

Agricultural Waste as Adsorbent for Removal of Chromium (VI) from Aqueous Solution

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A-R-T-I-C-L-E-I-N-F-O

Article Notes:

Received: Mar 27, 2016

Received in revised form:
Jul 29, 2016

Accepted: Sep 20, 2016

Available Online: Sep 27,
2016

Keywords:

Rice husk
Adsorption
Chromium (VI)
Isotherms
Iran

A-B-S-T-R-A-C-T

Background & Aims of the Study: Since the chromium (VI) is a toxic, carcinogenic and non-biodegradable element and can accumulate in the tissues, the presence and release of this element through the effluents is associated with dangerous effects on life cycle. Thus, it should be removed from the effluents. In the present study, biosorption of Cr(VI) from aqueous solutions using Rice husk was investigated.

Materials and Methods: The various parameters such as pH, initial Cr(VI) ion concentration, adsorbent dose, and contact time were optimized in batch adsorption system. The experimental data were modeled by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The pseudo-first order, pseudo-second order and intraparticle diffusion models were used to describe the kinetic data.

Results: The results indicated that Cr(VI) removal efficiency increases by increasing of contact time and adsorbent dosage. Langmuir models demonstrated the best fit of the adsorption data. The maximum adsorption capacity was 38.4 mg/g at optimum conditions of pH 5.0, contact time of 75 min, temperature of 30 °C and biomass dose of 5 g/L. The best correlation was provided by the second-order kinetic model.

Conclusion: It can be concluded that the Rice husk can be considered as an effective adsorbent to remove the Cr(VI) from aqueous solution.

Please cite this article as: Balarak D, Yari AR, Kord Mostafapour F, Mahdavi Y, Joghataei A. Agricultural Waste as Adsorbent for Removal of Chromium (VI) from Aqueous Solution. Arch Hyg Sci 2016;5(4):310-318.

Background

One of today's environmental challenges is the excessive use of heavy metals for industrial and domestic activities which it contaminates the ground and surface water; therefore, it is important to remove these elements from water and wastewater prior to discharge into the environment (1-3). Cr(VI) containing waste water discharged from various industries including mining, tanning, cement, production of steel and other metal alloys, electroplating operations, photographic material and corrosive

painting industries (4,5). The carcinogenic, mutagenic and toxic of Cr(VI) can negatively affect on the life cycle; thus, there is significant need to remove this element for the elimination of this element (6,7). The maximum permissible limit of Cr(VI) for the discharge to inland surface water is 0.1 mg/L and in potable water is 0.05 mg/L (8,9). Heavy metals can be removed from industrial wastewater using physico-chemical treatment technologies such as precipitation, ion exchange, electrochemical processes and membrane processes (10,11). However, these technologies are expensive and

energy-intensive and they can be driving factors towards a search of cheaper alternatives in both developing and developed countries (12-14). Activated carbon has been used as an adsorbent in wastewater treatment throughout the world, but this is not an economical adsorbent due to its high operation and regeneration costs (15-17). Currently, the researchers have exhibited more tendencies for the innovation of adsorbents to substitute the costly activated carbon. Many studies have been made on the use of different adsorbents like peat, coir pith, chitin, Azolla, Lemna minor, hardwood sawdust, bagasse pith, paddy straw, various blends of these (11-14). However, the studies are continuing for a cost-effective, efficient adsorbent. The use of agricultural waste, i.e., Rice husk has been identified as a paramount alternative because it is conveniently available in many countries like Iran (Particularly in the area North Iran) where agriculture is one of the major businesses (18). It is cheap and shows good sorption capacities when properly treated (19-21). In many countries, this adsorbent has been evaluated to remove different types of pollutants such as dyes and heavy metals and it has represented appropriate adsorption ability due to its adsorbing properties (22, 23).

Aims of the study:

The aim of the present study was a survey of the efficiency of agricultural waste as an adsorbent for the removal of chromium (VI) from an aqueous solution. Equilibrium isotherm models and kinetic models were conducted for a better understanding of the adsorption process.

Materials & Methods

2.1. Preparation of Adsorbent

In this study, the adsorption of Cr (VI) by Rice husk from an aqueous solution was investigated. The stalks of Rice husk were collected from the research farm of Tabriz agricultural school. These stalks were primarily washed with water to remove the contaminant and then were placed in the oven at 105°C for 5 h for drying.

Subsequently, they were treated by 0.1 M H₂SO₄ for 2 h and washed with distilled water and were dried at 105°C for 3 h (24). Finally, the adsorbent was crushed and was sieved to achieve the particle size of 18 mesh and was stored for the experiments.

2.2. Preparation of Standard Cr(VI) Solution

All the chemicals used in the study were of analytical grade and were obtained from Merck Co. The stock Cr(VI) solution (1000 mg/L) was prepared by dissolving 3.73 g of K₂CrO₄·2H₂O in 1000 mL of double distilled water. The desired initial concentrations for experiments were prepared by appropriate dilution of the stock Cr(VI) solution.

2.3. Batch Adsorption Studies

The Cr (VI) adsorption study was accomplished by varying pH, contact time, adsorbent dose, temperature, initial Cr(VI) concentration under the aspects of adsorption isotherms and kinetics. Therefore, the initial Cr(VI) concentration, adsorbent dosage, contact time and pH were selected in a range of 10-200 mg/L, 1-10 g/L, 10-180 min and 3-10, respectively (25). To carry out the adsorption experiments, 250 mL Erlenmeyer flasks were used to hold the total volume of 100 mL of the reaction mixture. The pH of the solution was adjusted by adding 0.1 M NaOH or HCl. After shaking (3600 rpm for 10 min), all sample solutions were filtered through a 0.45-µm membrane filter paper (Sartorius, Germany) and the filtrate was analyzed. The kinetic studies were carried out by agitating of 250 mL flasks containing 5 g/L of biomass and 100 mL Cr(VI) solutions of different concentrations i.e. from 10 to 200 mg/L. The residues of the Cr (VI) in the samples were measured by UV-visible spectrophotometer (25,26). All the experiments were carried out in triplicate.

The following equation was used to calculate the amount of Cr(VI) adsorbed per unit mass of the adsorbent (27):

$$q_e = \frac{(C_0 - C_e)V}{W}$$

Where C_0 and C_e are the initial and equilibrium Cr(VI) concentrations in solution, respectively (mg/L), V the volume of the solution (L) and m is the mass (g) of the adsorbent used.

Results

Effect of pH and Contact time

Figure 1 shows the effect of pH on the biosorption of Cr(VI) ions onto Rice husk biomass.

The highest removal was obtained at pH=3.0. The Cr(VI) ions removal was 99.1% at pH=3.0, but this rate decreased to 78% at pH=7.0 and decreased to 47% at pH=10.0.

Fig. 2 represents the effect of contact time on Cr(VI) biosorption. As it can be observed, the removal of Cr(VI) by biomass increased with increasing contact time and maximum value at 75 min and thereafter, it remains almost constant. After the equilibrium time, there was not observed more Cr(VI) removal.

Effect of Adsorbent Amount

The Effect of Adsorbent Amount onto the Cr(VI) adsorption is shown in Fig. 3 for a constant initial Cr(VI) concentration of 50 mg/L in the solution. The percentage of Cr(VI) removal increases with an increase in the adsorbent dose from 1 to 5 g/L. the Cr(VI) removal efficiency was observed to be 94.4 % at the biomass dosage of 5 g/L and there was not significant change in removal efficiency in higher biosorbent dosage.

Effect of Initial Cr(VI) Concentration

The equilibrium adsorption capacity of the adsorbent for Cr(VI) increased with increasing initial Cr(VI) concentration, as is also shown in Fig. 4. The results show that an increase in Cr(VI) concentration from 10 to 200 mg/L decreases the removal percentage from 99.4% to 81.5% and increases the adsorption capacity from 1.98 to 32.6 mg/g.

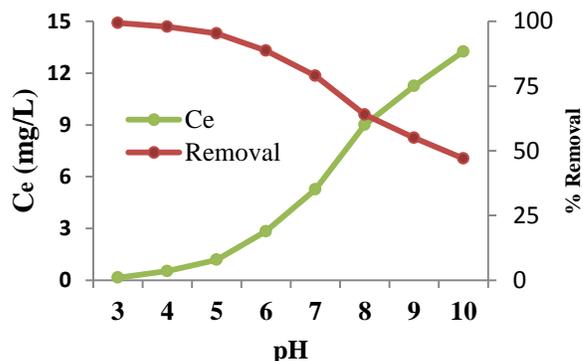


Figure 1) Effect of pH on Cr(VI) removal efficiency ($C_0 = 25$ mg/L, adsorbent dose of 5 g/L, Time = 75 min and Temp: 30 °C)

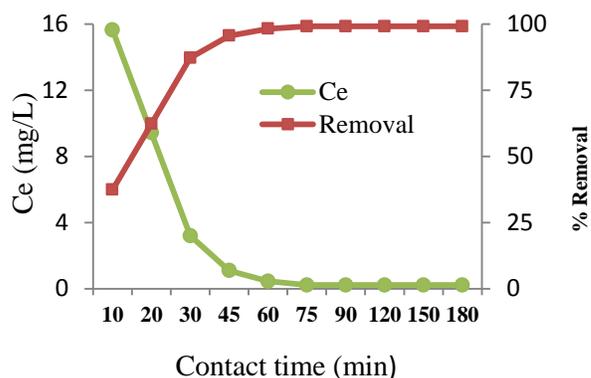


Figure 2) Effect of contact time on removal efficiency (pH = 3, adsorbent dose 5 g/L, Con: 50 mg/L, Temp: 30 °C)

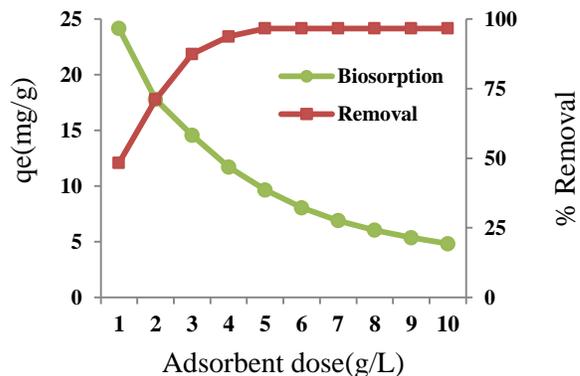


Figure 3) Effect of biomass dose on Cr(VI) biosorption ($C_0 = 50$ mg/L, pH=3, Contact time=75 min and Temp: 30 °C)

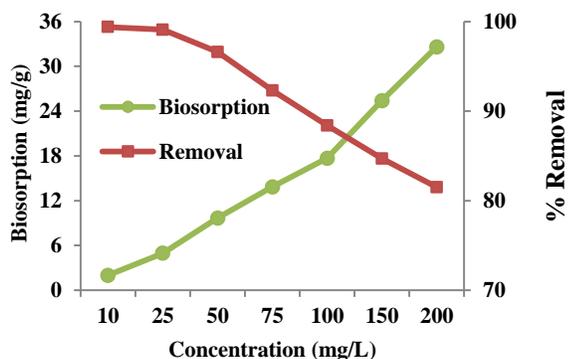


Figure 4) Effect of initial Cr(VI) concentration (Time: 75 min, pH=3, adsorbent dose: 5 g/L and Temp: 30 °C)

Adsorption equilibrium study

The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm models were selected in this study to evaluate the adsorption of Cr(VI) on Rice husk.

The linear form of Freundlich equation is expressed as (16):

$$\log q_e = \frac{1}{n} \log C_e + \log K_F$$

Where q_e is the Cr(VI) concentration on Rice husk at equilibrium, C_e (mg/L) is the concentration of Cr(VI) in solution at equilibrium, K_F and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The higher values for K_F shows the greater dependency for adsorbate. The values of the $1/n$ between $0 < 1/n < 1$ indicates that adsorption process is favorable.

The linear form of the Langmuir isotherm model is described as (28):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

Where C_e (mg/L) and q_e (mg/g) are the concentration of Cr(VI) and the amount of Cr(VI) adsorbed by the Rice husk at equilibrium, respectively; the value of q_m (mg/g) indicates the maximum adsorption capacity related to

monolayer coverage; and K_L (L/mg) is the Langmuir constant. The q_m and K_L is calculated from plotting C_e/q_e versus C_e . In order to determine, the adsorption process is favorable or unfavorable, a dimensionless constant separation factor or equilibrium parameter R_L , is defined according to the following equation (28):

$$R_L = \frac{1}{K_L C_0}$$

Where K_L (L/mg) is the Langmuir constant and C_0 (mg/L) is the initial Cr(VI) concentration. The R_L value indicates adsorption process is irreversible when R_L is 0; favorable when R_L is between 0 and 1; linear when R_L is 1; and unfavorable when R_L is greater than 1.

The linear form of Temkin isotherm model is given by the equation (29):

$$q_e = B \ln(A) + B \ln(C_e)$$

Where $B = RT/b$, T is the absolute temperature in Kelvin and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). A is the equilibrium binding constant and B is corresponding to the heat of sorption.

The linear form of D-R isotherm model is expressed as (30):

$$\ln q_e = \ln q_m - K \varepsilon^2$$

Where K is a constant corresponding to the biosorption energy, q_m the theoretical saturation capacity and ε is the Polanyi potential which is calculated from equation below (31):

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$$

Where R ($\text{kJ mol}^{-1} \text{ K}^{-1}$) is the gas constant and T (K) is the absolute temperature. E was calculated from the K value by the following relation (32):

$$E = \frac{1}{(2K)^{1/2}}$$

The resultant values of the isotherm parameters for all the experiments in solutions with pH equal to 3.0 are presented in Table 1. The Langmuir isotherm is obeyed better than the Freundlich, Temkin and D–R isotherms, as is evident from the values of the regression coefficients. Langmuir isotherm parameter fits for Cr(VI) adsorption on Rice husk yielded isotherms that were in good agreement with observed behaviour ($R^2 \geq 0.998$). The Cr(VI) adsorption capacity at room temperature (303 K) was 24.56 mg/g.

Adsorption kinetics

The kinetic models is used to study the mechanism and rate-controlling step in the adsorption process. for this purpose, three kinetic models, i.e, pseudo-first-order, pseudo-second-order and intra-particle diffusion, were applied in this study.

The pseudo-first-order equation can be expressed as the following equation (33):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$$

Where q_e and q_t (mg/g) are the Cr(VI) adsorption capacity at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the rate constant of the pseudo-first-order.

The pseudo-second-order kinetic model can be expressed in linear form as follows (34):

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$$

Where k^2 (g/mg min) is the rate constant of the pseudo second order.

The intraparticle diffusion equation is written as follows (21):

$$q_t = K t^{0.5} + C$$

Where C is the intercept which describes the foundry layer thickness and K ($\text{mg/g min}^{1/2}$) is the rate constant of intraparticle diffusion.

The value of kinetic parameters obtained in this work is shown in table 2. The R^2 values listed for the pseudo first-order kinetic model were between 0.881-0.944. The values of R^2 for pseudo-second-order model were greater than 0.99, and it is clear that it is higher than the R^2 values obtained for the pseudo-first-order model. Therefore, the adsorption kinetics could be more favorably described by the pseudo-second-order kinetic model for Cr(VI) adsorption onto Rice husk.

Table 1) The adsorption isotherms constants for the removal Cr(VI)

Tem(°C)	Langmuir model				Freundlich model			Temkin model			Dubinin–Radushkevich			
	q_m	R_L	K_L	R^2	n	K_F	R^2	B	A	R^2	K	q_m	E	R^2
10	22.16	0.541	0.59	0.998	2.17	3.11	0.886	11.4	0.44	0.945	0.96	18.65	9.142	0.784
20	23.65	0.623	0.78	0.999	2.89	5.76	0.854	8.86	0.71	0.937	1.22	18.92	10.921	0.801
30	24.56	0.452	0.94	0.997	1.74	7.79	0.873	6.14	0.88	0.954	1.47	19.46	11.558	0.826
40	24.92	0.712	1.14	0.998	2.29	8.42	0.821	5.19	0.99	0.912	1.96	20.19	12.341	0.849
50	25.35	0.842	1.39	0.999	3.11	9.18	0.879	3.75	1.04	0.939	2.14	20.71	13.205	0.823

Table 2) The adsorption kinetic model constants for the removal Cr(VI)

C ₀	Pseudo second-order model			Pseudo first-order model			Intraparticle diffusion		
	k ₂	R ²	q	K ₁	R ²	q	K _{dif}	C	R ²
10	0.96	0.993	1.72	0.074	0.894	0.95	0.136	2.25	0.786
25	0.45	0.995	5.11	0.067	0.939	2.94	0.412	3.17	0.812
50	0.31	0.999	9.74	0.071	0.881	4.71	0.673	5.64	0.746
100	0.22	0.998	17.95	0.089	0.944	11.45	0.894	4.19	0.783
200	0.19	0.991	33.41	0.097	0.903	20.64	1.04	8.42	0.804

Discussion

pH is an important factor to control the biosorption process. The pH can change the surface charge of the biosorbent and it also can affect on the degree of ionization and speciation of the heavy metal in solution (7). In addition, it considered as an important factor which can influence on the site dissociation as well as the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation are strongly influenced by pH and, strongly influences speciation and biosorption availability of the heavy metals. In present study, Cr(VI) removal process was significantly influenced by pH. The biosorption capacity (q_e) was decreased with the increase of the pH and the maximum adsorption capacity was observed in pH=3. It was also detected that Cr₃O₁₀ and Cr₄O₁₃ species are formed at pH=3, but HCrO₄⁻ and Cr₂O₇⁻² ions are observed at pH ranges of 3–7. Furthermore, CrO₄⁻² is the predominant species in the solution at pH values more than 7 (35,36). At the lower pH values, the negatively charged chromium species is bonded to positively charged functional groups of the surface of adsorbent through electrostatic attraction, because most of functional groups are carrying positive charges. As pH increased, the overall surface charge on cell walls became negative and biosorption decreased. On the other hand, the reduction process of hexavalent to trivalent chromium requires a large amount of proton (37).

Biosorption of Cr(VI) on dried Rice husk was rapidly increased within the first 30 min and

then slowed from 30 to 60 min and it was finally reached to equilibrium after 75 min. The initial high biosorption rate of Cr(VI) on dried Rice husk within the first 30 min was attributed to the high the availability of binding sites on the surface of dried Rice husk, and the subsequent lower biosorption rate after 30 min was related to decrease the availability of binding sites on the surface of dried Rice husk due to the absorption of initial Cr(VI) molecules (30).

The investigation of the effect of dried Rice husk amount on Cr(VI) removal efficiency is important to understand the intercommunication between the adsorbent capacity and percentage removal of Cr(VI). The percentage of Cr(VI) removal increases from 48.3 to 94.4% with an increase in the biomass amount from 1 to 5 g/L. The increase in Cr(VI) removal with increase in Rice husk amount is due to the increase in surface area and adsorption sites available for adsorption (38). However, the adsorption capacity decreases from 24.15 to 4.72 mg/g by increasing the adsorbent amount from 1 to 10 g/L. The decreasing of adsorption capacity can mainly due to this fact that a lot of adsorption sites on adsorbent surface remain unsaturated during the adsorption process (36). Zubair et al, (39) found that the Cr(VI) removal efficiency by *Citrus reticulata* waste biomass increases with increasing adsorbent amount, which can be due to the large number of vacant adsorption sites and the greater surface area, hence favoring more Cr(VI) adsorption.

The results show that the increasing of Cr(VI) concentration from 10 to 200 mg/L is led to decrease the percentage removal from 99.4% to

85.5%, but it can increase adsorption capacity from 4.98 to 41.45 mg/g. Since the adsorbent has a limited number of active site, these sites is saturated after a certain concentration of Cr(VI) which this event is led to decrease the Cr (VI) removal percentage (40). The increase in adsorption capacity with increase in Cr(VI) concentration may be due to the higher adsorption rate and utilization of all active sites available for the adsorption at higher concentration (41). For the 25 mg/L of initial Cr(VI) concentration, the optimum values of Cr(VI) removal and adsorption capacity are found to be 99.4% and 28 mg/g respectively.

The isotherm models are identified as an essential part of the adsorption studies which they are successfully used to determine the maximum capacity of adsorption. It also provides a panorama of the course taken by the system in a concise form and it indicates efficacy level of an adsorbent to adsorb and it also clears whether the adsorbent is a cost-effective adsorbent (1). The Freundlich isotherm is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent (14). The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites (12). The Temkin isotherm model assumes that the adsorption energy is linearly decreased with the surface coverage ratio due to adsorbent-adsorbate interactions (9). The D-R isotherm model is a semi-empirical equation where adsorption follows a pore filling mechanism. This isotherm model assumes a multilayer feature to adsorption process and reveals that the Van der Waals force participates in the process; this model is applicable for physical adsorption processes (30). The Freundlich constant, KF, is increased with increasing of the temperature which it clarifies that the adsorption process is endothermic. This further supports the findings

that the adsorption of Cr(VI) onto Rice husk particles is a chemisorption process.

The correlation coefficient for the D-R isotherm is the lowest when compared to other three isotherm models. This suggests that the Cr(VI) adsorption onto Rice husk particles is not a physical process. The mean sorption energy, E, indicates the information about adsorption mechanism. If E 8 kJ/mol, the adsorption process was physical in nature and in the ranges from 8 to 16 kJ/mol, it was chemical in nature (42,43). The estimated values of E were 9.142 kJ/mol, 10.921 kJ/mol, 11.558 kJ/mol, 12.341 kJ/mol and 13.205 kJ/mol for different temperature which suggested the adsorption process was chemical in nature i.e. the indication of chemical bond formation between metal ion species and the functional group of the adsorbents.

The kinetic data were well fitted by a pseudo-second order model. These indicate that the adsorption system is probably best described by the pseudo-second order kinetic model. On the other hand, it has shown a better performance of the pseudo-second order kinetics model in the case of adsorption of chromium from aqueous solutions on treated sawdust (38). Balarak *et al.* (7) has obtained similar conclusions in the case of adsorption of Cr(VI) onto Canola. Ghanizadeh *et al.* has been studied the bone charcoal ability for Cr (VI) removal (44). The results of their study showed that adsorption of hexavalent chromium using this biosorbent complies with pseudo-second-order kinetics.

Conclusion

The efficiency of Cr(VI) ions removal from aqueous solution by onto Rice husk biomass as a natural biosorbent was evaluated. The effect of parameters such as contact time, pH, Cr(VI) concentration, adsorbent doses and temperature were analyzed. In general, the best, efficiency of Cr(VI) removal by Rice husk biomass was obtained at pH 3.0, dose adsorbent of 5 g/L,

initial concentration of Cr(VI) of 10 and 25 mg/L and contact time 75 min. The adsorption isotherms studies showed the best applicability of the Langmuir isotherm to describe the equilibrium data, on other hand, the Langmuir isotherm was found to be better than other studied isotherms. The rate of adsorption was found to conform to pseudo-second-order kinetics with a good correlation. The increase in temperature increased the Rice husk biomass monolayer adsorption capacities. Finally Rice husk biomass, an inexpensive and easily available material, can be an alternative for more costly adsorbents used for Cr(VI) ions removal in wastewater treatment processes.

Footnotes

Acknowledgments

The authors would like to acknowledge from Qom University of medical sciences for the financial support this study.

Conflict of Interest:

The authors declared no conflict of interest.

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