

Adsorptive Removal of Chromium (VI) by Papaya Seed from Aqueous Media

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Abstract

Batch adsorptive removal of chromium (VI) from aqueous solution using raw papaya seed powder (RPS) was investigated as a function of pH, equilibrium time, amount of adsorbent and concentration of chromium(VI). Adsorption efficiency is highly pH dependent and the results indicate that the optimum removal was achieved at pH 1. Kinetics and isotherm modeling studies demonstrated that the experimental data best fitted a pseudo-second order and Langmuir isotherm model, respectively. The maximum Langmuir adsorption capacity was found to 106.25 mg/g.

Key Words: *Chromium(VI), Adsorption, Papaya Seed, Isotherm, Kinetic*

Introduction

Chromium is a common and very toxic pollutant introduced into natural waters from a variety of industrial wastewaters. The main industrial sources of chromium in water are leather tanning, electroplating, dyeing, steel fabrication, agricultural runoff. Chromium is also used in explosive, ceramics and photography^{1,2}.

Chromium exists in environment both as trivalent and hexavalent forms of which hexavalent form of chromium is 500 times more toxic than trivalent one. Human toxicity of Cr(VI) includes skin irritation, lung cancer, as well as kidney, liver and gastrum damage². Hexavalent chromium which is primarily present in the form of chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) possesses significantly higher level of toxicity than other valency states³. Cr(VI) ions mostly exists in anionic form at highly acidic medium (pH=1). At pH 2-6 there is equilibrium between the anionic species⁴. Hexavalent chromium has been reported to be carcinogenic. The tolerance limit for Cr(VI) for discharge into inland surface water is 0.1mg/l and potable water is 0.05 mg/l⁵. To comply with the limit, industrial effluents need to be treated to reduce the Cr(VI) to acceptable level.

A number of treatment methods have been reported for removal of metal ions from aqueous solutions. The most commonly employed process of treating waste water containing Cr(VI) include its reduction to trivalent state by addition of reducing agents (e.g. NaHSO_3 and FeSO_4) followed by alkaline precipitation of $\text{Cr}(\text{OH})_3$ ⁶. This method is reliable but requires large settling tanks for precipitation of voluminous hydroxides and subsequent sludge treatment and its disposal. Other methods are ion exchange,

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electrodialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis and adsorption on activated carbon.⁷ But most of these methods suffer from drawbacks due to high capital investment, high operational and maintenance cost and safe disposal of the residual metal sludge. These methods are limited by technical and economical constraints, especially when concentration is below 100 mg/L. In such cases adsorption is promising technique⁸. Adsorption has advantages over the other methods because it is simple in design and requires low operational cost⁹.

Recently, agro wastes containing functional groups associated with proteins, polysaccharides and cellulose as major constituents have been used as adsorbents for the removal of metal ions from aqueous solutions since it offers flexibility in design and operation with the advantages such as: low cost, high efficiency, minimization of sludge, regeneration ability and possibility of metal recovery.^{10, 11} The metal ion binding occurs as a result of physiochemical interactions, mainly ion exchange or surface complex formation between metal ions and the acidic functional groups present on the surface of adsorbent.¹²

The effectiveness of different biological materials such as cactus and pine needles², sphagnum moss peat³, maize bran¹³, saw dust¹⁴, rice husk¹⁵, activated cow dung carbon¹⁶, filamentous algae¹⁷, tamarind hull¹⁸, grape waste¹⁹, moss²⁰, corn cob²¹, coconut husk and palm pressed fibres²², sunflower waste²³, green Moringa tea leaves²⁴, wheat straw and *Eupatorium adenophorum* stem²⁵, rice straw²⁶ towards the adsorption of chromium(VI) from aqueous media have been reported by a number of researchers.

Papaya seed is one of the commonly discarded agro-waste. Papaya seed is composed of lignin and cellulose as major constituents and contain other polar functional groups of lignin, which include alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups. These groups have ability to bind heavy metal ions by donation of an electron pair from these groups to form complexes with the metal ions in solution.²⁷ The use of papaya seeds as adsorbent is very interesting from environmental and economic point of view since it is an agricultural residue that is available at low cost.

In this study, papaya seed from agricultural waste is explored for the adsorptive removal of Cr(VI) from aqueous solution at room temperature.

Experimental Methods

Metal ion solution preparation

Chromium(VI) stock solution was prepared by dissolving predefined amount of an analytical grade, potassium dichromate in distilled water in volumetric flask, so as to achieve concentration of 1000 mg/L. Laboratory distilled water was used for the preparation of standard chromium(VI) samples from the stock solution.

Preparation of Adsorbent

Raw papaya seed collected was washed thoroughly with distilled water to remove dust particles. It was left at room temperature for 1 day to ooze out excess water and was dried in air dry oven at 105 °C for 24 hours. The dried papaya seed was then grinded in to small particle size and was sieved by 212 micron mesh to obtain definite particle size raw papaya seed powder (RPS).

Adsorption experiments and analysis

Experiments were performed in 125 mL reagent bottle in batch mode taking 25 mL, pH adjusted synthetic working solutions of chromium(VI) of predetermined initial concentrations and pre-defined amounts of adsorbent, raw papaya seed powder (RPS), at room temperature. The reagent bottle was shaken in mechanical shaker at speed of 200 rpm to attain equilibrium. The equilibrated solution was filtered using ordinary filter paper and the filtrate was analyzed for the residual concentration of chromium(VI) ions. The metal concentration before and after adsorption were determined by using WPAS-104 Spectrophotometer, at 540nm using 1,5-Diphenyl carbazide solution in acidic medium.²⁸ The pH of each solution was adjusted to the desired value using 0.1 M HNO₃ and 0.1 M NaOH solutions. pH measurements were carried out using pH meter. All experiments were performed in triplicate and average values are reported. Concentration of chromium(VI) retained in the adsorbent at equilibrium (q_e ; mg/g), and the adsorption efficiency (% removal), were computed according to the expressions (1) and (2).

$$q_e = \frac{(C_i - C_e) V}{m} \text{ mg/g} \quad (1)$$

$$\% \text{ Removal} = \frac{(C_i - C_e) 100}{C_i} \quad (2)$$

Where C_i and C_e are the initial and equilibrium or final concentrations of the chromium(VI) in mg/L respectively, V is volume of the chromium(VI) solution taken in litre (L) and m is the mass of the adsorbent in gram(g).

The effect of initial pH, adsorbent dose, contact time, and initial chromium(VI) concentration were investigated by varying any one of the process parameters keeping the others constant.

Results and Discussion

Effect of pH

To evaluate the influence of pH on the sorption process, experiments were carried out at different initial pH. The effect of pH on the sorption efficiencies of chromium(VI) on the raw papaya seed powder is shown in figure 1.

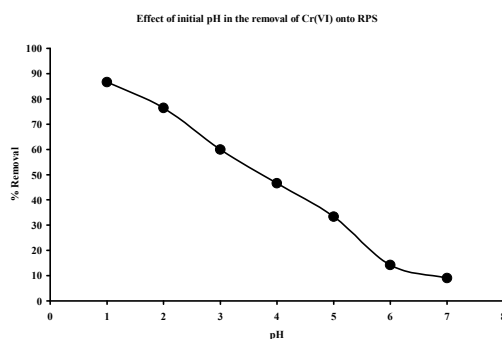


Figure 1: Effect of pH on the adsorption onto RPS.

Removal of chromium(VI) decreased with the increase in pH and the optimum pH for the maximum uptake was found to be 1. The high degree of adsorption at low pH can be explained by the fact that at low pH, Cr(VI) exists in the form of oxyanions such as HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , etc and lowering of pH caused the surface of the adsorbents to be protonated to a greater extent as a result a strong electrostatic attraction exists between the oxyanions of Cr(VI) and the positively charged surface of the adsorbents. As a consequence the uptake increases with decrease in pH of the solution, whereas at high pH adsorbent surface will be negatively charged there by causing hindrance in the adsorption of oxyanions of Cr(VI) resulting in decrease in removal efficiency at high pH, which indicates that sorption of Cr(VI) in aqueous solution through anion sorption mechanism. Similar findings have been reported by others.^{14,29}

Effect of Adsorbent Dose

The effect of adsorbent dose was studied by varying the amount of adsorbent from 25 mg to 150 mg and equilibrated for 24 hours at pH 1 and at initial Cr(VI) ion concentration 5 mg/L. The effect of adsorbent dose on the adsorption efficiency of Cr(VI) by RPS is shown in figure 2 which shows that the adsorption of Cr(VI) was found to be increased with an increase in adsorbent dose initially but adsorption remains almost unchanged after adsorbent dose of 100 mg.

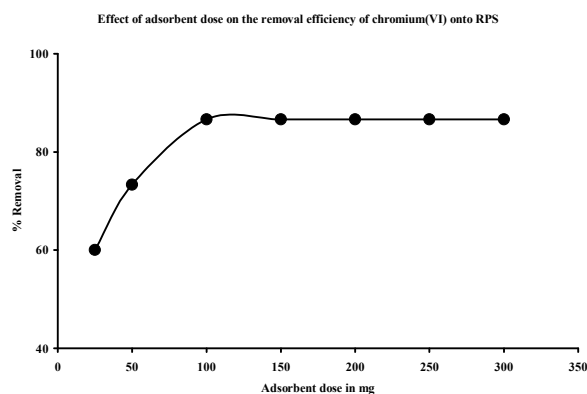


Figure 2: *Effect of adsorbent Dose on the adsorption onto RPS.*

Increase in adsorption with increase in adsorbent doses attributed to the availability of large surface area and more adsorption sites. At low adsorbent dose, the adsorbent surface becomes saturated with Cr(VI) and the corresponding residual Cr(VI) ion concentration in the solutions is large.³⁰

Effect of contact time

The effect of contact time on the adsorption of Cr(VI) was studied by taking 50 mL aliquot of 5 mg/L Cr(VI) solution with 50 mg of adsorbent, and shaking at a speed of 200 rpm in the range 2 to 120 minutes.

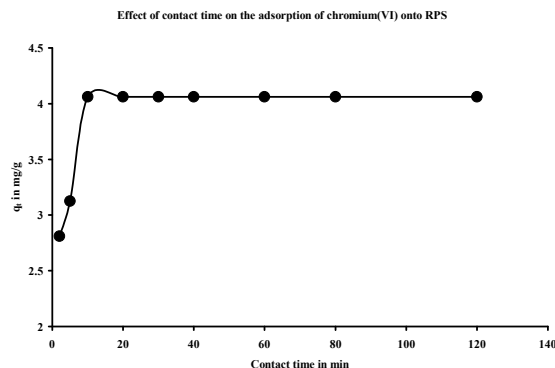


Figure 3: Effect of Contact Time on the adsorption onto RPS.

The equilibrium contact time for adsorption of Cr(VI) on to RPS reached within the first 10 minutes as shown in figure 3. The experimental results showed that the adsorption rate was rapid at first because of the presence of large number of adsorption sites so that large amount of Cr(VI) oxyanions attached selectively to the adsorbent sites initially. The chromium(VI) removal gradually reduced till it attained equilibrium at specific time for the adsorbents beyond which there was no significant increase in adsorption rate due to decrease in active adsorption sites in the adsorbent and after reaching the saturation point adsorption becomes constant. Significant adsorption efficiency of RPS could be attributed to the higher availability of different oxyanion selective surface functional groups.^{27, 30}

Effect of Initial Concentration

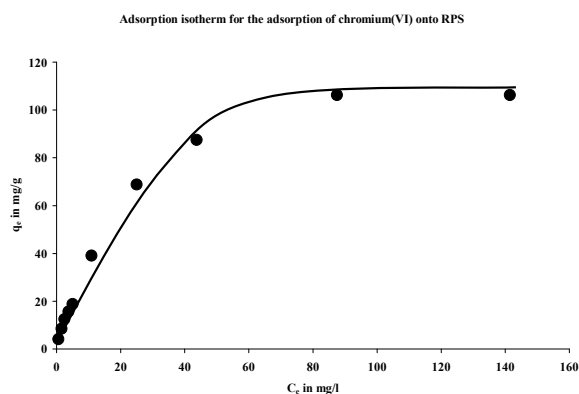


Figure 4: Effect of Initial Concentration on the adsorption onto RPS.

The effect of Cr(VI) concentration is shown in figure 4 which shows that adsorption of Cr(VI) on raw papaya seed powder increases with increase in initial concentration of Cr(VI) solution and attains equilibrium which is attributed to the availability of limited adsorption sites. The increase in concentration of Cr(VI) increases the mass transfer driving force and therefore increases the rate at which Cr(VI) ions pass from the bulk solution to the particle surface that would results in higher adsorption.³¹

It was found that on changing the initial concentration of Cr(VI) from 5 to 250 mg/L the amount adsorbed increased from 4.06 mg/g to 106.25 mg/g at optimum pH 1 signifying that the RPS is effective for the adsorptive removal of Cr(VI) from aqueous solution.

Isotherm modeling

The experimental data for the adsorptive removal of chromium(VI) from aqueous solution was analyzed by using Langmuir and Freundlich isotherm models. The Langmuir isotherm^{32, 33} assumes monolayer adsorption onto a surface with a finite number of identical sites with homogeneous adsorption energy, and its linear form can be expressed as follows:

$$C_e/q_e = 1/q_m b + C_e/q_m$$

Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in (mg/g), C_e is the equilibrium concentration of the adsorbate in mg/L, q_m is the maximum adsorption capacity (mg/g) and ‘b’ is the Langmuir adsorption equilibrium constant 1/mg.

The Freundlich equation^{32, 33} proposes an empirical model that is based on sorption on heterogeneous surface and has the linear form:

$$\log q_e = \log K + 1/n \log C_e$$

Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L); ‘K’ and ‘n’ are Freundlich equilibrium coefficient, which are considered to be the relative indicators of adsorption capacity and adsorption intensity.

Table 1: Results of chromium(VI) adsorption isotherm modeling on RPS.

S.N.	Adsorbent	Langmuir isotherm			Freundlich isotherm		
		q_m (mg/g)	b (L/mg)	R^2	K (mg/g)	$1/n$	R^2
1	RPS	106.25	0.044	0.9931	6.70	0.633	0.9678

Langmuir and Freundlich parameters shown in and table 1 were determined from their respective plots. The values of Langmuir equilibrium parameter between 0 and 1 indicated that equilibrium data fits well with Langmuir adsorption isotherm. The values of 1/n between 0 and 1 indicated that adsorption process was favorable.

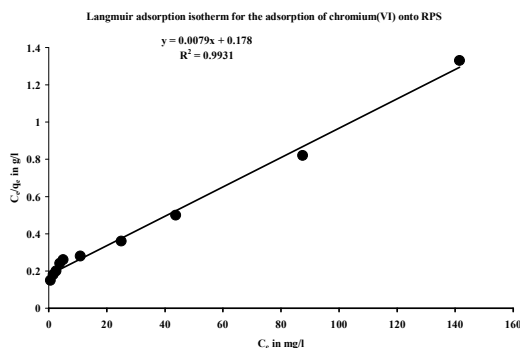


Figure 5: Langmuir Adsorption Isotherm for the adsorption of chromium(VI) onto RPS.

However, the correlation coefficient values for Langmuir isotherms were found to be greater than that of Freundlich isotherms indicating that the adsorption process is better defined by the Langmuir adsorption isotherm model than by the Freundlich, indicating the homogeneous distribution of active sites on the surface of adsorbents. According to the Langmuir adsorption isotherm as shown in figure 5, the monolayer sorption capacity was found to be 106.25 mg/g.

Kinetic Modeling

The kinetics for the adsorption of chromium(VI) onto RPS was analyzed using pseudo-first order^{34, 35}, Pseudo-second order³⁶ models. The linear form of the pseudo first order equation of Lagergren model can be expressed as:

$$\log (q_e - q_t) = \log q_e - K_1 t/2.303$$

Where q_e and q_t is the amount of lead(II) ions adsorbed per gram on surface of adsorbent at equilibrium and at time 't' in mg/g, K_1 is the rate constant of pseudo-first order adsorption (min^{-1}).

The pseudo second order kinetic rate equation can be expressed as:

$$t/q_t = 1/K_2q_e^2 + t/q_e$$

Where, K_2 is the rate constant for pseudo-second order adsorption in ($\text{g mg}^{-1} \text{min}^{-1}$), q_e and q_t are the amount of lead(II) ions adsorbed (mg/g) at any time 't' and at equilibrium time(e) respectively.

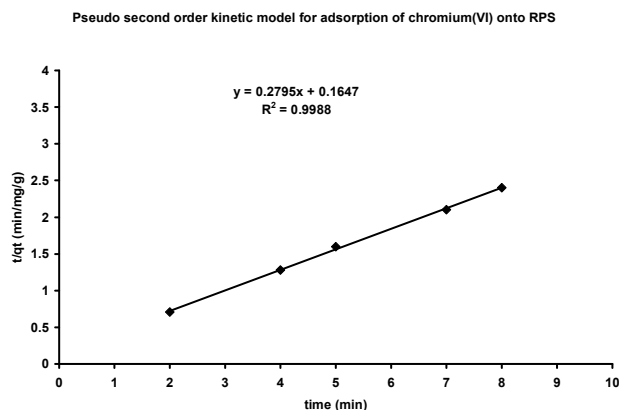


Figure 6: Pseudo second order kinetic model for adsorption of chromium(VI) onto RPS.

The correlation coefficient for pseudo second order was found to be 0.9988 for RPS whereas the correlation coefficient (R^2) for the pseudo-first order was lower than that of pseudo-second order. This fitness of the experimental data to pseudo second order model as shown in figure 6 (plot of t/q_t versus t) implies that the rate – limiting step for the adsorption of chromium(VI) onto RPS may be chemisorptions involving valence forces through sharing or exchange of electrons between adsorbent and chromium(VI) ions.^{36, 37}

Conclusions

Removal of chromium(VI) by using agro biomass raw papaya seed powder (RPS) was investigated. Basic adsorption experiments indicated that the adsorption of chromium(VI) onto RPS was an adsorbate, adsorbent dependent process and the optimum adsorption capacity for RPS was achieved at pH 1, with equilibrium contact time of 10 min, initial concentration of 5 mg/L and adsorption dose of 100 mg. The maximum adsorption capacity was found to be 106.25 mg/g for RPS and results revealed that Langmuir adsorption isotherm model was found to be more applicable than Freundlich adsorption isotherm model for the better description of the adsorption behavior of chromium(VI) ion onto raw papaya seed powder, indicating surface homogeneity. The kinetic data were best fitted by the pseudo-second order kinetic model, which indicated that chemisorptions were the rate – limiting step in the adsorption process. Hence it can be concluded that raw papaya seed powder possesses significant potentiality towards the adsorptive removal of chromium(VI) from aqueous solution.

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