



Studies on Removal of Cr (VI) From Aqueous Solutions Using Powder of Mosambi Fruit Peelings (PMFP) As a Low Cost Sorbent

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Abstract: The powder of mosambi fruit peelings (PMFP) was used as an adsorbent for the removal of heavy metal like Cr (VI) from aqueous solutions was studied using batch tests. The influence of physico-chemical key parameters such as the initial metal ion concentration, pH, agitation time, adsorbent dosage, and the particle size of adsorbent has been considered in batch tests. Sorbent ability to adsorb Cr (VI) ions was examined and the mechanism involved in the process investigated. The optimum results were determined at an initial metal ion concentration was 10mg/lit, pH=2, agitation time –60min, an adsorbent dose (150 mg/50ml) and the particle size (0.6mm). The %adsorption, Langmuir constants [$Q_0=7.51(\text{mg/g})$ and $b=1.69(\text{mg/lit})$] Freundlich constant($K_f=2.94$), Lagergren rate constants($K_{ad}(\text{min}^{-1})=5.75 \times 10^{-2}$) for [Cr(VI)] 10 mg/lit were determined for the adsorption system as a function of sorbate concentration. The equilibrium data obtained were tested using Langmuir, Freundlich adsorption isotherm models, and the kinetic data obtained were fitted to pseudo first order model.

Keywords: Adsorption, pH, Powder of Mosambi Fruit Peelings (PMFP), Adsorption Kinetics and isotherm, Lagergren rate constant.

Introduction

Chromium is omnipresent in the environment occurring in air, rocks, soil, water and biological materials. Chromium is most commonly found in trivalent state, but hexavalent compounds are also found in small quantities. The trivalent form is an essential nutrient for man required in amounts of 50-200 $\mu\text{g/day}$ whereas the hexavalent form is carcinogenic to man and animals. It ranks 21st in abundance among all elements with an average

concentration of 100 ppm chromium enters the environment through natural and anthropogenic sources. Among natural sources, volcanic emissions, biological cycling and weathering of soils and rocks contribute as much as 10^5 tones of chromium per annum. The anthropogenic sources include, burning of oil and coal, production of ferrochromium, chromate chromium steels, fungicides, cement, pigments, catalysts, and oxidants. It is also used in metal plating, tanneries, and oil well drilling. These sources annually release 10^6 tones of chromium in the form of fly ash, industrial effluents, particulates, dust and fumes into air, soil and water. Phytoremediation of chromium contaminated water environments was tried by several authors using plant species possessing hyper-accumulative properties. The adsorption mechanism between Chromium ions and *L. hexandra* biomass was best studied using infrared spectroscopy. Acylamide, carbonyl, amino, carboxy and hydroxyl groups were found to act as ligands to immobilize the chromium ions¹ were the first to study the kinetics that play a very important role in the adsorption kinetics. The size of the particles and quantity of adsorption are inversely proportional. As the size of the particles decrease the adsorption of heavy metals increase. The need for effective and economical removal of toxic heavy metals from sewage and industrial waste resulted in for a search of non conventional methods and materials. The extent and pace of contamination had increased alarmingly since last century as a result of rapid industrialization.^{2,3} reviewed the literature on non-conventional adsorbents for the removal of dyes and heavy metals from waste waters. In an effort to evolve a useful user-friendly, eco-friendly and economical process, the present study was taken up. The present study includes the adsorption studies on Chromium (VI) using powder of mosambi fruit peelings. The efficiency of this adsorbent was studied and maximum adsorption and lowest equilibrium time for this adsorbent was recorded.

Experimental

Powder of Mosambi Fruit Peelings (PMFP)

Easy availability, economical to use and proven potential for other metals, have been the reasons for selection of these adsorbent Powder of Mosambi Fruit peelings (PMFP) was used to adsorb chromium (VI). Mosambi fruits are very famous in India. They are citrus family members and are popularly called as sweet limes. It is the first choice of many Indians as fruit juice. The peelings of the fruits were collected from the shops, dried and chopped, cleaned and soaked in distilled water for 24 hrs. The soaked pieces of peelings were sun-dried and powdered. Size of the particles selected for the study was 0.6 mm.

Measurement of pH of the adsorbent

Five grams of adsorbent powder was taken into a 1000 ml beaker. To this 150ml of freshly boiled and cooled water was added and then heated to boiling. The contents were digested for ten minutes and kept for ten minutes. The solution was filtered and pH was measured. The metal ion solutions for standard solutions and further dilutions were prepared by the following procedures described in reference⁴.

Analysis of Chromium (VI)

Chromium(VI) was estimated using UV – visible spectrophotometer (ELICO-SL 150) by Diphenyl Carbazide (DPC) method. Different dilutions of Cr(VI) solutions containing less than 30 mg /lit of chromium concentrations were added with 2.5 ml of Diphenyl Carbazide

solution. The diphenyl carbazide solution was prepared by dissolving 200 mg of 1.5 diphenyl carbazide in 100 ml of 95% alcohol. The contents were mixed with an acid solution of 40 ml of concentrated H₂SO₄ and 360 ml of distilled water. The contents were refrigerated for not less than 24 hrs, and to a maximum of one month. The absorbance was measured in the UV – visible spectrophotometer at 540 nm. The reagent blank was also measured following the same procedure. A calibration curve was prepared for Cr (VI) standard solutions and absorbance. The concentration in the sample was established by reading from the calibration curve. The results for a heavy metal concentration were expressed in mg/lit while those of the concentration equilibrium, equilibrium time, and adsorption capacity etc., were compared with the Langmuir and Freundlich isotherms.

The Langmuir isotherm was expressed in the following formula

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (1)$$

Where C_e was the equilibrium Concentration (mg/l) q_e was the amount adsorbed at equilibrium time (mg/g) and Q₀ and b are Langmuir constants related to adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. The equilibrium parameter R_L that was given⁵ by:

$$R_L = \frac{1}{1 + bC_i} \quad (2)$$

Where C_i is the initial concentration (mg/l) and b is the Langmuir constant. The interpretations are made using the standard Table 1.

Table 1.

Sl. No.	R _L	Type of isotherm
1	R _L > 1	Unfavorable
2	R _L = 1	Linear
3	0 < R _L < 1	Favorable
4	R _L = 0	Irreversible

The Freundlich isotherm is generally used for mathematical description of adsorption in aqueous system and describes heterogeneous surface energies. The equation is expressed in logarithmic form as:

$$\log x / m = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

Where (x/m) was the amount adsorbed in mg/lit), C_e was the equilibrium concentration (mg/l) and K_f and n were Freundlich constants. K_f [mg/g, L/mg] was the capacity of the adsorbent and n indicated the favorability of adsorption. The kinetics of Cr(VI) adsorption followed the first order rate. Equation given by Lagergren was:

$$\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303} t \quad (4)$$

Where q and q_e were the amounts of metal ion adsorbed (mg/g) at time t (min) and at equilibrium time, respectively and K_{ad} was the rate constant of adsorption (min^{-1}).

Batch Equilibrium Method

All experiments were carried out at (27°C) in batch mode. Batch mode was selected because of its simplicity and reliability. The experiments were carried out of taking 50 ml metal ion sample and known amount of the adsorbent in a 100 ml Stoppard conical flask. The flasks were agitated at 160 rpm for predetermined time intervals using a mechanical shaker at room temperature (27°C). Control experiments were conducted without adsorbent to given correction for metal ion adsorption on the walls of the container.

Results and Discussion

The Characteristics of PMFP is discussed in the table 2.

Table 2. Characteristics of PMFP.

S. No	Parameter	Value
1	Apparent Density (g/ml)	1.5673
2	Moisture Content % (w/w)	70.90%
3	Loss on ignition % (w/w)	95.80
4	p ^H	4.69
5	Particle size (MM)	0.6mm
6	Calcium as Ca	1.04
7	Lignin Content % (w/w)	7.3
8	Cellulose % (w/w)	2.9

Effect of pH

Studies were carried out to obtain optimum pH for the adsorption of Chromium (VI) using 150 mg of PMFP adsorbent in 50ml solution of 10mg/lit of Cr (VI) concentration adjusted to different pH values from 2.0 to 9.0. The solutions after equilibrium were centrifuged and analyzed for Cr (VI) content. The results obtained were presented in (Figure 1). It was evident from the figure.1, that maximum removal of 91.28% was achieved at pH 2.0 and the per cent removal was found to be almost constant after pH range 6 to 9. In the absence of adsorbent, precipitation started at pH greater than 6.0 and in the presence it started at 7.0. Since the aim of the work is to study only the adsorption phenomenon, it was decided to maintain pH value at 2.0 for all further experiments⁶. Many reports revealed that maximum adsorption of Cr (VI) are in the pH range of 2-6. The results obtained for the adsorption of Cr (VI) on powder of Mosambi fruit peelings adsorbent are in good agreement with the removal of Cr (VI) by saw dust and pine leaves⁷ at pH 2.0.

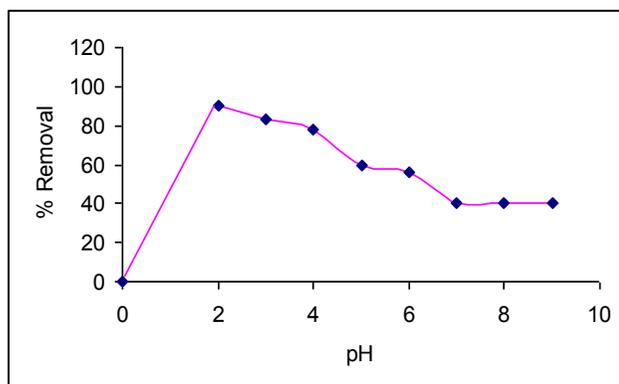


Figure 1. Relationship between pH and % removal of chromium (VI)

Effect of Equilibrium Time and Initial Cr (VI) Concentration

Equilibrium experiments were carried out by agitating 50ml of different concentration of Cr (VI) solutions (10-30 mg/lit) adjusted to pH 2.0 along with 150 mg of PMFP adsorbent. After equilibrating for different time periods, the solutions were centrifuged and analyzed for chromium (VI) content. Cr (VI) adsorption as a function of time and different concentrations were shown in Table 3. It was evident from the table that the solutions equilibrated for 80 minutes showed maximum adsorption and the equilibrium time was independent of initial ion concentration. The rate of uptake was rapid in the beginning and became slow in the later stages and reached saturation. This is due to the fact that the metal ion occupied the sites in a random manner because of maximum availability of sites, as the time passed, the active sites were blocked and hence the rate decreased. For maximum removal of Chromium (VI) by the adsorbent, the solutions should be equilibrated for 60 min irrespective of the initial concentration. The amounts of chromium (VI) adsorbed were 3.04, 5.03 and 6.62 mg/g for Cr (VI) concentrations of 10, 20 and 30mg/lit, respectively.. The formation of monolayer of Cr (VI) ions on the outer surface of the adsorbent is suggested based on the observation that the curves shown in (Figure 2). Were single, smooth and continuous. The equilibrium time observed in this experiment was equal with that observed for chromium adsorption by other adsorbents like activated soya bean hull⁸ and rice husk ash⁹.

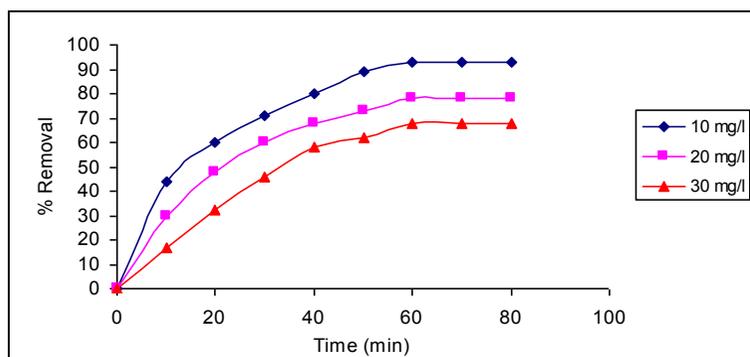


Figure 2. Relationship between agitation time and %removal of Chromium (VI).

Table 3. Adsorption of Cr (VI) at different agitation times at different concentration.

Agitation time in minutes	Concentration of Chromium (VI) in mg/l								
	10 mg/lit			20 mg/lit			30 mg/lit		
	Amount of Cr(VI) adsorbed q (mg/lit)	qe-q	% Removal	Amount of Cr(VI) adsorbed q (mg/lit)	qe-q	% Removal	Amount of Cr(VI) adsorbed q (mg/lit)	qe-q	% Removal
10	1.43	1.61	43.16	1.98	3.05	29.80	1.78	4.84	17.89
20	2.00	1.04	60.12	3.10	1.93	46.58	3.25	3.37	32.55
30	2.38	0.66	71.68	3.87	1.16	58.14	4.61	2.01	46.16
40	2.67	0.37	80.11	4.39	0.64	65.90	5.59	1.03	55.96
50	2.89	0.15	86.78	4.78	0.25	71.79	6.18	0.44	61.80
60	3.04	-	91.28	5.03	-	75.46	6.62	-	66.23
70	3.04	-	91.28	5.03	-	75.46	6.62	-	66.23
80	3.04	-	91.28	5.03	-	75.46	6.62	-	66.23

Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption of Cr (VI) was studied by varying amounts of the adsorbent from 25-200 mg. The adsorbent was added to 50ml of Cr (VI) solutions of concentration 10 mg/lit and equilibrated for 60 min. After equilibrium time, the solutions were centrifuged and analyzed for Chromium (VI) content. The results shown in Table 4 reveal that 100% adsorption was possible with 200mg of adsorbent dose.

Table 4 . Quantity of chromium (VI) adsorbed and % removal at different doses of adsorbent.

Adsorbent dose mg/50ml	% Removal	Equilibrium Concentration Ce (mg/lit)	Amount Adsorbed mg/g
25	26.80	7.32	5.36
50	47.65	5.24	4.76
75	62.80	3.72	4.18
100	75.50	2.45	3.77
125	85.10	1.49	3.40
150	91.20	0.88	3.04
175	96.30	0.37	2.75
200	100.00	0.00	2.50

From the (Figure 3). It was also evident that, an increase in adsorbent dose increased the percent Cr (VI) removal and a complete removal was possible with a dose of 200 mg/50 ml of Cr (VI) concentration 10mg/lit. This was attributed to an increase in number of binding sites as the dosage of adsorbent increased.

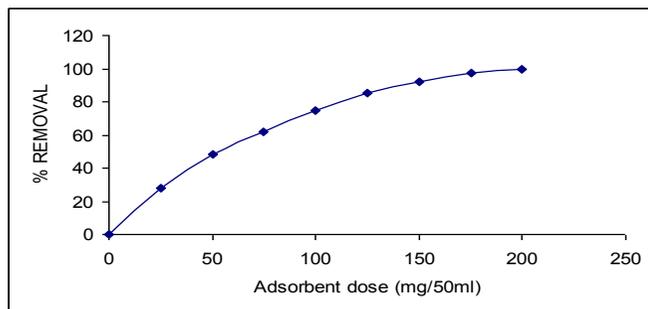


Figure 3. Relationship between adsorbent dose (mg/50 ml) and % removal of chromium (VI).

Effect of Particle Size

To study the effect of particle size, adsorbent particles of sizes 0.6 mm, 0.8 mm and 1.7 mm were used. In each study 150 mg of adsorbent in 50 ml of 10 mg/lit of Cr(VI) solution was agitated to equilibrium time of 60 min, the adsorbent was separated and the supernatant solution was analyzed for chromium concentration and the values are noted in Table 5, the amounts adsorbed for 0.6 mm, 0.8 mm and 1.7 mm particle size were 3.01, 2.66 and 2.34 mg/g, respectively. It is evident from (Figure 4). That increase in particle size decreased the percent removal. At a fixed adsorbent dosage, the decrease in particle size increases the metal uptake. The increase in the uptake by smaller particles was due to the greater accessibility to pores and to the greater surface area for bulk adsorption per unit mass of the adsorbent. Similar trend had been observed on removal of Cr(VI) by using *Pitchellobium dulce* Benth – A Kinetic Study¹⁰

Table 5. Adsorption of chromium (VI) on different particle sizes (mm) of the adsorbent.

Agitation time in minutes	Particle size in mm								
	0.6 mm			0.8 mm			1.7 mm		
	Amount of Cr(VI) adsorbed q (mg/lit)	qe-q	% Removal	Amount of Cr(VI) adsorbed q (mg/lit)	qe-q	% Removal	Amount of Cr(VI) adsorbed q (mg/lit)	qe-q	% Removal
10	1.33	1.68	40.18	1.13	1.53	34.20	0.94	1.40	28.40
20	2.09	0.92	62.75	1.75	0.91	52.50	1.47	0.87	44.22
30	2.48	0.53	74.69	2.12	0.54	63.85	1.82	0.52	54.74
40	2.77	0.24	83.11	2.43	0.23	72.95	2.08	0.26	62.50
50	2.94	0.07	78.02	2.60	0.06	78.02	2.21	0.13	66.46
60	3.01	-	90.58	2.66	-	80.05	2.34	-	70.13
70	3.01	-	90.58	2.66	-	80.05	2.34	-	70.13
80	3.01	-	90.58	2.66	-	80.05	2.34	-	70.13

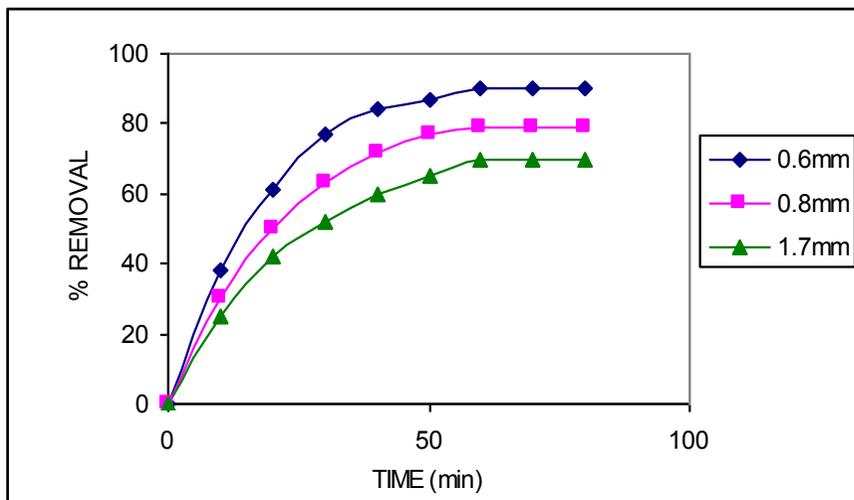


Figure 4. Relationship between particle size, % removal at different times.

Adsorption Isotherm

The data for Langmuir adsorption isotherm was presented in Table 6. It was fitted well in Langmuir adsorption isotherm. The Langmuir constants Q_0 and b calculated from the slope and intercept of the plot of C_e/q_e Vs C_e from (Figure 5) are 7.51(mg/g) and 1.69(L/g) respectively.

Table 6. Langmuir adsorption isotherm calculations for different initial concentrations.

Initial Concentration C_i (mg/lit)	C_e (mg/lit)	Q_e (mg/g)	C_e/q_e (g/lit)
10	0.872	3.04	0.286
20	4.908	5.03	0.975
30	10.130	6.62	1.530

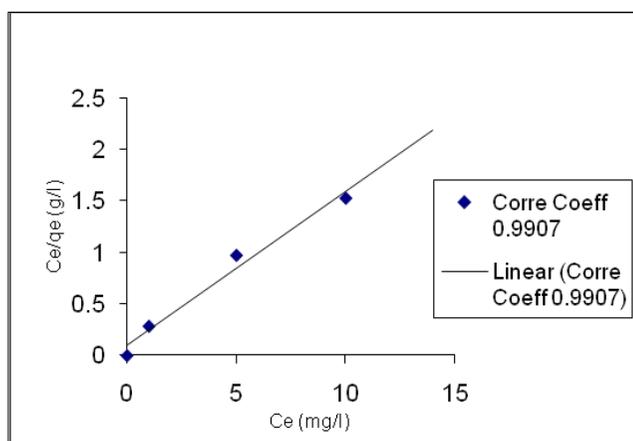


Figure 5. Langmuir adsorption isotherm for equilibrium concentrations and initial concentration.

Comparison of these values with the literature data ¹¹ indicated that Q_0 obtained for powder of mosambi fruit peelings - adsorbent was less than that of Q_0 (91.64 mg/g) obtained for Bengal Gram Husk. The characteristic equilibrium parameter R_L of Langmuir isotherm was calculated and the values of 0.055, 0.028 and 0.019 for the metal ion concentration of 10, 20 and 30 mg/l, respectively and all the values were between zero and one indicating the favorable adsorption of chromium on the adsorbent. The plot of $\log(x/m)$ Vs $\log C_e$ indicated in (Figure 6). Was linear, indicated that adsorption data obeyed Freundlich adsorption isotherm. The Freundlich constant K_f was 2.94 which is compared with the value of Bengal gram husk (2.81). According to ¹² the value of n between 2 and 10 indicates good adsorption. The calculated value of n for the adsorption of Cr(VI) is 3.41, showing very good efficiency for chromium adsorption by powder of mosambi fruit peelings adsorbent

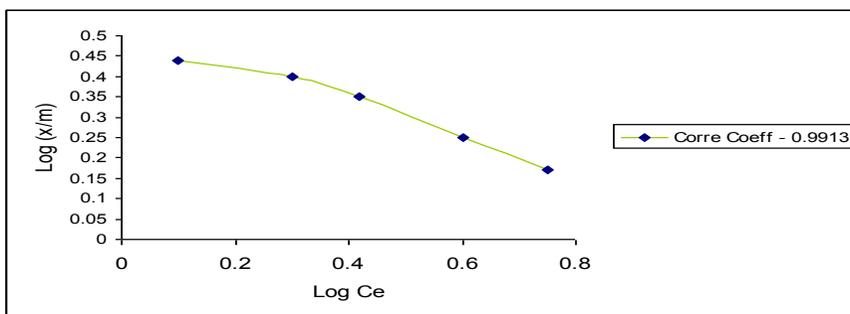


Figure 6. Logarithmic relationship between adsorption and equilibrium adsorption.

Adsorption Kinetics

The adsorption data were fitted in the Lagergren equation (4). The straight line plots of $\log(q_e - q)$ Vs time for Chromium (VI) Concentrations of 10,20 and 30mg/l, are shown in(Figure 7). The rate constants of adsorption K_{ad} determined from the slope of the plots are given in Table 7. From this table it is evident that the initial concentration did not have much significant effect on rate constant.

Table 7 . Calculated values of the rate constant for different concentrations of Cr(VI).

Cr(VI) (mg/lit)	Rate Constant K_{ad} (min^{-1})
10	5.75×10^{-2}
20	6.05×10^{-2}
30	5.91×10^{-2}

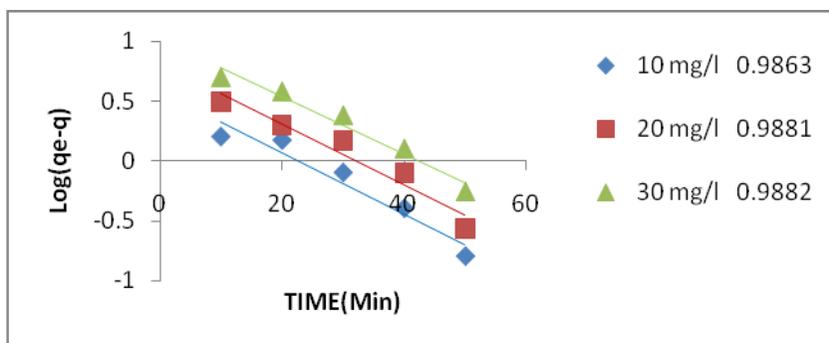


Figure7. Relationship between adsorption and time as per Lagergren equation.

Effect of Particles Size on Lagergren Rate Constant

The effect of particle size on the rate of adsorption was shown in (Figure 8). And the rate constant K_{ad} values calculated are given in Table 8. For the adsorption of Cr (VI), increase in particle size from 0.6 mm to 1.7 mm decreased the rate of adsorption from 6.01×10^{-2} to $4.37 \times 10^{-2} \text{ min}^{-1}$. The higher rate of metal uptake by smaller particles was due to greater accessibility to pores and greater surface area for bulk adsorption per unit weight of the adsorbent¹³ have stated that the breaking up of larger particles to form smaller ones opens some tiny sealed channels that will be available for adsorption and therefore the rate of uptake by smaller particles was higher than that larger particle.

Table 8 . Lagergren rate constants calculated for different particle sizes (mm).

Particle size (mm)	Rate Constant K_{ad} (min^{-1})
0.6	6.01×10^{-2}
0.8	5.21×10^{-2}
1.7	4.37×10^{-2}

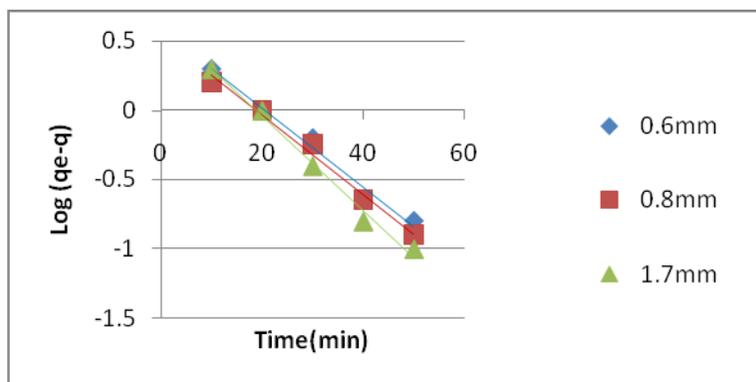


Figure 8. Relationship between different particle size and time of adsorption.

Conclusions

A) In this study the heavy metal, namely, chromium (VI) was selected for removal from aqueous solutions using adsorption technique. Batch experiments were conducted to study the impacts of particle size, pH, agitation time, adsorbent dose and initial metal ion concentrations. A particle size of 0.6 mm was observed to be highly efficient for chromium (VI). A decrease in the size of the particle increased the adsorption, as a decrease in size of the particle increased the availability of the number of active sites. The increase of pH showed a negative impact on the adsorption of chromium (VI). Maximum adsorption was recorded at pH 2.0 for Cr (VI). An increase in the adsorbent dosage gave increased adsorptions for chromium, whereas the adsorption decreased with increase of initial metal ion concentrations.

B) The adsorbent selected for the present study proved to be good adsorbent which was evident with the adsorption data obeying the Langmuir and Freundlich isotherms. The Langmuir capacities for chromium (VI) are 8.86; 7.51 and 5.68 mg/g, by PMFP. Freundlich adsorption Capacities K_f for Cr (VI) is 3.46, 2.94 and 1.46 by PMFP. The equilibrium parameter R_L in Langmuir isotherm and n values in Freundlich Isotherm indicated that the

adsorption of Cr (VI) on PMFP was favorable. The kinetics of the adsorption of the metal ions also obeyed Lagergren equation.

C) The present study provides available and economic procedure(s) for the removal of heavy metal like Cr (VI) using the aforesaid adsorbents. The procedure using powder of mosambi fruit peelings may be given a thought for removal of metals like Cr (VI) in small and medium scale industries for developing countries. Heavy metal removal with the above adsorbent appears to be technically feasible, user-friendly, eco-friendly and economical process and with high efficacy.

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