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Removal of chromium (VI) ions from aqueous solutions by using Kiwi shell

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Abstract. Kiwi shell, an waste material, was investigated as an adsorbent for the removal of Cr(IV) toxic metal from aqueous solutions. Batch experiments have been performed as a function of pH, contact time, dose of sorbent, initial Cr(IV) concentration, strength ionic and temperature. The experiments showed that the adsorption process was quick and the equilibrium attained within 20 min. Evaluation using Langmuir gave sorption capacity 6.23 mg g^{-1}. Chromium uptake by Kiwi shell was best described by pseudo-second order model. Using the equilibrium concentration constants obtained at different temperatures, various thermodynamic parameters, have been calculated. The results indicated that Chromium adsorption was feasible, spontaneous, and exothermic.

Keywords: *Removal; Chromium; Kiwi shell, kinetics*

1. INTRODUCTION

Nowadays, the contamination of waters by toxic heavy metals through waste effluent is a worldwide environmental problem. Hexavalent chromium, Cr(VI), is widely used in manufacturing and processing plants. Cr(VI) is present in high concentrations in the industrial wastewater of petroleum refineries, leather tanneries, electroplating and metal finishing plants as well as dye production, wood preservation and pulp production facilities [1]. In aqueous phase chromium mostly exists in two oxidation states such as trivalent chromium (Cr^{3+}, $Cr(OH)^{2+}$or $Cr(OH)^{2+}$, etc.) and hexavalent chromium ($HCrO_4^-$, CrO_4^2- or $Cr_2O_7^{2-}$etc.). Most of the hexavalent compounds are carcinogenic, toxic, and mutagenic and even can cause lung cancer also [2,3]. Cr(III) is essential for human (especially in glucose metabolism) and it is relatively immobile and innocuous. Cr(VI) ions mostly exists as H_2CrO_4 form at high acidic medium (pH~1.0). At pH 2–6 there is equilibrium between $HCrO_4^-$ and $Cr_2O_7^{2-}$ species, if Cr(VI) concentration is greater than 0.02 M, the dichromate ion ($Cr_2O_7^{2-}$–) is the predominant species and when the Cr(VI) concentration is less than 0.02 M, $HCrO_4^-$ is predominant form, under alkaline conditions (pH >8) it exists as chromate CrO_4^{2-} ion [4]. The maximum exit Cr(VI) concentration based on US-EPA guidelines for potable water is 0.05 mg/L and the United Nations Food and Agricultural Organization recommended maximum level for irrigation waters 0.1 mg/L [5].

A wide range of processes have been applied to eliminate the Cr(VI) from water and wastewater such as electrochemical reduction, chemical precipitation, sulphide precipitation, cementation, ion-exchange, reverse osmosis, elecrodialysis, solvent extraction and evaporation, etc. [6]. However, these processes have not been used extensively because of high cost. Hence, more economical techniques such as adsorption and the use of low-cost sorbents for removal of toxic metals from wastewater has been a focus. Therefore, there is a need to search an effective low cost adsorbent for economical wastewater treatment.

In recent years, Low cost adsorbents are widely used to remove heavy metals from waters. Adsorbents, such as sawdust [7], tourmaline [8], rice husk [9], chitosan [10], manure compost [11], charcoal [12], lawny grass [13], activated carbon [14,15], tea waste [16] and pistachio hull biomass [17], have been successfully applied for physical removal of heavy metals. The aim of

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this work is examination the potential of kiwi shells to adsorb Cr(VI) ions from aqueous solutions. The effect of the solution pH, contact time, temperature, and adsorbent doses on the removal of Cr(VI) ions was studied. The adsorption isotherms and probable mechanism are explained. The thermodynamic and kinetics parameters for the adsorption of Cr(VI) ions have also been computed and discussed.

2. MATERIALS AND METHODS

An atomic absorption spectrometer model Sens AA (Dandenong, Victoria, Australia) equipped with deuterium lamp background corrector was used for determination of Cr in air-acetylene flame. The instrumental settings of the spectrometer were as follows: wavelength, 357.9 nm; slit width, 0.2; lamp current, 7 mA; acetylene flow 1.5 L min-1 and air flow 3.5 L min-1. A mechanical shaker KS 130 basic (Deutschland, Germany) having speed control and timer was used for batch experiments. A 691 Metrohm pH meter (Herisau, Switzerland) was employed for pH measurements.

All the reagents used were in the analytical grade. The stock solution (1000 mg L^{-1}) of Cr(VI) ions used in this work was prepared by dissolving an accurate quantity of $K_2Cr_2O_7$ 99.99% (Merck, Darmstadt, Germany) in deionized water. Other concentrations prepared from the stock solution. Fresh dilutions were diluted daily prior to use and the solutions pH was adjusted to be desired values with 0.1 M HNO_3 or 0.1 M NaOH. NaCl and $CaCl_2$ 99%obtained from Merck were used for ionic strength examination. Kiwi shells were washed several times with distilled water to remove all dirt particles. The washing process was continued till the wash water contained no color. The washed shells were then dried in an oven at 50 ◦C for 12 h. The dried material was then ground, using a ball mill. The adsorbent was sieved through 40 mesh size and used without any pretreatment.

Batch adsorption experiments were carried out by shaking 0.5 g of the shells with 25 mL of the aqueous solutions 30 µg mL-1 of Cr(VI) ions in 125 mL stoppered pyrex glass flask, at a fixed temperature. The initial pH of the solutions was adjusted about 2 with diluted HNO3 and the shaking speed was 400 rpm for 20 min. At the end of the adsorption period, the mixtures were filtered out and analyzed for its metal ion concentration using flame atomic adsorption spectrometer. The amount of Cr(VI) ions adsorbed was obtained from equation:

$$q_e = V (C_0 - Ce) / M \qquad (1)$$

where q_e is the amount of adsorbed ion per gram of the adsorbent, C_0 is initial concentration and C_e is the equilibrium concentration of the metal ion (mg L^{-1}) that is obtained from calibration curve and M is the mass of dry adsorbent used (g).

The removal efficiency (%) was calculated as follow:

$$R\% = (C_0 - C_e) / C_0 \qquad (2)$$

3. RESULTS AND DISCUSSION

Effect of the sample pH: Figure 1 shows the effect of pH on percentage removal of chromium. It was observed that the removal of Cr(VI) decreased with increase in initial pH. The maximum removal was occurred at pH about 2.0. Adsorption of Cr(VI) at this pH is due to the bind of the negatively charged chromium species ($HCrO_4^-$) occurred through electrostatic attraction to the positively charged (due to more H^+ ions) surface functional groups of the adsorbent. At higher pH due to more OH^- ions adsorbent surface carrying net negative charges, which tend to repulse the metal anions (CrO_4^{2-})[18]. However, there is also some percentage adsorption at pH >2.0 but the rate of adsorption is reduced. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent or physisorption due to weak undirected Vander Waals forces of attraction [19,20].

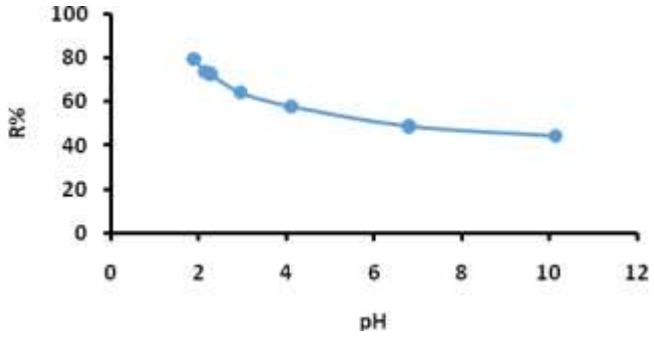

Figure 1. *Effect of pH on removal of chromium (adsorbent: 0.3 g, C_0: 30 µg mL^{-1}, T: 291 K, time: 20 min).*

Effect of adsorbent dosage: Amount of adsorbent is an important parameter, because this factor determines capacity of an adsorbent. The influence of adsorbent dosage on Cr(VI) sorption was studied by varying the amount of adsorbent. Figure 2 depicts that the percentage removal of chromium increased from 56.1% to 92.5% with increase of adsorbent dosage from 0.03 to 0.3 g. This trend is obvious because as adsorbent dose increases the number of adsorbent particle also increases, that makes the greater availability of exchangeable sites for adsorption. 0.3 g of adsorbent was selected for after steps.

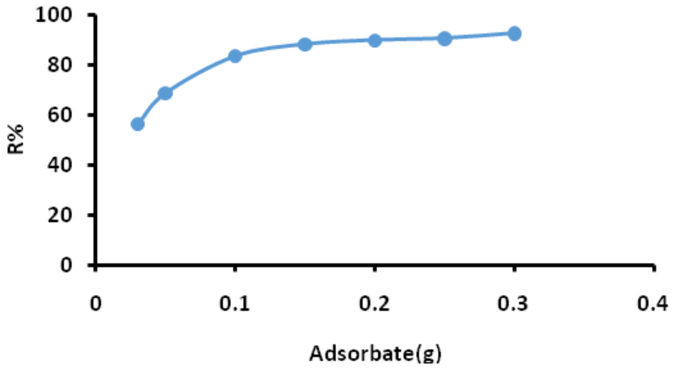

Figure 2. *Effect of adsorbent dosage on removal of chromium (pH~2, C_0: 30 µg mL^{-1}, T: 291 K, time: 20 min)*

Effect of contact time: The data obtained from the adsorption of Cr(VI) ions showed that the adsorption rate was very fast initially; about 78.6% of total Cr(VI) was removed within 5 min. Thereafter, the adsorption capacity remained constant after 20 min. Further increasing the time after equilibrium shows the rate of adsorption becomes almost constant up to the end of the experiment. Thus, 20 min was selected as equilibration time, which was sufficient for the removal of Cr(VI) by this adsorbent.

Effect of initial concentration and adsorption isotherms: The effect of Cr(VI) concentration on the sorption by kiwi shells was investigated with varying solution concentrations (20 to 70 mg/L). With increasing concentration of the solution, qe increased, while R% decreased. At low initial solution concentration, the surface area and the availability of adsorption sites were relatively high, and the metal ions were easily adsorbed and removed. At high initial solution concentration, the total available sites are limited, thus resulting in a decrease in percentage removal of the ions. The increased q_e at high initial concentration can be attributed to enhanced driving force.

Langmuir and Freundlich isotherms have both been used to describe observed adsorption phenomena on the adsorbent. The sorption data of the have been analyzed according to the linear form of the Langmuir isotherm, as represented in Eq. (3)

$$C_e/q_e = (1/Qb) + (1/Q)\ C_e \qquad (3)$$

b is Langmuir constant which is a measure of energy of adsorption and Q is adsorption capacity expressed in mg/g.

The Freundlich equation predicts that the concentration of metal ions on the adsorbent will increase as long as there is an increase in the metal ion concentration in liquid, as represented in Eq. (4)

$$q = K_f\ C_e n \qquad (4)$$

where n is the Freundlich constant, and K_f is the adsorption coefficient, q is the weight adsorbed per unit weight of adsorbent. Taking logs gives Eq. (5).

$$\log q = \log K_f + n \log C_e \qquad (5)$$

The results showed the adsorption processes can be correlated with Freundlich isotherm. The values of constants obtained from intercepted and slope of plots and values of calculated according to Eqs. (3) and (5) are given in Table 1.

Table 1. *Langmuir and Freundlich isotherm constants for biosorption of MB.*

Sorbent	Langmuir isotherm			Freundlich isotherm		
	Q(mg.g^{-1})	b(L. mg^{-1})	R^2	K_f	n	R^2
kiwi shell	6.23	0.018	0.754	0.066	1.33	0.972

Effect of ionic strength: The effect of various amounts of NaCl, $CaCl_2$ and Na_2SO_4 on the biosorption of Cr(VI) was examined. It was seen that the there was no significant decrease in the percent removal efficiency. As, even at high concentration of the salt, the shells still have big percent removal efficiency and can be used to efficiency remove Cr(VI) from aqueous solutions.

Adsorption kinetics: The adsorption kinetics described by the relationship between Cr(VI) uptake and contact time that is discussed below.

In many researches, the adsorption kinetics by plant adsorbents has been tested for the first order expression given by Lagergren. However, Several investigators have shown that pseudo-second-order kinetics can describe the adsorbent-Cr(VI) interactions very well for plant adsorbents [21-23].

The integral form of Lagergren equation is:

$$\log(q_e - q_t) = \log q_e - (k_1 / 2.303)\, t \qquad (6)$$

The pseudo-second-order equation is:

$$(t/q_t) = (1/k_2 \,.\, q_e^2) + t / q_e \qquad (7)$$

where q_t is the amount of solute adsorbed at ‘t’ time (mg/g), q_e is the amount of Cr(VI) adsorbed at equilibrium (mg/g), t is the contact time (min) and k_1 is the adsorption equilibrium rate constant of pseudo-first-order reaction (min^{-1}) and k_2 is the rate constant of pseudo-second-order adsorption ($g\ mg^{-1} min^{-1}$). The slope and intercept of plot of log ($q_e - q_t$) against time were used to determine the first-order rate constant k_1. The calculated values of R^2, $q_{e,cal}$ and $q_{e,exp}$ were presented in Table 2.

It was observed that correlation coefficient (R^2) was low and experimental data are not fitted well for pseudo-first-order reaction. Hence, the adsorption mechanism cannot be well described by pseudo-first-order kinetics. The pseudo-second order rate constant k_2 was calculated from the slope and intercept of the plot t/q_t against time (Figure 3). The $q_{e,cal}$ was very close to $q_{e,exp}$ value and correlation coefficient was high (Table 2). In the view of these results, it can be concluded that the pseudo-second order model provides a good correlation for adsorption of Cr(VI) on kiwi shells.

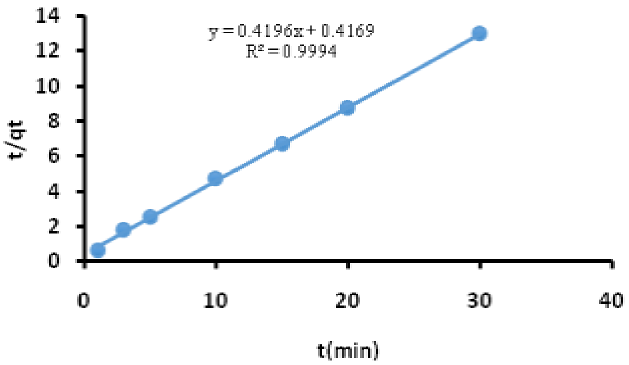

Figure 3. *Pseudo-second order kinetic plot for adsorption of chromium*

Table 2. *Adsorption kinetic constants for chromium adsorption by kiwi Shell.*

Concentration (mg/L)	First-order kinetic model				Second-order kinetic model		
	$q_{e,exp}$ (mg/g)	k_1(1/min)	$q_{e,\,cal}$ (mg/g)	R^2	k_2(1/min)	$q_{e,\,cal}$ (mg/g)	R^2
30	2.31	-0.072	1.93×10^{-7}	0.94	0.423	2.38	0.99

Effect of temperature and thermodynamic parameters: Study of the temperature dependence of adsorption gave valuable knowledge about the enthalpy and entropy changes during adsorption. The removal of Cr(VI) onto adsorbent was examined at 298, 302, 305 and 315 K to determine the adsorption thermodynamic parameters. Adsorption ability of the shells decreased with increasing temperature, illustrating that adsorption of Cr(VI) onto shells is an exothermic process.

The Gibbs free energy change, ΔG0, is fundamental criterion of spontaneity. The biosorption process of Cr(VI) can be summarized by the following reversible process. The apparent equilibrium constant (K_c) of the biosorption is defined as:

$$Kc=(C_0 - C_e)/C_e \qquad (8)$$

where C_e is the concentration of Cr(VI) on the adsorbent at equilibrium. The K_c value is used in the following equation to determine the Gibbs free energy of biosorption.

$$\Delta G^0= - RTlnK_c \qquad (9)$$

The enthalpy (ΔH^0) and entropy (ΔS^0) can be obtained from the slope and ntercept of van 't Hoff equation of ΔG^0 versus T.

$$\Delta G^0= \Delta H^0-T\ \Delta S^0 \qquad (10)$$

R the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K). The obtained ΔG^0 values were -732.18, -514.77, -481.86 and -185.17 J mol^{-1} at 298, 302, 305 and 315 K, respectively. These negative values of ΔG^0 confirm the spontaneous nature of biosorption with high performance of Cr(VI) on the shells. The values ΔS^0 and ΔH^0 were 30.49 J mol^{-1} $K^{-}1$ and -9.78 kJ mol^{-1}, respectively. The positive value ΔS^0 shows the increase in degree of freedom or increase the disorder of adsorption and the negative value ΔH^0 indicates that adsorption process is exothermic.

4. CONCLUSION:

The new biosorbent showed to be a good system for removal of Cr(VI) from aqueous solutions. In comparison with many sorbents equilibrium time is very short (20 min). Adsorption of Cr(VI) on kiwi shells followed pseudo-second order kinetic model. Equilibrium studies showed that the adsorption of Cr(VI) ion onto the new biosorbent followed the Freundlich isotherm model. Negative values of ΔG° for the adsorption of Cr(VI) on kiwi shells indicated that the adsorption process was feasible and spontaneous in nature. Negative value of

ΔH° suggested the adsorption process was exothermic in nature. Positive value of ΔS° described the increase in randomness at the adsorbent-solution interface during the adsorption.

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