

Adsorption Studies of hexavalent Chromium Ion from Aqueous Solution Using Lenus Esculent (Masoor)

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Research Article

Abstract: The use of masoor seedhusk as a low-cost adsorbents was investigated for the replacement for currently costly methods of adsorption Cr (VI) ions from aqueous solutions. Batch adsorption studies showed that masoor seedhusk was able to adsorb Cr (VI) ions from aqueous solution. The effect of contact time, effect of initial concentration, effect of adsorbent dose, effect of salt, effect of temperature, effect of pH etc. have been reported. Equilibrium data were analyzed using the Langmuir Freundlich isotherms whereas the adsorption kinetic data were evaluated by the pseudo-first-order and pseudo-second-order kinetic models. The results obtained indicate that the adsorption of Cr (VI) on masoor seed husk is better at lower metal ion concentration and higher adsorbent dose. The maximum adsorption capacity was found to be 95.15% which was obtained at 5 mg/L. Cr (VI) ion concentration and 10gm/l adsorbent dose. pH 7.1 was chosen as the optimum pH and better adsorption occurred at 302k temperature. The results demonstrated that masoor seed husk have potential to be employed as the adsorbent for the adsorption of Cr (VI) metal ions from aqueous solution.

Keywords: Chromium; masoor seed husk; adsorption; isotherm; aqueous solution; kinetics; thermodynamic parameters.

1. Introduction

The presence of toxic heavy metals in industrial effluent has become a matter of environmental concern, chromium (VI) is known to be one of the heavy metals and widely used in many industries including leather tanning, explosives, ceramics, photography, wood preservatives [1,2] paints and pigments [3]. Disposal of untreated effluent in these industries contains a considerable amount of Cr (VI), which spreads into the environment through soil and water streams and accumulates along the food chain, resulting in a high risk to human health, as high concentration of chromium will cause dermatitis, allergic skin reactions ulceration of intestine. It is also reported to be carcinogen to animals [4]. As Chromium does not degrade biologically, the control of chromium pollution has special importance for both organisms that live in water and those that benefit from water. The removal of heavy metals from industrial

effluent has several advanced techniques to decrease their impact on the environment such as physicochemical, biological and thermal processes. A physicochemical technique includes adsorption, coagulation, chemical precipitation, ultra filtration, etc. Among of these methods adsorption is the most effective and economical because their relative low cost. In recent years different bio-adsorbents were developed from agro-wastes and used for heavymetals removal such as maize leaf [5], bajra powder [6], rice husk [7], sawdust [8], pine bark [9], sugar beet pulp [10], wood and bark [11], tea-waste [12], and papaya seeds [13]. Bio-adsorbent which produced from agro-wastes may act as a significant material for Chromium adsorption. Masoor seed husk is an agro useless waste material. It is an abundant, readily available, low cost and, eco-friendly bio-material considering the above criteria, masoor seed husk was selected to prepare the Bio-adsorbent. The main aim of this research was to determine potentially and adsorption capacity of masoor seed husk as bio-adsorbent. The present study aimed to investigate the efficiency of masoor seed husk as adsorbents for the adsorption of Cr (VI) from aqueous solutions. Experiments were conducted to investigate the effect of contact time, effect of initial concentration, effect of adsorbent dose, effect of salt, effect of temperature, effect of pH etc. on adsorption efficiency of Cr (VI) by masoor seed husk. Adsorption equilibrium and kinetics had been studied under the optimum adsorption conditions. The Langmuir and Freundlich adsorption isotherms were applied to evaluate the adsorption properties in the batch technique. In addition, the pseudo-first and pseudo-second order kinetic model were also applied to examine the kinetics of the adsorption process.

2. Materials and methods

2.1 Materials

The stock solution of chromium was prepared by dissolving 0.2828 gm. of potassium dichromate (K₂Cr₂O₇) in one liter distilled water and used for all experiments with required dilution. All the chemicals used were of A. R. grade from M/S S. D. Fine Chemicals Ltd, Mumbai.

2.2 Preparation of Adsorbent

Masoor seeds were collected from local market and soaked in distilled water up to 24 hrs. Remove the husk of seeds from its pulses and dried in the absence of sunlight. The dried material was grind to fine powder and passed through sieves of different sizes. Powder obtained of 60 mesh size was kept in an air tied bottle for experimental uses.

2.3 Batch adsorption experiments

Batch adsorption studies were carried out using glass stoppard conical flask, the pH of the solution was adjusted with 0.1N HCl and 0.1N NaOH solutions by using Elico-digital pH meter model No.615 with combined glass electrode. The conical flask containing sample solution and adsorbent was shaken for the required time period with a mechanical stirrer. The experiments were carried out at room temperature (302 K) except while studying the temperature effect. After the appropriate time the contents of the flask were filtered and amount of chromium metal ion was determined using diphenylcarbazide by spectrophotometrically(Elico-minispec-171 model).

To examine the effect of pH, adsorption experiments were conducted at different pH ranging from 2 to 11 at 5 mg/L of Cr (VI) solution. The optimum pH was determined from this study [14] .The adsorption studies were also conducted in batch experiments as a function of adsorbed dose 0.5 to 2.0 gm. metal ion concentration 5,10,15, and 20 mg/L.

The percentage of Cr (VI) ion adsorption by masoor seed husk computed using equation,

$$\text{Percentage adsorption} = \frac{(C_0 - C_t)}{C_0} * 100(1)$$

Where, C₀ is the initial concentration of Cr (VI) metal ions (mg/L), and C_t is concentration of Cr (VI) metal ions at any time t in solution.

Adsorption capacity was calculated by using the mass balance equation for the adsorbent

$$q = \frac{V(C_0 - C_t)}{M}(2)$$

Where, q is the adsorption capacity(mg/ g), C₀ is the initial concentration of Cr (VI) metal ions (mg/L), and C_t is concentration of Cr (VI) metal ions at any time t in solution. V is the volume of Cr (VI) metal ion solution (L) and M is the weight of the adsorbent (gm).

3. Result and Discussion

3.1 Effect of contact time

The adsorption of the Cr (VI) metal ions by masoor seed husk was studied at various time intervals (0 to 35 min.).100 ml,5 mg/L concentration of Cr (VI) metal ion solution was taken in different conical flask and each flask adds one gm. of adsorbent, then filtered after 5,10,15,20,25,30,35min.time intervals respectively. The filtrates were then analyzed using spectrophotometer. The amount of metal ions adsorbed was calculated for each sample, and graph is plotted percentage adsorption capacity against time. It is shown in <Fig.1>.

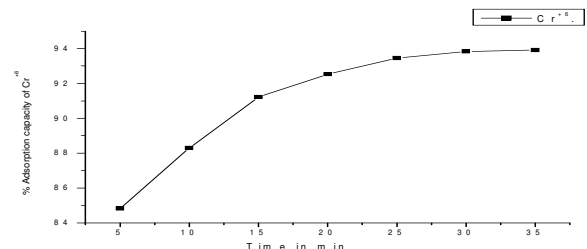


Fig.1. Effect of contact time. [Initial conc. = 5 mg/L., Adsorption dose = 1.0 gm., Temperature = 302 K, pH = 7.1]

3.2 Effect of adsorbent dosage

The adsorption studies of Cr (VI) metal ions at temperature 302 K by varying the quantity of adsorbent from 0.5 to 2.0 gm. while keeping the concentration of the metal ion solution constant at pH = 7.1. The influence of adsorbent dosage on percent adsorption capacity of Cr(VI) metal ions is shown in <fig.2>

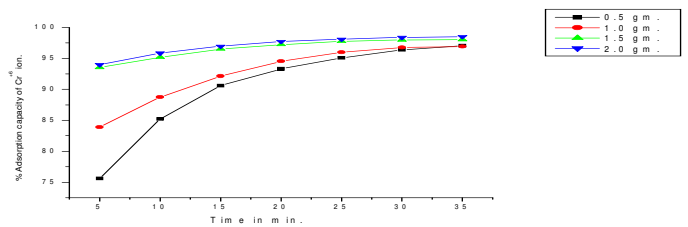


Fig.2 Effect of adsorbent dose. [Initial conc. = 5 mg/L., Temp. = 302 K, pH = 7.1]

The result from fig.2 indicates that the adsorption increase with the increase in the dose of the adsorbent. The increase in the percentage adsorption capacity is due to the increase in active sites on the adsorbent and thus making easier penetration of the Cr (VI) metal ions to the adsorption sites.

3.3 Effect of initial concentration of metal ion

In batch technique the initial concentration of metal ion in the solution plays a vital role on driving force to overcome the mass transfer resistance between the solution and solid phase. The effect of initial ion concentration of metal ion ranging from 5 mg/L to 20 mg/L on masoor seed husk was studied by taking different concentrations of Cr (VI) metal ion solution at pH 7.1 while keeping the adsorbent dose 0.5 gm.,100ml.volume of Cr (VI) metal ion solution constant

and temperature at 302⁰K. Thus the result is shown in <Fig.3>

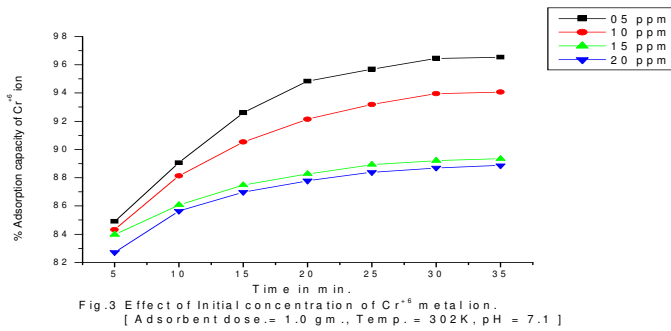
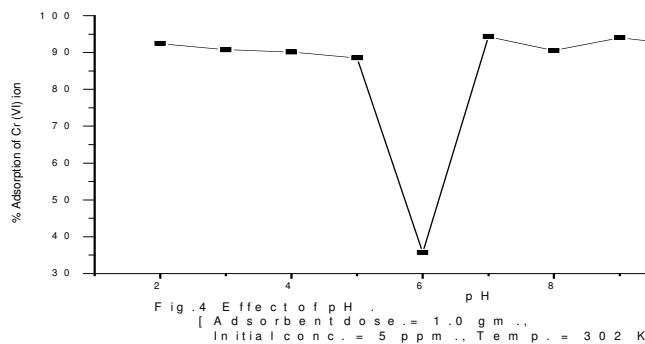


Fig.3 shows that the percent adsorption capacity decreases with increase of initial metal ion concentration. As the result of the above observations it is conclude that the adsorption process of Cr (VI) metal ion on masoor seed husk to be dependent on initial concentration of metal ion solution up to some extent.

3.4 Effect of pH

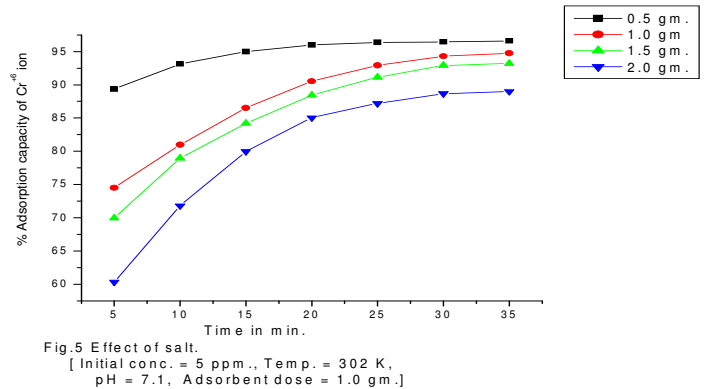
The effect of pH on adsorption of Cr(VI) metal ion was studied by mixing of 5 mg/L Cr (VI) metal ion 50 ml. solution with 0.5 gm of adsorbent at different pH values (2 to 11) undertemperature 302 K. The pH was adjusted with 0.1M NaOH or 0.1M HCl solutions and measured by pH-meter. It is shown in <Fig.4>. It indicates that the percentage adsorption capacity of Cr (VI) ions decreases within increase in pH up to 6.0 and at 7.1 pH percentage adsorption capacity increased, after that percentage adsorption capacity decreases with increase in pH



3.5 Effect of salt

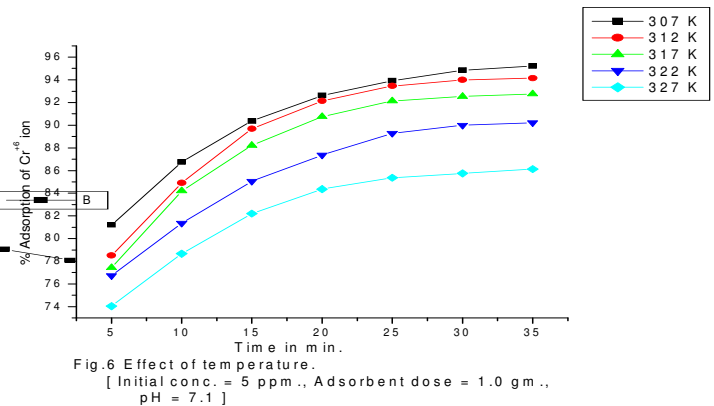
Experiments had been carried out using KCl of different concentration ranging from 0.5 gm. to 2.5 gm. Increase in salt concentration decrease the percentage adsorption capacity of Cr (VI) metal ion with increasing ionic strength, adsorption capacity decreased due to screening of the surface charges. The percentage

adsorption capacity of Cr (VI) ion is 96.69% by the addition of 0.5 gm salt, while the addition of 2.5 gm of salt the percentage adsorption capacity of Cr (VI) is 90.83%. Thus it shows that the percentage adsorption capacity of Cr (VI) metal ion is less at 0.5gm.of salt than the 2.5 gm of salt. The graphical representation is shown in < fig.5 >



3.6 Effect of temperature

The temperature dependence of Cr (VI) metal adsorption on husk of massore were examined over a temperature range of 302 to 327 K. It is shown in <Fig.6>



The results show that the percentage adsorption capacity of Cr (VI) metal ions decreases with increase in temperature.

The Gibb's free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes for the adsorption were determined by using equation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

$$\log \left(\frac{q_e m}{C_e} \right) = \frac{\Delta S^\circ}{2.303R} + \frac{-\Delta H^\circ}{2.303RT} \quad (4)$$

For the adsorbent concentration is unity (m = 1.0 gm) equation (4) becomes

$$\log \left(\frac{q_e}{C_e} \right) = \frac{\Delta S^\circ}{2.303R} + \frac{-\Delta H^\circ}{2.303RT} \quad (5)$$

Where, q_e is the amount of Cr (VI) ion adsorbed per unit mass of husk (mg/g), C_e is the equilibrium concentration (mg/L) and T is the temperature in K. $\frac{q_e}{C_e}$ is called adsorption affinity. The values of Gibbs's free energy (ΔG°) has been calculated by knowing the enthalpy of adsorption (ΔH°) and entropy of adsorption (ΔS°) and (ΔG°) was obtained from a plot of $\log(\frac{q_e}{C_e})$ versus $1/T$, from equation (4) and (5). Once these two parameters were obtained, (ΔG°) is determined from equation (3). In present study ΔG° values are negative, which indicates exothermic nature of adsorption. <Table.1>

Table 1: Thermodynamic parameters for the adsorption of Cr (VI) metal ion at different Temperatures

Temp ^o K	- (ΔG°) KJ / ^o K/ mole	- (ΔH°) KJ / ^o K/ mole	(ΔS°) KJ / ^o K/ mole
307	39.0619	20.4281	0.0607
312	39.3654	-	-
317	39.6688	-	-
322	39.9723	-	-
327	40.2758	-	-

3.7 Analysis of adsorption isotherm

The equilibrium study is important for an adsorption process as it shows the capacity of the adsorbent and describes the adsorption isotherm to express the surface properties and affinity of the adsorbent. In the present study the equilibrium data for Cr (VI) metal ion adsorption on masoor seed husk were evaluated by the Langmuir and Freundlich adsorption model.

3.8 Langmuir isotherm

The Langmuir isotherm is based on assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface, the energy of adsorption is constant there is no transmigration of adsorbate in the plane of the surface [15]. The data of the equilibrium studies for adsorption of Cr (VI) ions on husk follow the following form of Langmuir model.

$$\frac{c_e}{q_e} = \left(\frac{1}{Q_0}\right) * C_e + \frac{1}{bQ_0} \quad (6)$$

Where, C_e is the equilibrium concentration (mg/dm³), q_e is the amount of Cr (VI) ions adsorbed at equilibrium (mg/g). Q_0 and b are Langmuir constants related to adsorption capacity (mg/g) and energy of adsorption (dm³/mg). The values of Q_0 and b can be obtained from slope and intercept of a Plot $\frac{C_e}{q_e}$ versus C_e , respectively. < Table.2>

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L) which is given by following equation [16,17].

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

Where, b is the Langmuir isotherm constant and C_0 is the initial concentration of Cr (VI) metal ions. The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [14]. In the present investigation R_L values observed to be 0.00943 at initial concentration 5 mg/L, which indicates adsorption is favorable. <Table.3> and < Fig.7 >

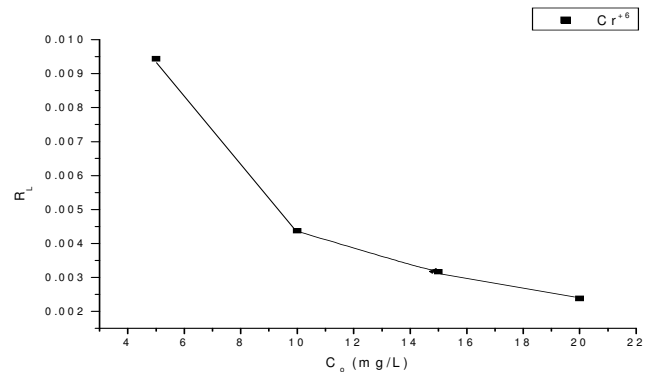


Fig.7 Plot of R_L values against initial concentration (C_0) of Cr(VI) ion.

3.9 Freundlich isotherm

The Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces and multilayer adsorption. It is expressed by the following equation,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (8)$$

For the analysis of Freundlich isotherm, a linear graph of $\log q_e$ against $\log C_e$ was plotted by reform to equation (8). The Freundlich constants n and K_f were determined from the slope and intercept of the plot respectively. The value of n between 2-10 indicates good adsorption [18]. The equilibrium data was also analyzed in the light of Langmuir adsorption model. <Table.3>

The constant n indicates the bond energies between metal ions and the adsorbent, where as K_f (mg/L) is related to bond strength [19]. From <Table.3> the Freundlich constant, $\frac{1}{n}$ denoting the intensity of adsorption indicates a favorable adsorption since $\frac{1}{n} < 1$ [20,21] the adsorption of Cr (VI) ions on masoor seed husk studied have been more favorable.

Table 2: Isotherm parameters for the adsorption of Cr (VI) metal ion

Langmuir isotherm			Freundlich isotherm		
Q_0 (mg/g)	b (L/mg)	R^2	K_f (mg/L)	n	R^2
211.5641	21.0075	0.975	281.8383	0.31	0.960

Table 3: R_L Values at different Initial Concentrations of Cr (VI) metal ion

Initial Concentration of Cr (VI) metal ion, C_0 (mg/L)	R_L Value
5	9.43×10^{-3}
10	4.37×10^{-3}
15	3.16×10^{-3}
20	2.37×10^{-3}

3.10 Analysis of adsorption kinetics

The study of adsorption kinetics is important in describing the adsorption process as it explains how fast the process occurs and also provides information on the factors affecting the adsorption rate. The adsorption of Cr (VI) ions on masoor seed husk at different contact time is shown in <Fig.1>. Figure indicates that the adsorption increased with increase in contact time, the adsorption occurred rapidly at first 15 minutes followed by slower adsorption phase after this the metal ion adsorption during the rapid phase was amounted to be around 83.0% and adsorption of the remaining Cr metal ions continued in the slower phase until the adsorption achieved almost 95.61% after 35 minutes.

Different models can be used to analyze the kinetics of the adsorption process. The pseudo-first-order

and pseudo-second-order kinetic equations of Lagergren are the most widely used for the adsorption of solutes from liquid solution [22]. The linear form of the pseudo-first-order and pseudo-second-order kinetic models can be represented by equation (9) and (10) respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303R} t \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

Where, q_t and q_e are the amount of Cr metal ion adsorbed (mg/g) at contact time t (min) and at equilibrium. k_1 and k_2 are the equilibrium rate constant for the pseudo first order (min^{-1}) and pseudo second order adsorption (g/mg min) respectively.

From the pseudo first order equation, a graph of $\log(q_e - q_t)$ versus t gave a straight line with slope $-\frac{k_1}{2.303R}$ and intercept $\log q_e$, and from pseudo-second-order equation; a graph of $\frac{t}{q_t}$ versus t gave a straight line with slope $\frac{1}{q_e}$ and intercepts $\frac{1}{k_2 q_e^2}$. Adsorption rates were calculated from the slope and intercept the calculated values of k_1 , k_2 , and q_e values are given in <Table.4>.

Table 4: Parameters of kinetic models for the adsorption of Cr (VI) metal ion on husk of masoor seeds

Initial Dye Conc. (ppm)	q_e expt. (mg/g)	First order Kinetic model			Second order kinetic model		
		q_e cal (mg/g)	k_1 (min^{-1})	R^2	q_e cal (mg/g)	$k_2/10^{-4}$ (g/mg.min)	R^2
5	483.82	81.2830	0.1425	0.982	492.2471	4.7437	0.999
10	968.41	149.6236	0.2142	0.969	975.6097	2.2840	0.999
15	1452.62	172.9816	0.0347	0.911	1369.8630	2.1316	0.999
20	1837.06	169.8244	0.0087	0.925	1813.2366	1.6008	0.999

4. Conclusion

This work clearly indicates the potential of using masoor seed husk as an excellent adsorbents for the adsorption of Cr (VI) metal ions from aqueous solutions. The optimum pH was found as pH 7.1 for the adsorption of Cr (VI) metal ions by masoor seed husk. The Langmuir adsorption isotherm was best fitted to the experimental data with a maximum adsorption capacity of 211.56 mg/g., this confirms that the monolayer adsorption process. Adsorption kinetics of Cr (VI) metal ions adsorbed on masoor seed husk followed by the pseudo-second-order kinetic model, where the chemisorption process may be the rate limiting step in the adsorption process. The values of (ΔG°) , (ΔH°) , and (ΔS°) results shows that masoor seed husk has potential as an adsorbent for adsorbing Cr (VI) metal ion. This study shows that masoor seed husk has high potential to be

employed as an effective adsorbent in adsorbing Cr (VI) metal ions and would be useful for the design of wastewater treatment plants for toxic heavy metal ions removal.

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