Adsorption, kinetic and isothermal studies of Chromium(VI) using Sapindus seed powder

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Abstract

The heavy metals are a major threat to water bodies as they pollute and make them inhabitable and non-consumable. Adsorption technique has been employed in estimating the metal removal efficiency at a medium level concentration by adopting adsorption isotherms. The aim of this study is to test the possibility of Sapindus as a potential adsorbent of chromium metal from its solution. Batch adsorption experiments have been used to analyze the percent reduction in chromium concentration using Sapindus fruit powder or soapnut powder. Different process variables are investigated like pH, adsorbent concentration, adsorbate concentration and contact time at which considerable reduction of metal in solution can be evaluated.

Keywords: Heavy metals, Sapindus, Adsorption, Isotherms, Chromium

1. INTRODUCTION

Heavy metal accumulation may cause serious health problems such as cancer and brain damage[1]. The discharge of chromium metal into the aquatic ecosystem by the leather tannery industries needs special attention as the maximum permitted concentration in drinking water for chromium is 0.05 mg/L[2].The removal of heavy metal ions using microorganisms, fungi, agricultural waste materials is known as biosorption and is receiving much attention due to its cost effectiveness and efficient removal of pollutants[3]–[5]. In this process, physical and chemical reactions take place simultaneously which allows the biomass to concentrate and bind contaminants to its surface. The origin of biomass, its composition, and processing varies the effectiveness of biosorption[5].

The heavy metal chromium exists in two main oxidation states, that is +6 (Dichromate) and +3 (Chromium trioxide) oxidation states [6]. They are used in various industries like textile dyeing, wood preservation, tanning, stainless steel, electroplating etc [7]. In both the valencies, chromium is known to be carcinogenic. A limited amount of Cr (III) in reduced form can enter cells and damage DNA causing cancer [8]. Cr (VI) in particular, has high oxidative properties which trigger oxidative reactions in bloodstream leading to hemolysis and kidney failure [9].

This study involves a plant material belonging to the genera of *Sapindus*. This tree has many beneficial effects to humans as hair conditioner, insecticide, folk medicine, and for the treatment of lice and dandruff. They have multiple utilities both in the industry and domestic purposes. The plant produces highly valuable soapberries or soapnuts which are about 2cm in diameter and are in spherical shape. Soapnut chemical composition is defined by (10-12%) saponin, 10% sugars and mucilage. The kernel contains 25-30% fatty acids. The oil from the kernel is also used as a biofuel that mixes with about 20% fossil fuels [10].

In this experiment, powdered soapnuts were used as sorbents for adsorbing chromium. The processed soapnut powder was added to a 100ml aqueous solution of chromium heavy metal by varying certain parameters. The concentration of the chromium left unabsorbed in solution was determined spectrophotometrically at 540nm using diphenyl carbazide reagent (DPC) after certain contact time has lapsed. The effect of parameters such as pH, contact time, adsorbent dose and adsorbate concentration on biosorption of chromium heavy metal is studied and reported.

2. MATERIALS AND METHODS

2.1 Preparation of Adsorbent

The soapnuts used in the present study were obtained from local retail store. The soapnuts were powdered using a domestic mixer and boiled several times to remove or reduce saponin content (which is a detergent molecule). The washing process continued till the lather formation reduced to little or no bubbles. The washed soapnut powder was then completely dried and used for adsorption experiments.The Soap Nut Powder of different dosages (2, 3, 5, and 7 g/L) were added each in 4 conical flasks containing 100 mL of Cr (VI) ion solution.

Figure 1 Powdered form of soapnuts

2.2 Preparation of Adsorbate

The heavy metal Cr (VI) ion solution was prepared using potassium dichromate salt (K2Cr2O7). A stock solution of 1000mg/l was prepared by mixing 1.414g of K2Cr2O7 in distilled water. 5ml of nitric acid (1:1) was added to the solution [11]. Different Cr (VI) ion concentrations were prepared by adding 2ml, 3ml, 5ml and 7 ml of stock solution to 100ml distilled water in conical flasks.

2.3 Adsorption Experiment

The adsorption of Cr (VI) from aqueous solution was studied in batch adsorption experiments. Different concentrations of soapnut were added to 100ml of metal solution in a 250ml conical flask.The pH of solutions was adjusted using 0.1N HCl and 0.1N NaOH. The flasks were placed on a gyratory shaker with a constant speed of 100 rpm at 37oC for three and half hours. Samples were collected at periodic intervals, centrifuged at 5000g for 2minutes and the amount of metal in the supernatant was determined spectrophotometrically at 540nm using diphenyl carbazide reagent.

Figure 2 Flasks containing chromium solution along with soapnut powder

2.4 Estimation of chromium

The reagent used for estimating chromium was prepared (0.25% w/v solution of diphenyl carbazide in acetone). 0.25g of DPC (diphenyl carbazide) was weighed and added to 50ml acetone. 15ml of each sample solutions, containing different concentrations of Cr (VI) were pipetted out into 25ml standard flasks. To this 2ml of H2SO4 (3M) was added along with 1ml of diphenyl carbazide and the total volume was made up to 25ml using double distilled water. The obtained solution was mixed and chromium concentration was estimated by the intensity of color complex formed by using a UV-visible spectrophotometer. The absorbance was measured against a reagent blank at a wavelength of 540 nm [12]. A standard graph (Absorbance vs concentration) was used to interpolate absorbance values to obtain the concentration of chromium left in the aqueous solution.

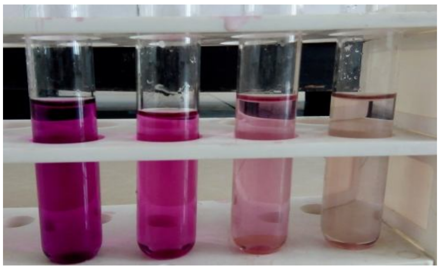

Figure 3 Estimation of reduction in chromium from samples

3. RESULTS AND DISCUSSION

3.1 Effect of pH

The pH of the solution was varied from 2-6 as it is an important factor that controls the oxidation of chromium. Figure 1 shows that pH- 2 is optimal for efficient removal of chromium. With the increase in pH, there was a steady decrease in adsorption phenomenon.

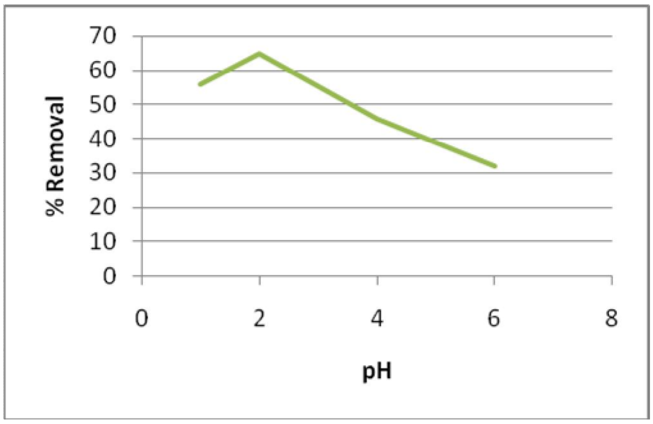

Figure 4 Adsorption of Cr (VI) with increasing pH

3.2 Effect of contact time

At different time intervals (15, 30, 60, and 90mins), the concentration of Cr (VI) ion was estimated. The effect of contact time was studied at initial metal ion concentration of 50mg/L, pH 2 and Soap Nut Powder dosage of 5 g/L. Fig.1 shows a plot of absorbance versus contact time. It can be observed that the percentage of adsorption increased steadily to time 60 minutes. At 90 minutes there was a significant rise in the adsorption percentage till 150 minutes and remained almost equal thereafter. Thus, 150 minutes is chosen as the equilibrium time for removal of Cr (VI) from solution.

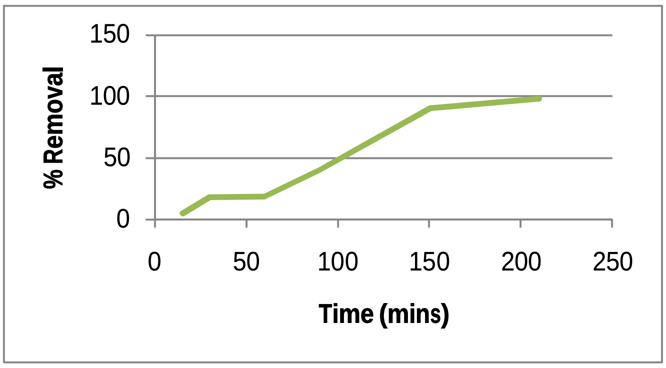

Figure 5 Adsorption of Cr with time

3.3 Effect of initial metal ion concentration

The initial metal ion concentrations were varied for 20, 30, 50 and 70 mg/L and their adsorption was studied for 150mins at fixed dosage of 5 g/L of Soap Nut Powder and pH 2. From fig. 3, it can be inferred that % adsorption was highest for 20 mg/L concentration. The % adsorption reduced at concentration 30 mg/L of Cr (VI) and increased slightly at 50mg/L which is assumed as optimum for adsorption at fixed dosage of 5g/L. Also, it is evident that when the initial metal ion concentration was increased, the time taken to reach equilibrium was longer. While at low initial concentrations the equilibrium time is 150 min.

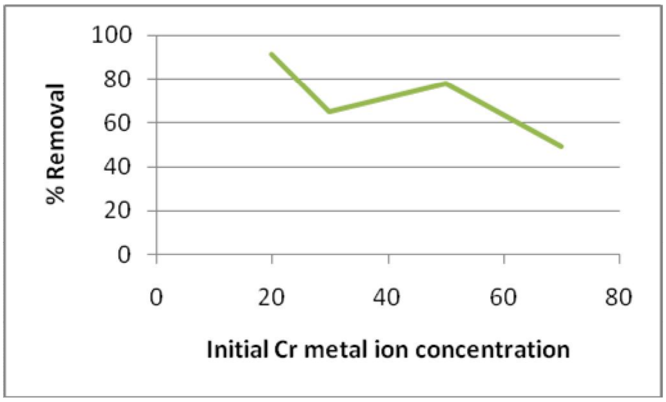

Figure 6 Adsorption of Cr at various concentration levels

3.4 Effect of adsorbent concentration

The effect of adsorbent dosages (soapnut powder) on the removal of Cr (VI) ions from its aqueous solution was carried out at different adsorbent doses ranging from 0.2-0.7 g using 50 mg/L as the fixed metal ion solution concentration ad pH as 2. As shown in fig.4, the graph is a rising curve. The increase in the percentage of adsorption with soapnut powder dosages can be attributed to increase in the surface area while expanding the number of adsorption sites available for adsorption. For higher adsorbent dosages, there may be a decrease in the percentage of adsorption due to the concentration gradient between the adsorbate and adsorbent.

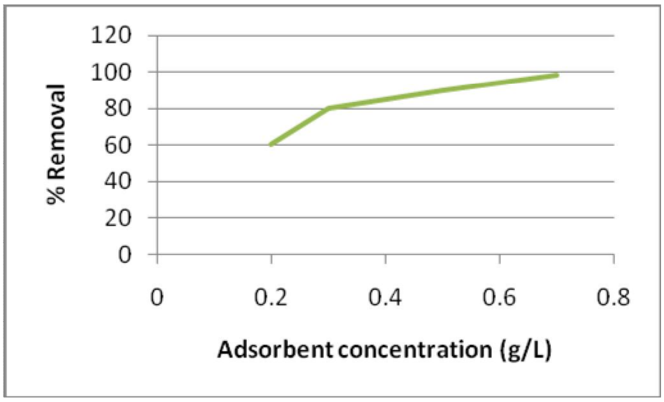

Figure 7 Adsorption of Cr under varying adsorbent concentrations

The line in all plots represents the concentration of Cr reduced due to adsorption phenomenon.

3.5 Equilibrium studies

The linear form of Langmuir equation is given below

$$\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{KLqm} \qquad (1)$$

where C_e (mg/L) is the equilibrium concentration of adsorbate, q_e (mg/g) is the quantity of adsorbed material (mg/g) at equilibrium, K_L is the Langmuir equilibrium constant related to the energy of sorption (L/mg) and q_m is the maximum amount of metal ions per unit weight of adsorbent to form a complete monolayer on the surface bound at high C_e. The isotherm models are used to analyze the equilibrium between Cr (VI) ions on the soapnut powder at a constant temperature. The Langmuir equation is suitable for monolayer adsorption on a homogenous surface with a limited number of identical sites with little or no interactions between the adsorbed species [6]. The values q_m and K_L are determined graphically.

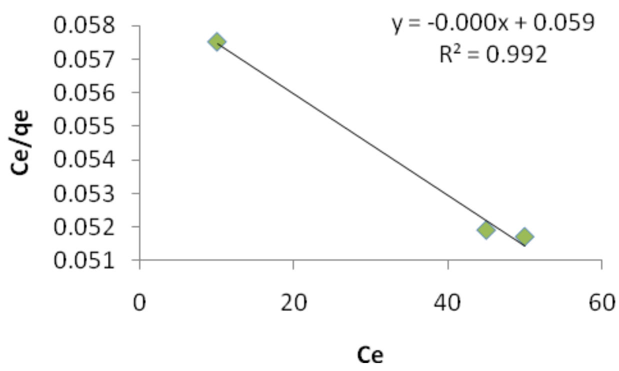

Figure 8 Langmuir adsorption isotherm

The Freundlich equation is given below

$$\text{Log } qe = \frac{1}{n} \text{Log } Ce + \log Kf \qquad (2)$$

where K_f (mg/g) and n (value between 0 and 1) are the Freundlich constants describing the characteristic of the system. K_f and n are indicators for adsorption capacity and adsorption intensity respectively. The Freundlich equation applies to multilayer sorption on a heterogeneous surface and can only be employed in the low intermediate concentration ranges.

The isotherms were plotted by assuming that maximum adsorption corresponds to a saturated monolayer of the solute molecules on the adsorbent surface, no transmigration of adsorbate on the plane of the surface and the molecules adhere with constant energy of adsorption. The plot of Langmuir isotherm from Figure 7 shows a decreasing trend, resulting in a negative slope. These values prove that the adsorption is not favored by Langmuir isotherm, as the slope is supposed to be positive. Whereas, Freundlich isotherm from Figure 8 indicates that the adsorption is favorable as it shows a positive slope.

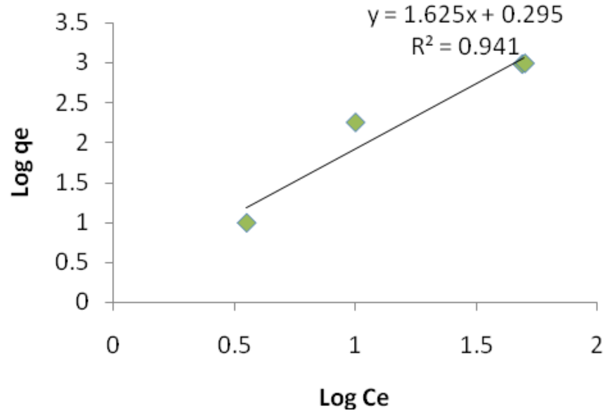

Figure 9 Freundlich isotherm

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Table 1: Isotherm constants for adsorption of Cr (VI) on soapnut surface

1. Langmuir Isotherm			**2. Freundlich Isotherm**		
3. Equation constant		**4.** Correlation coefficient R^2	**5.** Equation constant		**6.** Correlation coefficient R^2
7. q_m (mg/g)	**8.** K_L		**9.** n	**10.** K_f	
11. -500	**12.** 0.0033	**13.** 0.9929	**14.** 0.6153	**15.** 1.976	**16.** 0.9411

3.6 Adsorption kinetics

Kinetic mechanism of the experiment is tested using pseudo-first-order and pseudo second order models. Kinetic data were obtained at regular intervals of 5, 10, 15, 20, 25 and 30 minutes with an initial metal concentration of 50mg/L, an adsorbent dosage of 5g/L and pH 2. Equilibrium time was recorded as 30 minutes.

Pseudo first order equation is expressed as

$$\frac{dq}{dt} = K1(qe - q) \qquad (3)$$

Where, q_e is the amount of chromium adsorbed at equilibrium time (mg/g of adsorbate), q is the amount of metal adsorbed at regular intervals (mg) and K1 is the first-order adsorption rate constant (min^{-1}). Applying the limits, q = 0 at t = 0 and q = q_e at t = t and integrating; equation (3) becomes

$$Log\,(qe - q) = log\,(qe) - K1t \qquad (4)$$

The corresponding plot is presented in Figure 5. As the line possesses a negative slope and does not pass through all the data points, it is concluded that the rate of chromium removal by soapnut powder as adsorbate does not follow the pseudo first order kinetic equation.

The non-linear form of the pseudo-first-order equation is given by

$$\frac{dqt}{dt} = K\,(qe - qt) \qquad (5)$$

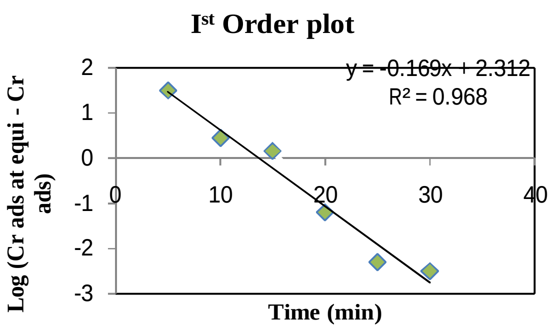

Figure10 First order kinetics

The pseudo second order model predicts the sorption capacity of soapnut over all the range of values. The rate limiting step is expressed as

$$\frac{dq}{dt} = K2(qe - q)^2 \qquad (6)$$

Where K_2 is the second order rate constant (units of g/mg.min). Using the integration limits same as that in the previous case, the integrated form of equation (6) becomes

$$\frac{t}{q} = \frac{1}{k2qe2} + \frac{t}{qe} \qquad (7)$$

The plot of equation 7 resulted in a straight line with a positive slope as shown in Figure 6.

The non-linear equation in integrated form for second order kinetics is given by

$$q = \frac{qe2\,K2t}{(1+qe2K2t)} \qquad (8)$$

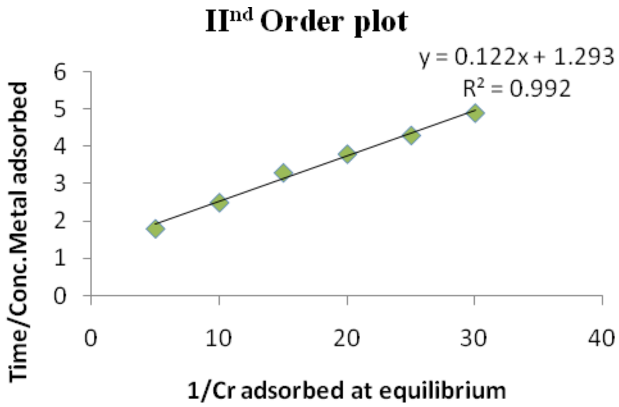

Figure 11 II order kinetics

By linear regression of the first order and second order plots, kinetic coefficient q, kinetic constant K, and coefficient of determination R^2 are obtained which are presented in Table 2.

Table 2: Kinetic coefficients

Pseudo-first-order		Pseudo-second-order	
q_{e1}	2.3127	q_{e2}	7.408
K_1	-0.1692	K_2	0.01696
R^2	0.9682	R^2	0.9923

Second order kinetics gave a reasonable fit with a coefficient of determination R^2 being equal to 0.9923. Its corresponding kinetic coefficient q_e is 7.408 and coefficient K_2 0.01696.

4. CONCLUSION

The equilibrium level of factors at 80% chromium removal are: contact time of 150 minutes, pH of 2, metal (adsorbate) concentration 50mg/L and a maximum soapnut powder (adsorbent) concentration. The adsorption of chromium on soapnut powder followed Freundlich adsorption isothermand it favored pseudo-second-order kinetics. The results indicated that *Sapindus* can be used as acheap bio-adsorbent for the removal of Cr (VI) from wastewater. *Sapindus*is a better alternative to traditional filters or other biofilters as they are low-cost alternatives and perform better.

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