

Removal of Toxic Metal Cr(VI) from Industrial Wastewater Using Sawdust as Adsorbent: Equilibrium, Kinetics and Regeneration Studies

Suresh Gupta, ¹B. V. Babu

Lecturer, Chemical Engineering Group, Birla Institute of Technology and Science (BITS),

Pilani- 333031, Rajasthan, India, Email: sureshg@bits-pilani.ac.in

¹Dean-Educational Hardware Division & Professor, Chemical Engineering Group, Birla Institute of Technology and Science (BITS), Pilani, -333031, Rajasthan, India.

Phone: +91-01596-245073 Ext. 259 / 212, Fax: +91-01596-244183.

Email: bvbabu@bits-pilani.ac.in ;

Homepage: <http://discovery.bits-pilani.ac.in/discipline/chemical/BVb/>

¹Corresponding Author

Abstract

Chromium is abundant in nature and has a dominant presence in most of the effluent streams as compared to other heavy metal ions. The presence of highly toxic and carcinogenic hexavalent chromium (Cr(VI)) in effluent streams is a major environmental issue. The electroplating and tannery industry effluents are the major source for the Cr(VI) production in wastewater streams. The present work deals with the determination of Cr(VI) removal capacity from synthetically prepared industrial effluent of electroplating and tannery industries using sawdust which is a low cost adsorbent. In the present study, batch experiments are carried out for an initial Cr(VI) concentration ranging from 50 – 500 mg l⁻¹. Experimental results demonstrate that the sawdust adsorbent has a significant capacity for adsorption of Cr(VI) from wastewater streams. The effect of various parameters such as pH, contact time, adsorbent amount, and initial Cr(VI) concentration for the adsorption of Cr(VI) on sawdust is investigated. The maximum adsorption of Cr(VI) on sawdust is obtained at pH 1. The equilibrium time obtained is 1050 min for Cr(VI) adsorption on sawdust. The equilibrium data for the adsorption of Cr(VI) on sawdust is being tested with various adsorption isotherm models such as Langmuir, Freundlich, Redlich-Peterson, Koble-Corrigan, Tempkin, Dubinin-Radushkevich and Generalized equation. The Langmuir isotherm model is found to be most suitable for the Cr(VI) adsorption using sawdust. The maximum adsorption capacity obtained using the Langmuir isotherm model is 41.5 mg g⁻¹ at pH 1. The dimensionless equilibrium parameter, R_L , signifies a favorable adsorption of Cr(VI) on sawdust adsorbent and is found to be between 0.00453 and 0.0435 ($0 < R_L < 1$). Various kinetic models such as pseudo first-order, second order and Elovich model are used to evaluate the mechanism of adsorption of Cr(VI) on sawdust. The adsorption process follows second order kinetics and the corresponding rate constants, for initial Cr(VI) concentration ranging from 100 – 400 mg/l, is found to be 3.39×10^{-3} to 4.3×10^{-4} g mg⁻¹ (min⁻¹). Desorption of Cr(VI) from sawdust using acid and base treatment exhibit higher desorption efficiency by more than 95%. A feasible solution is proposed, for the disposal of contaminant (acid and base solutions) containing high concentration of Cr(VI) obtained during desorption process. The present work also includes the effect of

interference of other ions which are generally present in electroplating and tannery industrial effluent streams on the Cr(VI) removal.

Keywords: Adsorption; Hexavalent Chromium; Sawdust; Kinetics; Adsorption Isotherm; Desorption; Regeneration; Interferences

1. Introduction

The most common forms of chromium are trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) which are commonly used in various industrial processes. Cr(VI) is also used in various other industries such as electroplating, glass, ceramics, fungicides, rubber, fertilizers, tanning, mining, metallurgical etc. [1-8]. Its ability to react with other elements makes hexavalent chromium a health hazard. Cr(VI) is highly mobile and is considered acutely toxic, carcinogenic and mutagenic to living organisms, and hence more hazardous than other heavy metals [9-14]. Therefore, it is necessary to eliminate Cr(VI) from the environment, in order to prevent the deleterious impact of Cr(VI) on ecosystem and public health. Because of stricter environmental regulations, a cost effective alternate technology for the treatment of Cr(VI) contaminated wastewater is highly desired by the industries [15].

Therefore, there is a dire need of a treatment method for Cr(VI) removal from wastewater which is simple, effective and inexpensive [16]. Adsorption when combined with an appropriate step of desorbing the Cr(VI) from adsorbent and avoiding the problem of disposal of adsorbent is a cost effective and versatile method for the removal of Cr(VI) [17]. The advantages of the adsorption process prompt to extend the use of other materials with structural, compositional or chemical characteristics suitable to make this technique with high Cr(VI) retention values and thus it has high potential for the Cr(VI) removal from wastewater streams [12]. It means that the selection of an adsorbent is a key factor for the use of adsorption as a treatment technique for Cr(VI) removal. The cost associated with commercial adsorbents make adsorption process very expensive which has led to the search for new strategies for developing low-cost materials with a good capacity for Cr(VI) removal [18-20].

The objective of the present study is to investigate the possible use of sawdust as an alternate adsorbent material for removal of Cr(VI) from wastewater. Batch experiments are carried out for kinetic studies on the removal of Cr(VI) from aqueous solution. The influence of various important parameters such as pH, time, adsorbent amount, and initial Cr(VI) concentration is investigated. The Langmuir, Freundlich, Redlich-Peterson, Koble-Corrigan, Tempkin, Dubinin-Radushkevich and Generalized equation models are used to fit the equilibrium isotherm models. Pseudo first-order, second-order and Elovich kinetic models are used to evaluate the mechanism of adsorption. In the present study, the desorption of Cr(VI) is proposed using acid and base treatment. The interference of other ions present in the wastewater generated in electroplating and tanning industries is studied on the removal of Cr(VI).

2. Materials and Methods

2.1. Adsorbent

Sawdust is collected from the institute workshop (BITS – Pilani). It is washed repeatedly with distilled water to remove dust and soluble impurities. Sawdust is kept for drying at room temperature in shade for 8 h.

2.2. Preparation of Cr(VI) solutions

All the chemicals used are of analytical grade. A stock solution of 1000 mg l⁻¹ of Cr(VI) is prepared by dissolving 2.8287 g of 99.9% potassium dichromate (K₂Cr₂O₇) in 1000 ml of distilled water. This solution is diluted as required to obtain standard solutions containing 50-500 mg l⁻¹ of Cr(VI). pH adjustment is carried out by using 0.5 N HCl and 0.5 N NaOH solutions.

2.3. Batch Experiments

The batch experiments are carried out in 100 ml borosil conical flasks. A specific amount of sawdust (adsorbent) is added in 25 ml of aqueous Cr(VI) solutions, and then stirred for a predetermined period (found out from kinetic studies) at 30⁰C in water bath-cum-mechanical shaker. Afterwards, the resultant solution is filtered using filter paper. Adsorption isotherm study is carried out with different initial concentrations of Cr(VI) ranging from 50 to 500 mg l⁻¹ while maintaining the adsorbent amount of 10 g l⁻¹. The effect of pH is studied at 30⁰C with an initial Cr(VI) concentration of 50 mg l⁻¹. The influence of time on Cr(VI) adsorption is studied at 30⁰C with initial Cr(VI) concentration ranging from 100 – 400 mg l⁻¹ with an adsorbent dosage of 10 g l⁻¹. The effect of adsorbent amount is studied by varying the adsorbent amount from 4 – 24 g l⁻¹ with Cr(VI) concentration of 50 mg l⁻¹ at 30⁰C.

2.4. Measurement of Cr(VI) concentration in Aqueous Solutions

The concentration of free Cr(VI) ions in the effluent is determined spectrophotometrically by developing a purple-violet color with 1,5-diphenyl carbazide in acidic solution as a complexing agent [21]. The absorbance of the purple-violet colored solution is read at 540 nm after 20 min.

2.5. Adsorption Isotherm Models

Various adsorption isotherm models such as Langmuir [22], Freundlich [23], Redlich-Peterson [24], Koble-Corrigan [25], Tempkin [26], Dubinin-Radushkevich [27], Generalized equation [28] are available in literature, a brief description of which is given below.

2.5.1. Langmuir Isotherm

The Langmuir isotherm is used to obtain the maximum adsorption capacity produced from complete monolayer coverage of adsorbent surface. The isotherm equation gives the fractional coverage (θ) in the form, as given by Eq. (1):

$$\theta = \frac{q_e}{Q_m} = \frac{bC_e}{1 + bC_e} \quad (1)$$

where, b is adsorption equilibrium constant (l mg⁻¹) that is related to the apparent energy of adsorption and Q_m is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent (mg g⁻¹) and q_e is the amount adsorbed on unit mass of the

adsorbent (mg g^{-1}) when the equilibrium concentration is C_e (mg l^{-1}). Eq. 1 can be rearranged to get the linear form, as given by Eq. (2):

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right)C_e \quad (2)$$

which shows that a plot of (C_e/q_e) vs. C_e should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium. The slope and the intercept of this line then give the values of constants Q_m and b .

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L [29], also known as the separation factor, given by Eq. (3):

$$R_L = \frac{1}{1 + bC_e} \quad (3)$$

The value of R_L lies between 0 and 1 for a favorable adsorption, while $R_L > 1$ represents an unfavorable adsorption, and $R_L = 1$ represents the linear adsorption, while the adsorption operation is irreversible if $R_L = 0$.

2.5.2. Freundlich Isotherm

For adsorption from solution, the Freundlich isotherm is expressed as given by Eq. (4):

$$q_e = K_f C_e^{n_F} \quad (4)$$

where, K_f ($\text{mg}^{1-1/n} \text{l}^{1/n} \text{g}^{-1}$) is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, and n_F is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient. The Freundlich coefficients can be determined from the plot of $\log q_e$ versus $\log C_e$ on the basis of the linear form of equation as given by Eq. (5):

$$\log q_e = \log K_f + n_F \log C_e \quad (5)$$

2.5.3. Redlich-Peterson Isotherm

Redlich-Peterson isotherm contains three parameters and is improvement over the Langmuir and the Freundlich isotherms. It can be described by Eq. (6):

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (6)$$

where A , B and g ($0 < n < 1$) are the Redlich–Peterson parameters.

2.5.4. Koble-Corrigan Model

Koble-Corrigan Model is another three-parameter empirical model for representing equilibrium adsorption data. It is a combination of the Langmuir and Freundlich isotherm models and is given by Eq. (7):

$$q_e = \frac{aC_e^n}{1 + bC_e^n} \quad (7)$$

where, a , b and n are the Koble-Corrigan parameters, respectively.

2.5.5. Tempkin isotherm

The nonlinear form of Tempkin equation is given by Eq. (8) [30]:

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad (8)$$

Eq. (8) can be linearized as given by Eq. (9)

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (9)$$

where, $B_T = (RT)/b_T$, T is the absolute temperature in Kelvin and R is the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. The constant b_T is related to the heat of adsorption, A_T is the equilibrium binding constant (l min^{-1}) corresponding to the maximum binding energy [31]. The slope and intercept from a plot of q_e versus $\ln C_e$ determines the isotherm constants A_T and b_T .

2.5.6. Dubinin–Radushkevich (D–R) isotherm

The nonlinear form of D-R equation is given by Eq. (10) [32]:

$$q_e = Q_m \exp(-K\varepsilon^2) \quad (10)$$

Eq. (10) is represented in a linear form as given by Eq. (11):

$$\ln q_e = \ln Q_m - K\varepsilon^2 \quad (11)$$

where K ($\text{mol}^2 \text{ kJ}^{-2}$) is a constant which relates to the adsorption energy; Q_m (mg g^{-1}) is the maximum adsorption capacity; and ε can be calculated from Eq. (12).

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (12)$$

The D-R isotherm constants, K and Q_m can be calculated from the slope and intercept of the plot between $\ln q_e$ and ε^2 .

2.5.7. Generalized Isotherm

A generalized isotherm can also be used to fit the equilibrium data. Linear form of the generalized isotherm is given by Eq. (13):

$$\log \left(\frac{Q_m}{q_e} - 1 \right) = \log K_G - N_b \log C_e \quad (13)$$

where K_G is the saturation constant (mg l^{-1}); N_b is the cooperative binding constant; and Q_m is the maximum adsorption capacity of the adsorbent (mg g^{-1}) (obtained from Langmuir isotherm model). The isotherm constants K_G and N_b are obtained from the

slope and intercept of the plot of $\log \left(\frac{Q_m}{q_e} - 1 \right)$ versus $\log C_e$.

2.6. Adsorption Kinetics

The kinetics of removal of Cr(VI) is explicitly explained in the literature using pseudo first-order, second-order, and Elovich kinetic models [33-35].

2.6.1. Pseudo First-order Kinetics

The non-linear form of pseudo first-order equation is given by Eq. (14):

$$\frac{dq_t}{dt} = k_{ad} (q_e - q_t) \quad (14)$$

where, q_e and q_t are the amounts of Cr(VI) adsorbed (mg g^{-1}) at equilibrium time and at any instant of time, t respectively, and k_{ad} (1 min^{-1}) is the rate constant of the pseudo first-order adsorption operation. The integrated rate law after application of the initial condition of $q_t = 0$ at $t = 0$, becomes a linear equation as given by Eq. (15):

$$\log(q_e - q_t) = \log q_e - k_{ad}t/2.303 \quad (15)$$

Plot of $\log(q_e - q_t)$ vs. t gives a straight line for the first-order adsorption kinetics, which allow the computation of the adsorption rate constant, k_{ad} .

2.6.2. Second-order Kinetics

Applicability of the second order kinetics has to be tested with the rate equation given by Eq. (16):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (16)$$

where, k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the second order rate constant. From the boundary conditions, $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of the equation becomes as given by Eq. (17):

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2t \quad (17)$$

Eq. (17) can be written in a linear form, as given by Eq. (18):

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \quad (18)$$

where, $h = k_2q_e^2$ that can be regarded as the initial sorption rate as $t \rightarrow 0$. Under such circumstances, the plot of t/q_t vs. t should give a linear relationship, which allows the computation of q_e , k_2 and h .

2.6.3. Elovich Kinetic Equation

Elovich equation is a rate equation based on the adsorption capacity commonly expressed as following Eq. (19):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (19)$$

where, α ($\text{mg g}^{-1} \text{min}^{-1}$) is the initial adsorption rate and β (g mg^{-1}) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorption. Eq. (19) is simplified by assuming $\alpha\beta \gg t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, as given by Eq. (20):

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (20)$$

The slope and intercept of the plot of q_t versus $\ln t$ determines the kinetic constants, α and β .

2.7. Desorption Study

Desorption studies are conducted by batch experiments. The 15 g of saturated sawdust with Cr(VI) is first treated with 150 ml of 1 N NaOH solution for 1 day. After

the NaOH treatment, sawdust is separated from the solution and washed with distilled water. Washed adsorbent is further regenerated with 150 ml of 1 N HCl. The sawdust is washed with distilled water and dried at room temperature (~30 °C) for 6 h. Desorption experiments are carried out with different initial concentrations of Cr(VI) from 50 to 500 mg l⁻¹ while maintaining the adsorbent amount of 10 g l⁻¹ and an initial pH value of 1 at 30 °C.

2.8. Interference Studies

Batch experiments are conducted to investigate the influence of other ions such as iron (Fe²⁺), lead (Pb²⁺), sodium (Na⁺), calcium (Ca²⁺), Magnesium (Mg²⁺), Zinc (Zn²⁺), Cadmium (Cd²⁺), sulphate (SO₄⁻²), and Nickel (Ni²⁺) that are present in the industrial effluent stream. These experiments are carried out by maintaining the initial Cr(VI) concentration, pH, and adsorbent amount constant at 200 mg l⁻¹, 1, and 10 g l⁻¹ respectively. Experiments are conducted for different concentration (mg l⁻¹) ranges of other ions which is given in Table 1. Based on the tannery effluent composition reported by Contreras-Ramos et. al. [36] and electroplating industry effluent by Kumar et al. [6], synthetic solutions are prepared and concentration of other ions present in these effluent streams are given in Table 1.

Table 1. Concentration range of other ions and composition of synthetically prepared electroplating and tannery effluent

S No	Other Ion	Concentration Range (mg l ⁻¹)	Concentration of other ions in synthetically prepared electroplating effluent (mg l ⁻¹)	Concentration of other ions in synthetically prepared tannery effluent (mg l ⁻¹)
1	Fe ²⁺	10 – 40	10	40
2	Pb ²⁺	5 – 30	-	10
3	Na ⁺	200 – 800	-	800
4	Ca ²⁺	200 – 800	-	800
5	Mg ²⁺	200 – 800	-	800
6	Zn ²⁺	100 – 400	250	-
7	Cd ²⁺	25 – 100	-	25
8	SO ₄ ⁻²	200 – 500	450	-
9	Ni ²⁺	25 – 100	50	-

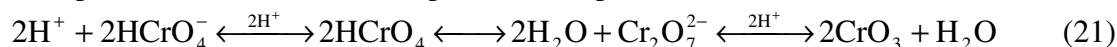
3. Results and Discussion

In the present study, sawdust is used as an adsorbent for Cr(VI) removal from wastewater. It is found that, using the sawdust as an adsorbent, the maximum capacity obtained for Cr(VI) adsorption is 41.52 mg g⁻¹. The comparison of adsorbent capacity of different low cost and commercially available adsorbent is shown in Table 2. When compared with other adsorbents, the results of the present study indicate that sawdust as an adsorbent has better adsorption capacity in almost all cases (S. Nos. 5-32 in Table 2) except for activated neem leaves, activated carbon, and bentonite clay (S. Nos. 1-3 in Table 2). The results of the present study indicate that sawdust proves to be a cost effective adsorbent that can be used for the removal of Cr(VI) from wastewater. Adsorption also depends on various parameters such as pH, contact time, adsorbent

amount, and initial Cr(VI) concentration. Based on the results obtained in the present study, the effect of these parameters is studied in detail.

3.1. Effect of pH

It is well known that the pH of a system is an important parameter in the adsorption of Cr(VI) [56]. In the present work, effect of pH on the adsorption of Cr(VI) using sawdust as an adsorbent is studied in the initial pH range of 1-11. The relation between the initial pH of the solution and percentage removal of Cr(VI) is shown in Fig. 1. Removal efficiency is increased from 6.9 to 99.89% with decreasing initial pH from 11 to 1. The following reaction (Eq. 21) and the subsequent reaction mechanism for adsorption of Cr(VI) at different pH values explain the observed trend:



At lower pH (pH = 1), dominant form of Cr(VI) is HCrO_4^- while the surface of adsorbent is charged positively. The stable forms of chromium such as H_2CrO_4 and CrO_3 exist as polynuclear species at high chromium concentration [57] and hence the low pH value of 1 results in a higher percentage removal of Cr(VI) using sawdust.

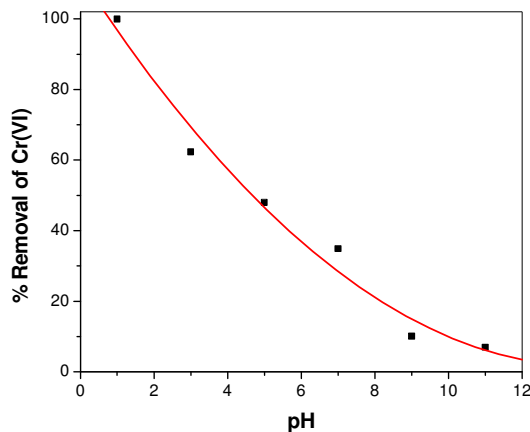


Fig. 1. Effect of pH on the adsorption of Cr(VI) using sawdust at 30 °C

Table 2. Maximum adsorbent capacity of various commercial and low cost adsorbents

S NO	Adsorbent	Maximum Adsorbent Capacity, q_m (mg g ⁻¹)	Optimum pH	Reference
1	Activated neem leaves	62.97	2	[16]
2	Activated Carbon (Filtrasorb-400)	57.7	-	[37]
3	Bentonite clay	49.75	3.0	[38]
4	Sawdust	41.52	1.0	Present Study
5	Coconut husk fiber	29	2.05	[39]
6	Tea factory waste	27.24	2.0	[8]
7	Leaf Mould	25.9	2.5	[40]
8	Pine needles	21.50	2.0	[41]

9	Coconut shell based activated carbon	20	2.5	[42]
10	Sugar beet pulp	17.2	2.0	[43]
11	Palm pressed-fibers	15.0	2.0	[39]
12	Maize cob	13.8	1.5	[43]
13	Sugar cane bagasse	13.4	2.0	[43]
14	Activated charcoal	12.87	2.0	[44]
15	Activated tamarind seeds	11.08	7.0	[45]
16	Almond	10	2.0	[41]
17	Polymer grafted sawdust	9.4	3.0	[46]
18	Maple sawdust	8.2	4.0	[47]
19	Activated alumina	7.44	2.0	[44]
20	Cactus	7.08	2.0	[41]
21	Coal	6.78	2.0	[41]
22	Biomass residual slurry	5.87	2.0	[48]
23	Distillery sludge	5.7	2.5	[49]
24	Calcined bauxite	2.02	3.8	[13]
25	Fly ash impregnated with aluminum	1.8	2.0	[50]
26	Waste tea	1.55	-	[51]
27	Fe(III)/Cr(III) hydroxide	1.43	5.7	[48]
28	Walnut shell	1.33	-	[51]
29	Agricultural waste biomass	0.82	2.0	[52]
30	Rice husks	0.6	-	[53]
31	Soya cake	0.28	1.0	[54]
32	River bed sand	0.15	2.5	[55]

3.2. Effect of Time

The effect of contact time on Cr(VI) adsorption on sawdust is investigated to study the rate of Cr(VI) removal. Fig. 2 shows the percentage removal of Cr(VI) for different value of initial Cr(VI) concentration ranging from 100 to 400 mg l⁻¹ at pH 1. It is evident from Fig. 2 that time is an important parameter for the adsorption of Cr(VI) on sawdust. While increasing the Cr(VI) concentration from 100 to 400 mg l⁻¹, the percentage removal decreases from 86 to 66% for initial 250 min of contact time. After that, the percentage removal of Cr(VI) reaches slowly to 99% and 81% for the initial Cr(VI) concentration of 100 mg l⁻¹ and 400 mg l⁻¹ respectively till 1050 min (Fig. 2). Hence the equilibrium time obtained is 1050 min for the Cr(VI) adsorption on sawdust. The rate of Cr(VI) removal using sawdust is increased rapidly till 250 min. A further increase in the contact time has a negligible effect on the rate of adsorption of Cr(VI). The nature of adsorbent and available adsorption sites affect the rate of adsorption of Cr(VI). The mechanism of solute transfer to the solid includes diffusion through the fluid film around the adsorbent particle and diffusion through the pores to the internal

adsorption sites. In the initial stage of adsorption of Cr(VI), the concentration gradient between the film and the available pore sites is large, and hence the rate of adsorption of Cr(VI) is faster. The rate of adsorption decreases in later stage of the Cr(VI) adsorption probably due to the slow pore diffusion of the solute ion into the bulk of the adsorbent.

3.3. Effect of Adsorbent Amount

Study on the effect of sawdust amount for Cr(VI) removal is important to get the trade-off between the adsorbent capacity and percentage removal of Cr(VI) resulting in optimum sawdust amount. The influence of sawdust amount, varying from 4 – 24 g l⁻¹ onto the Cr(VI) adsorption is shown in Fig. 3 for a constant initial Cr(VI) concentration of 50 mg l⁻¹ in the solution. The percentage of Cr(VI) removal increases from 98.3 to 99.8% with an increase in the sawdust amount from 4 to 24 g l⁻¹ respectively. The increase in Cr(VI) removal with increase in sawdust amount is due to the increase in surface area and adsorption sites available for adsorption. However, the adsorption capacity decreases from 12.28 to 2.06 mg g⁻¹ by increasing the adsorbent amount from 4 to 24 g l⁻¹. The drop in adsorption capacity is basically due to the sites remaining unsaturated during the adsorption process. For the 5.4 g l⁻¹ of adsorbent dosage, the optimum values of Cr(VI) removal and adsorption capacity are found to be 99.0% and 8.7 mg g⁻¹, respectively.

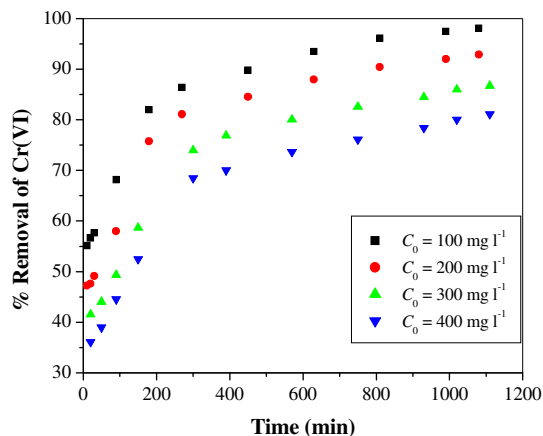


Fig. 2. Effect of contact time on the adsorption of Cr(VI) using sawdust at 30 °C and pH = 1 for different initial Cr(VI) concentrations

3.4. Effect of Initial Cr(VI) Concentration

Cr(VI) adsorption is significantly influenced by the initial concentration of Cr(VI) in aqueous solutions. In the present study, the adsorption experiments are performed to study the effect of initial Cr(VI) concentration by varying it from 50 to 500 mg l⁻¹ while maintaining the sawdust amount 10 g l⁻¹ and obtained results are presented in Fig. 4. The results show that with increase in Cr(VI) concentration from 50 to 500 mg l⁻¹, the percentage removal decreases from 99.9% to 89.9% and adsorption capacity increases from 4.98 to 41.45 mg g⁻¹. The decrease in percentage removal can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration. The increase in adsorption capacity with increase in Cr(VI) concentration may be due to the higher adsorption rate and utilization

of all active sites available for the adsorption at higher concentration. For the 216 mg l^{-1} of initial Cr(VI) concentration, the optimum values of Cr(VI) removal and adsorption capacity are found to be 93.5% and 28 mg g^{-1} respectively.

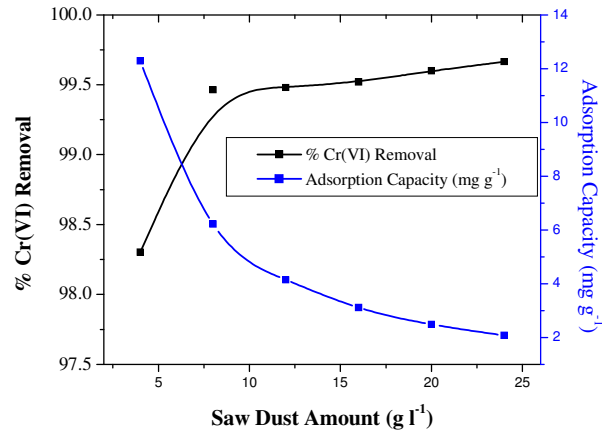


Fig. 3. Effect of amount of sawdust on the adsorption of Cr(VI) at initial Cr(VI) concentration, 50 mg l^{-1} ; temperature, $30 \text{ }^{\circ}\text{C}$; and initial pH, 1

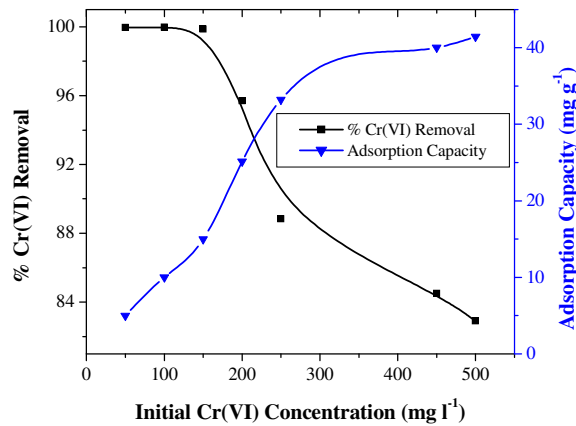


Fig. 4. Effect of initial Cr(VI) concentration on adsorption of Cr(VI) using sawdust at $30 \text{ }^{\circ}\text{C}$ and initial pH 1

3.5. Adsorption Isotherm Study

In the present study, seven equilibrium models are analyzed to investigate the suitable adsorption isotherm.

3.5.1. Langmuir Isotherm

The isotherm data has been linearized using the Langmuir equation and is plotted between C_e/q_e versus C_e . The Langmuir constant q_m , which is a measure of the monolayer adsorption capacity of sawdust is obtained as 41.52 mg g^{-1} in the initial pH range of 1-3. The Langmuir constant, b , which denotes adsorption energy, is found to be 0.4388 l mg^{-1} . The high value of regression correlation coefficient ($R^2 = 0.993$) is obtained which

indicates a good agreement between the experimental values and isotherm parameters and also confirms the monolayer adsorption of Cr(VI) onto the sawdust surface. The dimensionless parameter, R_L , which is a measure of adsorption favorability is found in the range of 0.00453 and 0.0435 ($0 < R_L < 1$) which confirms the favorable adsorption process for Cr(VI) removal using sawdust.

3.5.2. Freundlich Isotherm

The applicability of the Freundlich isotherm is analyzed based on adsorption on heterogeneous surface using the same equilibrium data of Cr(VI) adsorption on sawdust. Freundlich constants, K_f and n are obtained by plotting the graph between $\log q_e$ versus $\log C_e$. The values of K_f and n are 16.66 and 0.2095 respectively. It is found that the regression correlation coefficient obtained from Freundlich isotherm model for sawdust is 0.931 which is lower than that for Langmuir isotherm model as given in Table 3. Freundlich isotherm model is widely used but does not provide the information on the monolayer adsorption capacity. The obtained result indicates that the equilibrium data is not fitted well with the Freundlich isotherm model.

3.5.3. Redlich-Peterson Isotherm

Redlich-Peterson isotherm constants are not possible to obtain using graphical method because of three unknown parameters. So the three isotherm constants are obtained using a professional graphics software package ORIGIN (version 6) and are listed in Table 3. The regression correlation coefficient for Redlich-Peterson isotherm model is obtained as 0.987 which shows a good applicability of this model for the adsorption of Cr(VI) using sawdust as an adsorbent. The correlation coefficient obtained for Redlich-Peterson isotherm model is greater than that of Freundlich isotherm model but less than that of Langmuir isotherm model.

3.5.4. Koble-Corrigan Isotherm

The three isotherm constants of Koble-Corrigan model are also evaluated using a professional graphics software package ORIGIN (version 6) and are listed in Table 3. The regression correlation coefficient for Koble-Corrigan isotherm model is obtained as 0.986 which shows that equilibrium data obtained for the adsorption of Cr(VI) using sawdust also follows Koble-Corrigan isotherm model. This indicates the combination between heterogeneous and homogeneous adsorption of Cr(VI) using sawdust.

3.5.5. Tempkin Isotherm

A plot of q_e versus $\ln C_e$ at constant temperature is used to calculate the Tempkin isotherm constants, A_T and b_T . The constants A_T and b_T , obtained for Tempkin isotherm model are 235.49 and 642.485 and also tabulated in Table 3. The obtained regression correlation coefficient for Tempkin isotherm model is 0.965 which confirms the better fit of equilibrium data as compared with the Freundlich isotherm model. But Tempkin isotherm model is not as good as Langmuir, Redlich-Peterson, and Koble-Corrigan isotherm models as can be seen from the reported values of correlation coefficient in Table 3.

3.5.6. Dubinin-Radushkevich Isotherm

The plot between $\ln q_e$ and ε^2 at constant temperature of 30°C used to calculate the constants, Q_m and K for Dubinin-Radushkevich isotherm model are 31.79 and 1.73×10^{-8} . The value of regression correlation coefficient ($R^2 = 0.872$) indicates that the Dubinin-Radushkevich isotherm model does not fit well with the equilibrium experimental data as compared with the other models considered. The maximum adsorption capacity, Q_m , obtained using Dubinin-Radushkevich isotherm model is 31.79 mg g^{-1} for adsorption of Cr(VI) by sawdust which is less than the Q_m (41.5 mg g^{-1}) obtained using the Langmuir isotherm model. The mean free energy of adsorption, E , is calculated as 5.37 kJ mol^{-1} . The typical E values for ion-exchange mechanisms are ranged between 1 – 16 kJ mol^{-1} , indicating that the adsorption of Cr(VI) using sawdust is physical adsorption, which is well established in the result obtained in the pH study.

3.5.7. Generalized Isotherm Equation

The generalized isotherm constants, K_G and N_b , are calculated by plotting the graph between $\log [(Q_m/q_e)-1]$ and $\log C_e$. The slope, N_b and intercept, $\log K_G$ of this plot determines the isotherm constants, N_b as 0.685 and K_G as 0.238. The regression correlation coefficient obtained for generalized isotherm model is 0.737 which is less than that of the other isotherm models as given in Table 3. That means equilibrium experimental data for adsorption of Cr(VI) on sawdust can not be represented by the generalized isotherm model.

Table 3. Isotherm constants and regression data for various adsorption isotherms for adsorption of Cr(VI) on sawdust

S No	Adsorption Isotherm	Isotherm Parameters		R^2
1	Langmuir	Q_m	41.52	0.993
		b	0.438	
2	Freundlich	K_F	16.66	0.931
		n_F	0.209	
3	Redlich– Peterson	A	1914	0.988
		B	104.5	
		g	0.818	
4	Koble–Corrigan	a	16.58	0.986
		b	-0.035	
		n	0.187	
5	Tempkin	A_T	235.5	0.965
		B_T	3.921	
		b_T	642.5	
6	Dubinin–Radushkevich	Q_m	31.79	0.872
		$K \times 10^8$	1.730	
		E	5.370	
7	Generalized	N_b	0.685	0.737
		K_G	0.238	

3.6. Adsorption Kinetics

In order to understand the kinetics of removal of Cr(VI) using sawdust as an adsorbent, pseudo first-order, second-order and Elovich kinetic models are tested with the experimental data.

3.6.1. Pseudo First-Order Kinetics

The plot of $\log (q_e - q_t)$ versus t gives a straight line which represents the pseudo first-order kinetics for the removal of Cr(VI) using sawdust. The values of first-order rate constants, k_1 and q_e for the initial Cr(VI) concentration ranges of 100-400 mg l⁻¹ by keeping the adsorbent amount 10 g l⁻¹ constant are calculated and listed in Table 4. The regression correlation coefficient is found to be in the range of 0.97-0.982 which seems to be good and shows the applicability of pseudo first-order kinetic model for the removal of Cr(VI) using sawdust. The true value of q_e obtained from experiments for 100, 200, 300, and 400 mg l⁻¹ of initial Cr(VI) concentrations are 9.81, 18.57, 26.01, and 32.439 mg g⁻¹ respectively which is not in agreement with the pseudo first-order model predicted values as given in Table 4.

3.6.2. Second-Order Kinetics

As a result of non-applicability of pseudo first-order, the kinetics for adsorption of Cr(VI) on sawdust is tested with the second-order kinetic model. Application of second-order kinetics by plotting t/q_t vs. t , yielded the second-order rate constant, k_2 , calculated equilibrium capacity q_e , and regression correlation coefficient for the initial Cr(VI) concentration ranging from 100 – 400 mg l⁻¹ are reported in Table 4. The calculated q_e values show a good agreement with the experimental values and the obtained values for regression correlation coefficients are more than 0.997 which indicates that the second-order kinetic model can be applied for the removal of Cr(VI) using sawdust as an adsorbent.

3.6.3. Elovich Kinetic Equation

The Elovich kinetic constants α and β are obtained from the intercept and slope respectively. The regression correlation coefficients (R^2) are obtained in the range of 0.962 - 0.976 for all values of initial Cr(VI) concentration (100-400 mg l⁻¹) which are found to be less than the values calculated using pseudo first-order and second-order kinetic model as shown in Table 4.

The regression correlation coefficients for second order kinetic model are more than the pseudo first-order and Elovich kinetic model for all values of initial Cr(VI) concentration. Thus the kinetics of Cr(VI) adsorption using sawdust as an adsorbent can be better explained by second-order kinetic model.

Table 4. Calculated kinetic parameters for pseudo first-order, second order and Elovich kinetic models for the adsorption of Cr(VI) using sawdust as an adsorbent

S No	C ₀ (mg l ⁻¹)	q _e (mg g ⁻¹) (experimental)	First-Order Kinetic Model			Second-Order Kinetic Model			Elovich Kinetic Model		
			k ₁ ×10 ³	q _e	R ²	k ₂ ×10 ³	q _e	R ²	β	α	R ²
1	100	9.81	3.98	4.27	0.982	3.39	9.96	0.998	0.97	13.7	0.976
2	200	18.57	3.79	8.09	0.982	1.47	18.9	0.999	0.45	8.92	0.962
3	300	26.01	3.66	14.5	0.970	0.59	27.1	0.998	0.26	3.15	0.964
4	400	32.44	3.34	18.6	0.970	0.43	33.9	0.997	0.20	2.89	0.967

3.7. Desorption Study

The saturated adsorbent which contains Cr(VI) is not safe for disposal due to the stringent environmental constraints. It is important and appropriate to propose a method for regeneration and reuse of adsorbent so as to reduce the load on environment in terms of disposal of polluted adsorbent. In the present study, sawdust is regenerated and is used for the removal of Cr(VI) at different initial Cr(VI) concentration in the range of 50 – 500 mg l⁻¹. Fig. 5 shows the comparison for the percentage removal of Cr(VI) using fresh and regenerated sawdust. Fresh and regenerated sawdust is used for the adsorption of Cr(VI) having 50 mg l⁻¹ and 500 mg l⁻¹ of initial Cr(VI) concentration, the percentage removal of Cr(VI) is decreased from 98.85% to 97.42% and 87.59% to 83.99% respectively. These results exhibit higher desorption efficiency by more than 95% for the removal of Cr(VI). Since, Cr(VI) adsorption is an example of physical adsorption, it is possible to regenerate the sawdust, which can be considered for reuse. The adsorption of Cr(VI) onto the sawdust is highly pH dependent. Hence, desorption of Cr(VI) is accomplished by increasing the solution pH.

The major problem of desorption process is the disposal of the acid and base solution obtained which contain high concentration of Cr(VI). One of the methods to tackle this problem is precipitation of Cr(VI) from the aqueous solution using barium chloride. Addition of barium chloride solution to a Cr(VI) solution precipitates bright yellow barium chromate, as given by the following reaction (Eq. 23)



The precipitated solid volume is very less as compared to the volume of the solution. Also the chromium present in the complex solid can be recovered and reused by the industries. So this way the problem of disposal which is a major disadvantage of adsorption operation can be solved effectively and efficiently.

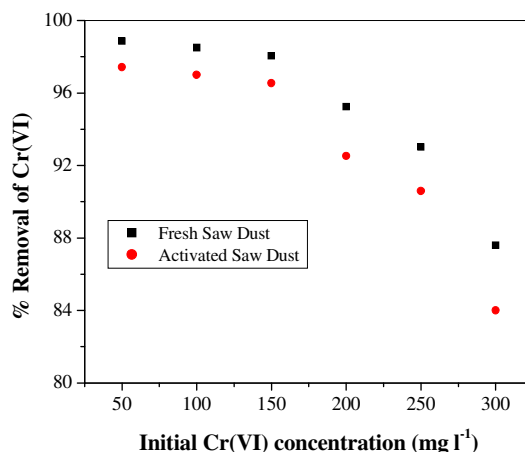
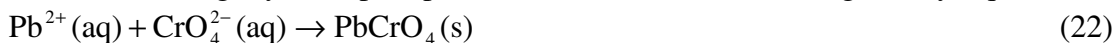


Fig. 15. Comparison for the percentage removal of Cr(VI) using fresh and regenerated sawdust

3.8. Interference of Other Ions

In the present study, the interference of other ions such as Fe²⁺, Pb²⁺, Na⁺, Ca²⁺, Mg²⁺, Zn²⁺, Cd²⁺, SO₄²⁻, and Ni²⁺ present in the electroplating industrial effluent [6] and tannery effluent [36] wastewater streams is studied for the Cr(VI) removal. The effect of initial concentration of each ion for varying ranges (Table 1) on the percentage removal

of Cr(VI) is plotted in Fig. 6. It can be seen from Fig. 6 that the percentage removal of Cr(VI) is marginally decreased (94.1% to 89%) by the presence of Ca^{2+} , Mg^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} ions. Hence, it can be concluded that the adsorption of Cr(VI) is not significantly affected by the presence of Ca^{2+} , Mg^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} ions. This may be due to the more ionic charge of the Cr(VI) which dominates in the adsorption as compared to the other divalent ions such as Ca^{2+} , Mg^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} ions present in the industrial effluent. However, the percentage removal of Cr(VI) is significantly affected by the presence of Fe^{2+} , Pb^{2+} , Na^+ , and SO_4^{2-} in industrial effluent. For the initial concentration of Fe^{2+} (0 – 40 mg l^{-1}), the percentage removal of Cr(VI) ion decreases from 96% to 72.89%. Similar trends have been observed for ions such as Na^+ , and SO_4^{2-} as shown in Fig. 6. But in the presence of lead ion, the percentage removal first decreases for 5 mg l^{-1} of Pb^{2+} concentration and then increases with increase in concentration of Pb^{2+} . This may be due to the precipitation of Cr(VI) ion in the presence of Pb^{2+} to the bright yellow precipitate of lead chromate which is given by Eq. (22):



The synthetic solution for electroplating industry and tannery industry effluents (Table 1) are treated with the sawdust which results in the decrease of percentage removal from 96% to 55.4% and 96% to 50.25% respectively. These results show that the adsorbent capacity for Cr(VI) removal is decreased approximately by 50% for the synthetic electroplating and tannery effluents.

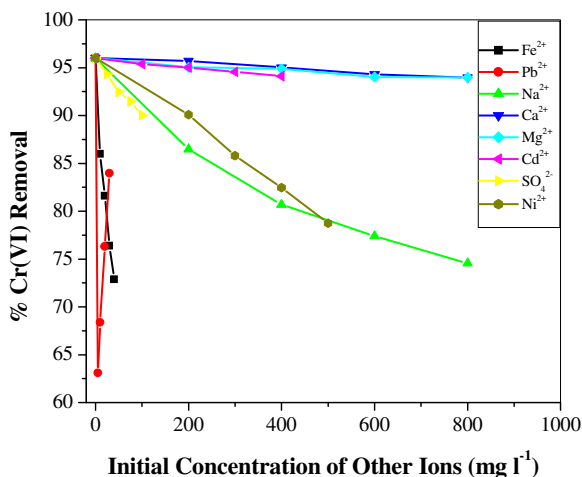


Fig. 16. Effect of other ions on the removal of Cr(VI) using sawdust

4. Conclusions

Utilization of waste material such as sawdust for the removal of Cr(VI) from the industrial wastewater streams is investigated. Sawdust is found to be a better adsorbent for the removal of Cr(VI) as compared to other low cost and commercially available adsorbents. The maximum percentage removal of Cr(VI) is obtained at $\text{pH} = 1$. The dominant form of Cr(VI) is HCrO_4^- and the surface of adsorbent is charged positively at lower pH . It is found from the kinetic studies that the adsorption rate of Cr(VI) is faster for initial 250 min and then it decreases in the later part of adsorption. The equilibrium time for Cr(VI) adsorption on sawdust is obtained as 1050 min. With the increase of

adsorbent amount the percentage removal of Cr(VI) increases and the adsorption capacity of sawdust to adsorb Cr(VI) decreases because of availability of more unsaturated adsorption sites. The percentage removal decreases and the adsorption capacity increases with an increase in initial Cr(VI) concentration. The equilibrium adsorption data are satisfactorily fitted with various isotherm models such as Langmuir, Freundlich, Redlich-Peterson, Koble-Corrigan, Tempkin, Dubinin-Radushkevich, Generalized isotherm models. The equilibrium data are best fitted with Langmuir isotherm model which confirms the monolayer adsorption of Cr(VI) onto the sawdust. The maximum adsorption capacity is obtained with the application of Langmuir isotherm model as 41.52 mg g^{-1} , which is comparatively good adsorption capacity. The kinetics of Cr(VI) adsorption using sawdust as an adsorbent for different values of initial Cr(VI) concentration is explained by the second-order kinetic model. The presence of other ions such as Fe^{2+} , Pb^{2+} , Na^+ and SO_4^{2-} in aqueous solutions are found to have significant effect on Cr(VI) adsorption. Sawdust can be used to treat industrial wastewater streams (electroplating and tanney) containing large amount of Cr(VI). The saturated adsorption is regenerated by acid and base treatment. The desorption efficiency obtained is more than 95% for the removal of Cr(VI). The possible solution for the major problem of desorption process which is disposal of the acid and base solution obtained which contain high concentration of Cr(VI) is the precipitation of Cr(VI) as barium chromate.

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