduction:

Among the most important problems facing the world in the 21st century are those of securing supplies of clean water for humans; reducing pollution levels of surface water and sewage and environmental pollution by toxic contaminants [22]. Heavy metals cause environment pollution and can be harmful to living creatures. Metals transmitted to the environment can undergo change that has an adverse affect on public health and is detrimental to the economy. Among heavy metals in the environment, chromium has been classified as a primary contaminant [16]. Chromium is widely used in industry and is very important for the economy. It has widespread industrial application in plating, alloy, steel, pigment synthesis and colouring. Chromium usually enters the environment through industrial effluent and becomes a major contributor to environmental pollution if it is allowed to spread to water resources. Cr(VI) is toxic as a carcinogen and mutagen to living creatures [30]. Environmental pollution, including Cr(V1) caused by industrial effluent needs legal regulation to control serious environmental damage and to protect human health [25]. There are various approaches available to control pollutants; such as chemical deposition, evaporation, and ionic exchange; reverse osmosis and superficial absorption [3, 29]. In terms of efficiency and applicability, superficial absorption is the most commonly used method [31]. Recently, most research has considered the use of cheap absorbents. These absorbent materials are abundant and the cost of their preparation is low. Absorbent materials can be sourced from waste material such as that produced by industrial activity especially from agriculture; they mostly contain cellulose [18]. Samarghandi *et al.* (2009) reports the use of modified holly tree sawdust to omit Cr(VI) and tests determined that pH was an important factor for metals' removal [23]. Nikazar and Noorbakhsh (2006) applied water solutions from activated carbon of agricultural waste to remove the heavy metals (Pb(II), Cr(VI) and Cd(II)). It was reported that absorption rate decreased when the pH level of cadmium and lead was 5 or above and the pH of chromium was above 3; also reported was that rate of absorption decreased in relation to higher primary density [21]. Song Wang and co-workers (2009) removed Cr(VI) from water solutions using walnut shells. The results showed that absorption of chromium was dependent on pH of the solution and that maximum absorption (97.3%) took place when pH was 1, and that the absorption process followed the Langmuir and Freundlich isotherm [27]. The aims of this study were as follows: 1- to study elimination of Cr(VI) from water solutions using barberry leaf; 2- to study effects of certain factors of the absorption process such as contact time, pH level, amount of absorbent and primary density of chromium and 3- to determine the most suitable absorption isotherm and kinetics model for removal of Cr(VI) using barberry leaf. This work was the first to report on tests on barberry leaf as an adsorbent for removal of heavy metals from wastewater. Other ions were also tested for disturbance in this study.

2. Survey method:

Barberry leaf agricultural waste was dried at air temperature and then reduced to a powder using a number 60 filter with holes 0.25 mm in diameter. Potassium dichromate salt was used for the chromium solution and nitric acid and sodium hydroxide were used to adjust the pH level, provided by Merck Company, Germany. All salts used as reagents were of the highest degree of purity. The factors; pH of the solution, amount of absorbent, duration of the absorbent in contact with the solution and primary density of the metal solution were tested according to the following procedure. A sample of 100 ml of chromium solution was mixed with the determined density and pH and weight then put in an electrical machine set at the speed of 200 revolutions per minute (rpm) at 25^0 C. When the sample had cleared, density of the remaining chromium was determined by the Spectrophotometer method with Diphenyl Karbazayd. Also, the samples were expressed as a testament regarding to the Blank's sample. Each solution sample was provided daily using 2-distilled water. The reagent solution was provided every day with Merck's Acetone and kept in dark conditions until use. Optimum absorption conditions and analysis of acquired data was done using Langmuir and Freundlich's isotherms and by the first and second para-stage's synthetic models. Infrared (IR) spectra were provided before and after absorbing the Cr(VI) existing in barberry leaf.

3. Results and Discussion

3.1. Effect of pH

pH is one of the most important parameters for assessing the absorption capacity of an adsorbent for metal [15]. To improve pH, about 0.05 gr of leaf powder was added to 7 samples with different pH values each containing about 100 mL solution and 80 mg/L of chromium. Then, density of the remaining Cr was measured after 10 minutes. Results in Figure 1 show, a higher percentage of absorption in samples at pH level 2 and absorption decreased at a pH of more than 2. This result can be explained as follows, at lower pH the surface of the absorbent was surrounded by H^+ ions, so there was increased movement of negative ions $Cr_2O_7^{2-}$ towards the absorbent so that the removal rate of Cr(VI) in the solution increased when the absorbent surface had a higher positive charge. Therefore, pH level of the solution was a very important factor for the removal of Cr(VI) by barberry leaf [14]. A decrease in adsorption of Cr(VI) by an increase in pH level may be due to dual competition between the anions (CrO_4^{2-} and OH^-) to be adsorbed on to the surface of the adsorbent, of which OH^- predominates [9]. Thus it can be concluded that during the sorption process at a low pH, there was increased sorption of Cr(VI). Similar observations have also been reported in other research [4,12,26,28].

3.2. Effect of adsorbent dose

The effect of absorbent dose was tested by placing different weights of barberry leaf in contact with 100 mL solution containing 80 mg /L of Cr(VI) at pH level 2 to study the effect of weight of the absorbent on the rate of chromium removal. The density of chromium remaining after 10 minutes was then measured. Results are shown in Figure 2: These results demonstrate that an increased dose of adsorbent resulted in an increased percentage of chromium adsorption and the maximum removal was observed at adsorbent dose in the range of 0.3-0.5gr; hence, 0.3 gr adsorbent dose was justified for the purpose of economy. This trend determined that an increased adsorbent dose contributed to more adsorbent particles and thus a larger surface area for Cr(VI) attachment [20]. An increase in the percentage of adsorption in relation to adsorbent dose may be due to an increase in surface area of the adsorbent and availability of more adsorption sites [8,17]. It is obvious that barberry leaf adsorbed more Cr(VI) at higher dose, which resulted in increased efficiency. Similar observations have also been reported in other research [9,19].

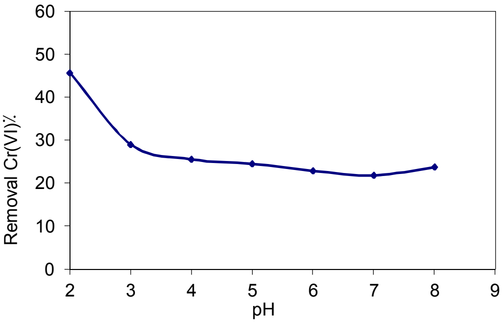

Figure 1- Effect of pH on the removal of Cr (VI) [chromium concentration = 80 mg/l; stirring speed = 200 rpm; contact time = 5 min; adsorbent dose = 0.05 g/100ml]

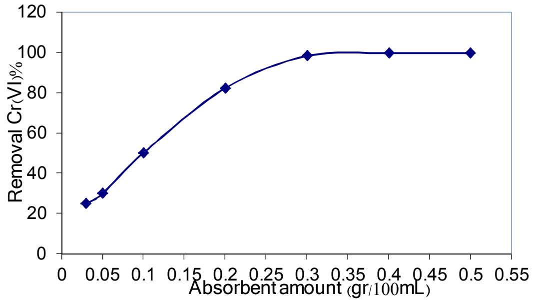

Figure 2- Effect of amount of adsorbent on the removal of Cr (VI) [chromium concentration = 80 mg/l; stirring speed = 200 rpm; contact time = 10 min; pH=2]

3.3. Effect of contact time

The rate of chromium removal by barberry leaf was examined at the various durations of 1, 3, 7, 9, 15, 30 and 60 minutes, at pH level 2 and at absorbent weight of 0.3 gr. The process was fast and most of the adsorption took place in the first 5 minutes. This was due to the nature of the adsorbent and amount of available adsorption sites, which affected the rate of Cr(VI) adsorption . Similar observations have been reported in other research [9]. All discontinuous tests were examined at 10 minutes to ensure equilibrium was reached.

3.4. Improving the density of metallic solution

With the improved condition of bed weight, contact time and solution pH, different densities of chromium were placed in contact with the bed and the rate of omission determined for each case. Results shown in Fig.3 show that the rate of absorption decreased under a higher density of metallic ions. The ratio of available surface area to initial Cr(VI) was higher at lower concentration so there was a higher removal rate. And at higher ratio of available surface to initial Cr(vl), the percentage removal was less [13]. This can be explained as follows; when the first density of chromium was increased the then there was also a decrease in the proportionate number of active sites that of absorbed samples. Also, the limitation of absorbent cell size and the electrostatic repulsed power among negatively charged ions of absorption caused a decrease of the rate of absorption so, the percentage of metallic ions decreased. The percentage of removal decrease was related to the increase in Cr(VI) density, but the amount of absorbed Cr(VI) increased according to the mass unit of the absorbent [1,5]. These results are consistent with those reported in other research [6,7], namely that removal of Cr(VI) decreases according to an increased chromium concentration.

3.5. Survey of the inconvenient effect of other ions on removal of Cr by barberry leaf

The effects of chloride, nitrate, and sulphate anions were researched because of a survey on the effect of other anions on the rate of removal of Cr(VI) by barberry leaf. Tests on removal of chromium were done under improving conditions. But the difference was that an inconvenient sample was tested in each step, in addition to Cr(VI), with a non-specific density. The results showed that chloride and nitrate anions at the amount of 20 mg/L caused trouble, while inconvenience of sulphate anions was at a density of 50 mg/L.

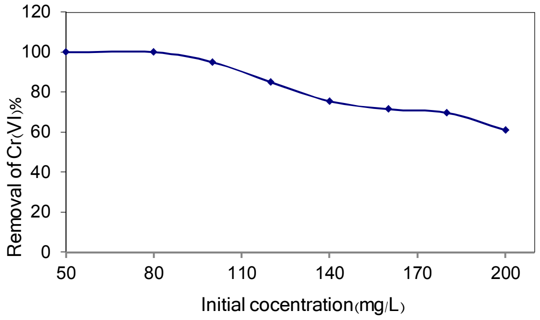

Figure 3- Effect of initial Cr (VI) concentration on the removal of Cr (VI) [pH=2; stirring speed = 200 rpm; contact time = 10 min; adsorbent dose = 0.3 g/100ml]

3.6. Search for efficiency of a new absorbent in the removal of Cr from original samples

Application of the use of barberry leaf for elimination of Cr was examined in a water sample from an aqueduct in the village of Amirabad in the region of Birjand city. The water sample was cleared by filter paper under laboratory conditions and then various different amounts of Cr(VI) were added. pH level of the water sample was adjusted and Cr(VI) was eliminated by barberry leaf in optimum conditions in the original water sample. This test was repeated 3 times for each density. Table 1 shows the results.

Table 1- Results from the water sample

RDS%	Percentage of Removal of Cr	Added chromium concentration(mg/L)	
0.005	99.5	40	1
0.03	99.6	60	2
0.14	99.4	80	3

This shows that the method has suitable efficiency for omitting Cr from real samples of contaminated water.

3.7. Analysis of leaf barberry's IR Spectrum

The results, shown in Figure 4 present a wide pick in the 3000-3600 cm^{1-} area of the IR spectrum of the barberry leaf sample that relates to the tension vibration of O-H groups. This visible pick relates to the tension vibration of the C-H group in the 2910 cm^{1-} area. The visible pick related to tension vibration of C=C of Aromatic chains in the 1625 cm^{1-} area and the vibration at 1725 cm^{1-} is related to the tension vibration of the C=O group. There is a small pick in the 2850 cm^{1-} area, which could be related to the C-H group tension vibration of Aldehyde.

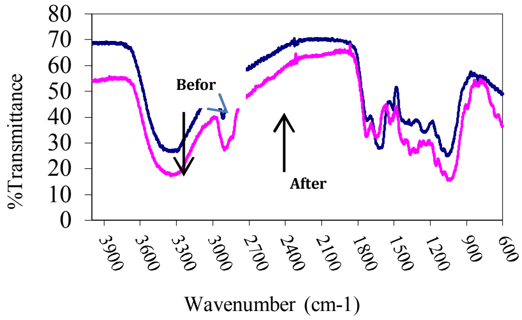

Figure 4 - IR spectra of barberry leaf

A replacement in some vibration of picks is seen in the IR spectrum of barberry leaf after coming into contact with the Cr solution, results are shown in Table 2.

Table 2 – shows changes in frequency of the functional groups of the adsorbent before and after contact

After contact	Before contacting	Functional groups
3350	3350	O-H
2910	2910	C-H
1735	1725	C=O
1650	1625	C=C
2840	2850	C-H)Aldehyde(

3.8. Absorption Isotherms

Absorption isotherms are equations used to describe the equilibrium state of an absorbed element between its fluid and solid phases. The amount of absorbed material that an absorbent article can absorb depends on characteristics of the absorbed material as well as characteristics of the absorbent and the acting environment. Data obtained from tests on absorption equilibrium in this study were examined by Freundlich and Langmuir's absorption isotherm models. Barberry leaf was applied to determine absorption isotherm as the absorbent. Tests were conducted with different primary densities of metallic ions (Cr(VI)) in pH=2 .

3.8.1. Langmuir Isotherm

Langmuir's isotherm model was used to calculate maximum absorption capacity of the absorbent, which is the amount of target species absorbed per unit of bed mass. Maximum capacity of the absorbent was achieved by test data with this model. In this model, it is supposed that absorption happens on homogenous places and a single layer. The Langmuir equation is:

$$\frac{C_e}{q_e}=\frac{1}{q_0 b}+\frac{C_e}{q_0} \quad \text{(linear form)} \qquad (1)$$

In this equation, C_e is the balanced density of absorbed sample (mg/L), q_e is the amount of absorbed sample at balanced state (mg/g), q_0 is the maximum capacity of an absorbent (mg/g) and b is the Langmuir's fixed amount (L/mg), which depends on energy of the absorption process. Considering form of the above equations, if drawing C_e/ q_e changes the curve proportion to $C_{e,}$ a straight line will be provided whose slope is $1/ q_0$ and its breadth is $1/ q_0 b$.

3.8. 2. Freundlich Isotherm

Freundlich's isotherm is a useful model for studying the absorption process in a solution. This model explains that absorption occurs on unlike absorption sites. The isotherm declares that absorption power decreases according to an increase of surface cover because of its heterogeneous surface. The Freundlich equation is:

$$log q_e = log k_f + \frac{1}{n} log C_e \quad \text{(linear form)} \qquad (2)$$

In this form C_e is the balance density of the absorbed sample (mg/L), q_e is the absorbent capacity or the amount of absorbent species in an equilibrium state for the unit of bed mass of absorbent (mg/g), and n,K_F are Freundlich fixed and show capacity and amount of absorption. By drawing the logarithm curve of q_e, according to C_e, a line will be present which these fixed points of slope and breadth are achieved [2,11,24].

Coefficients of correlation and absorption factors are provided in Table 3.

The results of test data with absorbed models show that test data had the best accordance with Langmuir's isotherm, and that the maximum absorbent capacity was 40.16 mL/g.

3.9. Chromium absorption Kinetics on leaf barberry

Absorption kinetics was studied using the first and second para-stage models.

3.9.1. First para-stage synthetic follows the expression:

$$Ln(q_e - q_t) = Lnq_e - k_1 t \qquad (3)$$

Where q_e, q_t are absorbent capacity at the moment of equilibrium and t time (mg/g) respectively, k_1 is the first stage of the synthetic's fixed (1/min), t is time in minutes.

3.9.2. Second para-stage synthetic follows the expression:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

Table 3- Correlation coefficients and other parameters of the model of absorption.

Freundlich isotherm			Langmuir isotherm		
n	KF	R2	B	q0	R2
10.30	27.62	0.8227	1.51	40.32	0.9965

In this equation q_e,q_t are, respectively, the absorbent capacity at the moment of equilibrium and t time (mg/g), k_2 is the second stage synthetic's fixed (g/min.mg), t is time according to minute [10,24]. Table 4 shows fixed coefficients and correlations.

Considering that correlation coefficients are achieved, it can be calculated that the absorption data follows the second para-stage synthetic model better than the first para-stage model.

Table 4- Fixed coefficients and correlations

Second para-stage synthetic					First para-stage synthetic				
a	b	qe	K1	R2	a	b	qe	K1	R2
0.016	0.0007	60.606	0.388	1	0.279	- 3.75	42.8	- 0.27	0.7838

4- Conclusion

In summary, the following conclusions are drawn:

- Maximum adsorption was observed in the acidic medium at pH 2, initial Cr(VI) concentration of 80 mg L−1 and temperature of 25 ◦C with contact time of 5 min at 200 rpm stirring speed.
- The process of (Cr(VI)) absorption isotherm by barberry leaf follows Longmuir's model and yielded maximum adsorption capacity of 40.16 mL/g.
- The rate of chromium removal by barberry leaf increased in relation to a decrease of solution density.

- The process of (Cr(VI)) absorption kinetics by barberry leaf correlated with the second para- stage kinetics model.
- Barberry leaf can be confirmed as a suitable absorbent for removal of chromium contaminated water.

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