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Removal of toxic metal Cr(VI) from aqueous solutions using sawdust as adsorbent: Equilibrium, kinetics and regeneration studies

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ABSTRACT

In the present study, a low-cost adsorbent is developed from the naturally and abundantly available sawdust which is biodegradable. The removal capacity of Cr(VI) from aqueous solutions and from the synthetically prepared industrial effluent of electroplating and tannery industries is obtained. The batch experiments are carried out to investigate the effect of the significant process parameters such as initial pH, change in pH during adsorption, contact time, adsorbent amount, and the initial Cr(VI) concentration. The maximum adsorption of Cr(VI) on sawdust is obtained at an initial pH value of 1. The value of pH increases with increase in contact time and initial Cr(VI) concentration. The equilibrium data for the adsorption of Cr(VI) on sawdust is 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 the most suitable one for the Cr(VI) adsorption using sawdust and the maximum adsorption capacity obtained is 41.5 mg g^{-1} at a pH value of 1. The adsorption process follows the second-order kinetics and the corresponding rate constants are obtained. Desorption of Cr(VI) from sawdust using acid and base treatment exhibited a higher desorption efficiency by more than 95%. A feasible solution is proposed, for the disposal of the contaminant (acid and base solutions) containing high concentration of Cr(VI) obtained during the desorption process. The interference of other ions which are generally present in the electroplating and tannery industrial effluent streams on the Cr(VI) removal is investigated.

1. Introduction

The increasing contamination of urban and industrial wastewaters by toxic metal ions causes significant environmental pollution [1–3]. All over the world, chromium is abundantly available in nature. 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 a metal particle that occurs naturally in rocks but is most commonly produced by industrial processes. Cr(VI) is present in many different compounds [ammonium dichromate, $(NH_4)_2Cr_2O_7$; calcium chromate, $CaCrO_4$; chromium trioxide or chromic acid, CrO_3; lead chromate, $PbCrO_4$; potassium chromate, K_2CrO_4; potassium dichromate, $K_2Cr_2O_7$; sodium chromate, Na_2CrO_4; strontium chromate, $SrCrO_4$; and zinc chromate, $ZnCrO_4$] which has a variety of industrial applications. Cr(VI) is also used in various other industries such as electroplating, glass, ceramics, fungicides, rubber, fertilizers, tanning, mining, metallurgical, etc. [4–11]. 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 the living organisms, and hence more hazardous than other heavy metals. In addition, it also has an effect on human skin, liver, kidney, and respiratory organs. This results in a variety of diseases such as dermatitis, bronchitis, perforation of nasal septum, bronchogenic carcinoma, liver damage, ulcer formation, etc. [12–17]. 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 the stricter environmental regulations, a cost effective alternate technology for the treatment of Cr(VI) contaminated wastewater is highly desired by the industries [18]. There are various treatment technologies available to remove Cr(VI) from wastewater such as chemical precipitation [19,20], ion-exchange [21,22], membrane separation [23], electrocoagulation [24], solvent extraction [25], reduction [26], reverse osmosis [25], and adsorption [16,27]. These techniques are economically expensive for the removal of Cr(VI) from wastewater. The above mentioned removal techniques have many disadvantages such as incomplete metal removal, high reagent and energy

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requirements, and generation of toxic sludge or waste products which require proper disposal without creating any problem to the environment [28–30].

Therefore, there is a dire need of a treatment method for Cr(VI) removal from wastewater which is simple, effective and inexpensive [3]. 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) [31]. The advantages of the adsorption process prompted 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 a high potential for the Cr(VI) removal from wastewater streams [15]. 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 [32–34]. In the recent years, several studies have been reported on various low-cost adsorbents such as wool [35], used tyres [36], seaweed [37], fungal biomass [38], green algae [39], maple sawdust [40], sugar industry waste [41], distillery sludge [42], soya cake [43], red mud [44], activated carbon derived from fertilizer waste [45], tea factory waste [46], Turkish brown coal [47], moss peat [48], hazelnut shell [49], coconut trees [50], lignocellulosic residues [51], rice brand [52], activated neem leaves [3], activated tamarind seeds [2], etc. However, many of these naturally available adsorbents have low chromium adsorption capacity. Thus, there is a need to develop or find innovative low-cost adsorbents with an affinity towards metal ions for the removal of Cr(VI) from aqueous solution which leads to high adsorption capacity [9].

The objective of the present study is to investigate the possible use of sawdust as an alternate adsorbent material for the 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, change in pH during adsorption, 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 experimental equilibrium isotherm data obtained in this study. Pseudo first-order, second-order and Elovich kinetic models are used to evaluate the mechanism of adsorption. A feasible method for the desorption of Cr(VI) from the used adsorbent 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). One of the method is proposed to tackle the problem of disposal of the acid and base solution obtained during desorption process which contain high concentration 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 the dust and soluble impurities. It is then kept for drying at room temperature in shade for 8 h. The specific surface area of sawdust is measured using BET surface area analyzer (Smart Sorb 92/93, Smart Instruments Co. Pvt. Ltd., Thane).

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 ($K_2Cr_2O_7$) in 1000 mL of solution. This solution is diluted as required to obtain the standard solutions containing 50–500 mg L^{-1} of Cr(VI). pH adjustment is carried out by using 0.5N HCl and 0.5N 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) solution, and then stirred for a predetermined period (found out from the kinetic studies) at 30 °C in water bath-cum-mechanical shaker. Afterwards, the resultant solution is filtered using a filter paper. Adsorption isotherm study is carried out with different initial Cr(VI) concentrations ranging from 50 to 500 mg L^{-1} while maintaining the adsorbent amount of 10 g L^{-1}. The pH of the solution is also measured during course of adsorption. The effect of pH is studied at 30 °C with an initial Cr(VI) concentration of 50 mg L^{-1}. The influence of time on Cr(VI) adsorption is studied at 30 °C with an initial Cr(VI) concentration ranging from 100 to 400 mg L^{-1} with an adsorbent dosage of 10 g L^{-1}. The effect of the adsorbent amount is studied by varying it in the range of 4–24 g L^{-1} with the Cr(VI) concentration of 50 mg L^{-1} at 30 °C.

The amount of Cr(VI) adsorbed by the sawdust and the percentage removal of Cr(VI) are calculated using the following Eqs. (1) and (2) respectively.

$$q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

$$\%\,\text{Removal of Cr(VI)} = \frac{C_i - C_0}{C_i} \times 100 \tag{2}$$

where, q is the adsorption capacity in mg g^{-1}, C_i, C_0 and C_e are the initial, outlet and equilibrium concentration of Cr(VI) in mg L^{-1}, V is the volume of Cr(VI) solution in mL and W is the total amount of sawdust in g.

2.4. Measurement of Cr(VI) concentration in aqueous solutions

In the present study, di-pheynl carbazide method is used for the analysis of Cr(VI) in the solution which only measures the amount of Cr(VI). This method has been reportedly used in many studies for analysis of Cr(VI) at low pH [11,51]. The concentration of 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 [53]. The absorbance of the purple-violet colored solution is read at 540 nm after 20 min. To calculate the deviation of analytical method of Cr(VI) concentration, calibration curve is prepared from standard solutions. The standard deviation obtained for the calibration curve is 0.00453 which is indicative of a good fit of the data and within the error limits of ±1.64%. This ensured high confidence limits of the experimental measurements.

2.5. Adsorption isotherm models

Adsorption isotherms are expressed in terms of a relationship between the concentration of adsorbate in the liquid and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. There may not be a simple expression which is capable of describing the equilibrium relation between the adsorbate in liquid phase and the adsorbate in solid phase, because of the complex nature of liquid-phase adsorption on the microporous substances. It is important to get an accurate equilibrium relationship between the solid and liquid-phase concentrations of Cr(VI). In the present study, as the adsorbent developed is new, it is essentially required to test the equilibrium data obtained for Cr(VI) removal using sawdust with different isotherm models available in the literature so as to know which one is the best suited out of all the reported isotherms. Various adsorption isotherm models such as Langmuir [54], Freundlich [55], Redlich–Peterson [56], Koble–Corrigan [57], Tempkin [58], Dubinin–Radushkevich [59], and Generalized equation [60] which are available in the literature are described in the following sections bringing out the differences among them and the significance of the characteristic parameters of each isotherm model.

2.5.1. Langmuir isotherm

Langmuir isotherm has been extensively used for the adsorption of heavy metals, dyes, organic pollutants, etc. [61,62]. It is applicable for monomolecular layer adsorption. This isotherm is described as a homogeneous one assuming that all the adsorption sites have equal adsorbate affinity and that the adsorption at one site does not affect the adsorption at an adjacent site [54]. The Langmuir isotherm is used to obtain a maximum adsorption capacity produced from the complete monolayer coverage of adsorbent surface. The isotherm equation is represented in term of the fractional coverage (θ) as given by Eq. (3):

$$\theta = \frac{q_e}{Q_m} = \frac{bC_e}{1+bC_e} \tag{3}$$

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. (3) can be rearranged to get the linear form, as given by Eq. (4):

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right) C_e \tag{4}$$

which shows that a plot of (C_e/q_e) versus 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 yield the values of constants Q_m and b respectively.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L [63], also known as the separation factor, given by Eq. (5):

$$R_L = \frac{1}{1+bC_0} \tag{5}$$

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

Freundlich isotherm describes that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of solute in the solution is not constant at different concentrations. For many systems, the heat of adsorption decreases in magnitude with increasing the extent of adsorption [55]. This has been well taken care of by the Freundlich isotherm, previously considered to be an empirical isotherm. For adsorption from solution, the Freundlich isotherm is expressed by Eq. (6):

$$q_e = K_f C_e^{n_F} \tag{6}$$

where, K_f (mg$^{1-1/n}$ L$^{1/n}$ 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. (7):

$$\log q_e = \log K_f + n_F \log C_e \tag{7}$$

2.5.3. Redlich–Peterson isotherm

Redlich–Peterson isotherm contains three parameters and is an improvement over the Langmuir and Freundlich isotherms. It has a linear dependence in the numerator and an exponential dependence in the denominator on concentration which makes it an overall complex and non-linear dependence on C_e. It can be described by Eq. (8):

$$q_e = \frac{AC_e}{1+BC_e^g} \tag{8}$$

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 the equilibrium adsorption data. It is a combination of the Langmuir and Freundlich isotherm models and is given by Eq. (9):

$$q_e = \frac{aC_e^n}{1+bC_e^n} \tag{9}$$

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

2.5.5. Tempkin isotherm

Tempkin isotherm equation [58] contains a factor that takes into account of the adsorbent–adsorbate interactions. It is based on the assumption that the heat of adsorption of all the molecules in the layer decreases linearly with the coverage of molecules due to the adsorbate–adsorbate repulsions and the adsorption of adsorbate is uniformly distributed [64]. In addition, it also assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich isotherm. The non-linear form of Tempkin equation is given by Eq. (10) [65]:

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \tag{10}$$

Eq. (10) can be linearized as given by Eq. (11)

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{11}$$

where, $B_T = (RT)/b_T$, T is the absolute temperature in K and R is the universal gas constant (8.314 J mol^{-1} 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 [66]. The slope and the 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

Dubinin and Radushkevich have proposed another isotherm which can be used to analyze the equilibrium data [59]. It is not based on the assumption of homogeneous surface or constant adsorption potential, but it is applied to estimate the mean free energy of adsorption (E). If the value of E is between 1 and 16 kJ mol^{-1}, then physical adsorption prevails, and if the value is more than 16 kJ mol^{-1}, then chemisorption prevails. The non-linear form of D–R equation is given by Eq. (12) [67]:

$$q_e = Q_m \exp(-K\varepsilon^2) \tag{12}$$

Eq. (12) is represented in a linear form as given by Eq. (13):

$$\ln q_e = \ln Q_m - K\varepsilon^2 \tag{13}$$

where K ($\mathrm{mol^2\,kJ^{-2}}$) is a constant which relates to the adsorption energy; Q_m ($\mathrm{mg\,g^{-1}}$) is the maximum adsorption capacity; and ε can be calculated from Eq. (14).

$$\varepsilon = RT\,\ln\left(1+\frac{1}{C_\mathrm{e}}\right) \tag{14}$$

The D–R isotherm constants, K and Q_m are estimated from the slope and intercept of the plot between $\ln q_\mathrm{e}$ and ε^2.

2.5.7. *Generalized isotherm*

The generalized isotherm is a combination of Langmuir and Freundlich isotherms. It depends on the value of cooperative binding constant (N_b). A generalized isotherm can also be used to fit the equilibrium data [60]. The linear form of the generalized isotherm is given by Eq. (15):

$$\log\left(\frac{Q_\mathrm{m}}{q_\mathrm{e}}-1\right) = \log K_\mathrm{G} - N_\mathrm{b}\,\log C_\mathrm{e} \tag{15}$$

where, K_G is the saturation constant ($\mathrm{mg\,L^{-1}}$); N_b is the cooperative binding constant; and Q_m is the maximum adsorption capacity of the adsorbent ($\mathrm{mg\,g^{-1}}$) (obtained from the Langmuir isotherm model). The isotherm constants K_G and N_b are obtained from the slope and intercept of the plot of $\log[(Q_\mathrm{m}/q_\mathrm{e})-1]$ versus $\log C_\mathrm{e}$.

2.6. *Adsorption kinetics*

The dynamics of the adsorption process in terms of the order and the rate constant can be evaluated using the kinetic adsorption data. The process of Cr(VI) removal from an aqueous phase by any adsorbent can be explained by using kinetic models and examining the rate-controlling mechanism of the adsorption process such as chemical reaction, diffusion control and mass transfer. The kinetic parameters are useful in predicting the adsorption rate which can be used as important information in designing and modeling of the adsorption operation. The kinetics of removal of Cr(VI) is explicitly explained in the literature using pseudo first-order, second-order, and Elovich kinetic models [68–70].

2.6.1. *Pseudo first-order kinetics*

Lagergren showed that the rate of adsorption of solute on the adsorbent is based on the adsorption capacity and followed a pseudo first-order equation [68,69]. The non-linear form of the pseudo first-order equation is given by Eq. (16):

$$\frac{dq_t}{dt} = k_\mathrm{ad}(q_\mathrm{e}-q_t) \tag{16}$$

where, q_e and q_t are the amounts of Cr(VI) adsorbed ($\mathrm{mg\,g^{-1}}$) at equilibrium time and at any instant of time, t, respectively, and k_ad ($\mathrm{L\,min^{-1}}$) 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. (17):

$$\log(q_\mathrm{e}-q_t) = \log q_\mathrm{e} - \left(\frac{k_\mathrm{ad}t}{2.303}\right) \tag{17}$$

The plot of $\log(q_\mathrm{e}-q_t)$ versus t gives a straight line for the pseudo first-order adsorption kinetics, from the adsorption rate constant, k_ad, is estimated.

Pseudo first-order kinetic equation differs from a true first-order equation in two ways: (i) the parameter $k_\mathrm{ad}\,(q_\mathrm{e}-q_t)$ does not represent the number of available sites, and (ii) the parameter $\log(q_\mathrm{e})$ is an adjustable parameter and often it is found that it is not equal to the intercept of the plot of $\log(q_\mathrm{e}-q_t)$ versus t, whereas in a true first-order model the value of $\log q_\mathrm{e}$ should be equal to the intercept [69]. Hence, pseudo first-order kinetic model (Eq. (16)) is used for estimating k_ad alone, which is considered as mass transfer coefficient in the design calculations.

2.6.2. *Second-order kinetics*

As pseudo first-order kinetic model gives only k_ad and as q_e cannot be estimated using this model, applicability of the second-order kinetics has to be tested for the estimation of q_e with the rate equation given by Eq. (18):

$$\frac{dq_t}{dt} = k_2(q_\mathrm{e}-q_t)^2 \tag{18}$$

where, k_2 ($\mathrm{g\,mg^{-1}\,min^{-1}}$) is the second-order rate constant. From the boundary conditions, $t=0$ to t and $q_t=0$ to q_t, the integrated form of the equation becomes Eq. (19):

$$\frac{1}{(q_\mathrm{e}-q_t)} = \frac{1}{q_\mathrm{e}} + k_2 t \tag{19}$$

Eq. (19) can be written in a linear form, as given by Eq. (20):

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_\mathrm{e}}\right)t \tag{20}$$

where, $h=k_2{q_\mathrm{e}}^2$ that can be regarded as the initial sorption rate as $t\to 0$. Under such circumstances, the plot of t/q_t versus t should give a linear relationship, which allows the computation of q_e and k_2.

2.6.3. *Elovich kinetic equation*

Elovich equation is a rate equation based on the adsorption capacity commonly expressed as Eq. (21) [70]:

$$\frac{dq_t}{dt} = \alpha\,\exp(-\beta q_t) \tag{21}$$

where, α ($\mathrm{mg\,g^{-1}\,min^{-1}}$) is the initial adsorption rate and β ($\mathrm{g\,mg^{-1}}$) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorption. Eq. (21) 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. (22):

$$q_t = \frac{1}{\beta}\,\ln(\alpha\beta) + \frac{1}{\beta}\,\ln t \tag{22}$$

The slope and intercept of the plot of q_t versus $\ln t$ result in the estimation of 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 1N 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 1N 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 $\mathrm{mg\,L^{-1}}$ while maintaining the adsorbent amount of 10 $\mathrm{g\,L^{-1}}$ 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 ($\mathrm{Fe^{2+}}$), lead ($\mathrm{Pb^{2+}}$), sodium ($\mathrm{Na^{+}}$), calcium ($\mathrm{Ca^{2+}}$), magnesium ($\mathrm{Mg^{2+}}$), zinc ($\mathrm{Zn^{2+}}$), cadmium ($\mathrm{Cd^{2+}}$), sulphate (${\mathrm{SO_4}}^{-2}$), and nickel ($\mathrm{Ni^{2+}}$) that are present in the industrial effluent stream. These experiments are carried out by maintaining the initial Cr(VI) concentration, initial pH, and adsorbent amount constant at 200 $\mathrm{mg\,L^{-1}}$, 1, and 10 $\mathrm{g\,L^{-1}}$ respectively. Experiments are conducted for different concentration ($\mathrm{mg\,L^{-1}}$) ranges of other ions as shown in Table 1. Based on the tannery effluent composition reported by

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	–

Contreras-Ramos et al. [71] and electroplating industry effluent by Kumar et al. [9], synthetic solutions are prepared and the concentration of other ions present in these effluent streams are given in Table 1.

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 the adsorbent capacity of different low cost and commercially available adsorbents 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. The metallic ions uptake on sawdust mainly depends on the ions concentration, and adsorption and reduction phenomena that simultaneously take place on the adsorbent surface [85–88]. These phenomena are strongly related to the solution pH. Various mechanisms such as electrostatic forces, ion-exchange, chemical complexation must be taken into account while discussing the mechanism of Cr(VI) adsorption on adsorbents. The solution pH plays a major role in the adsorption of Cr(VI) and it can be related to the type and ionic state of the functional group present on the adsorbent surface [89]. The ionic state of the functional group present on the adsorbent surface depends on the pH_{zpc} (zero point of charge) value of adsorbent. The obtained value of pH_{zpc} of sawdust is 6.2, and below this pH, the surface charge of the adsorbent is positive [18,31]. If the pH of the solution (pH 1) is less than the value of pH_{zpc}, then the active sites of sawdust are positively charged. In the present study, the initial pH of solution is maintained in the range of 1–3 and the equilibrium solution pH (after adsorption of Cr(VI)) is also obtained in the range of 1.23–1.55 for an initial Cr(VI) concentration ranging from 50 to $500\,mg\,L^{-1}$ and final Cr(VI) concentration from 0.02 to 85.46 mg/L. Within the solution pH range of 1.0–6.0, chromium ions can exist in different forms, such as Cr_2O^{7-}, $HCrO^{4-}$, $Cr_3O_{10}{}^{2-}$, $Cr_4O_{13}{}^{2-}$ of which $HCrO^{4-}$ predominates [3]. At lower solution pH value (1–3),

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	[3]
2	Activated carbon (Filtrasorb-400)	57.7	–	[72]
3	Bentonite clay	49.75	3.0	[73]
4	Sawdust	41.52	1.0	Present study
5	Activated tamarind seeds	29.7	2.0	[2]
6	Coconut husk fiber	29	2.05	[74]
7	Tea factory waste	27.24	2.0	[11]
8	Leaf mould	25.9	2.5	[75]
9	Pine needles	21.50	2.0	[35]
10	Coconut shell based activated carbon	20	2.5	[76]
11	Sugar beet pulp	17.2	2.0	[77]
12	Palm pressed-fibers	15.0	2.0	[74]
13	Maize cob	13.8	1.5	[77]
14	Sugar cane bagasse	13.4	2.0	[77]
15	Activated charcoal	12.87	2.0	[78]
16	Almond	10	2.0	[35]
17	Polymer grafted sawdust	9.4	3.0	[79]
18	Maple sawdust	8.2	4.0	[40]
19	Activated alumina	7.44	2.0	[78]
20	Cactus	7.08	2.0	[35]
21	Coal	6.78	2.0	[35]
22	Biomass residual slurry	5.87	2.0	[80]
23	Distillery sludge	5.7	2.5	[42]
24	Calcined bauxite	2.02	3.8	[16]
25	Fly ash impregnated with aluminum	1.8	2.0	[81]
26	Waste tea	1.55	–	[82]
27	Fe(III)/Cr(III) hydroxide	1.43	5.7	[80]
28	Walnut shell	1.33	–	[82]
29	Agricultural waste biomass	0.82	2.0	[61]
30	Rice husks	0.6	–	[83]
31	Soya cake	0.28	1.0	[43]
32	River bed sand	0.15	2.5	[84]

the increase in Cr(VI) adsorption is due to the electrostatic attraction between positively charged groups of adsorbent surface and the $HCrO^{4-}$. Another possible reason for the higher adsorption of Cr(VI) on sawdust could be the reduction of Cr(VI) to Cr(III) in acidic medium. At low pH, the presence of H^+ ions in the solution is high which causes the reduction of Cr(VI) to Cr(III) ions due to high redox potential (1.3 V at standard state) as shown in the reaction below [18,31].

$$HCrCO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \quad (23)$$

The oxidation product of this reaction is water. As the size of Cr(III) ions is small, they can be easily replaced by the positively charged ions present on the sawdust surface [36]. Though in principle, there is a possibility of reduction of Cr(VI) ion into Cr(III) at low pH, the earlier studies reported that the amount of total Cr and Cr(VI) at low pH is approximately same [9] which indicates that the presence of Cr(III) in the final solution is insignificant. So in this study, the amount of Cr(III) is not determined. The mechanism of electrostatic attraction between sawdust surface and $HCrO^{4-}$ is found more appropriate for explaining the Cr(VI) adsorption onto the sawdust.

Besides pH, another key factor which dominates the adsorption of Cr(VI) on sawdust is the available surface area. In general, naturally occurring adsorbents have less surface area which results in a lower adsorption capacity of Cr(VI) ions. The specific surface area of sawdust is obtained as 0.86 m^2/g, which is much higher as compared to other low-cost adsorbent such as tea factory waste which has a specific area of 0.39 m^2/g [11]. Large specific surface area is one of the important reason for the higher uptake of Cr(VI) on sawdust. Sawdust has a lesser bulk density (0.125 g/cm^3) because of which almost all the surface is available for adsorption. This is also one of the reasons for the higher adsorption capacity of Cr(VI) on sawdust.

In previous studies [1–3], it has been found that the chemically activated naturally occurring adsorbent has a higher surface area and shows a larger capacity of Cr(VI) removal. But in the present study, the sawdust which has not been activated is comparatively showing a better adsorption capacity as compared to other chemically activated or non-activated adsorbents which is shown in Table 2. Adsorption also depends on various parameters such as initial pH, change in pH during adsorption, 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 and discussed in detail in the following section.

3.1. 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. 1 shows the percentage removal of Cr(VI) for different values of the initial Cr(VI) concentration ranging from 100 to 400 mg L^{-1} at pH 1. It is evident from Fig. 1 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 and 400 mg L^{-1} respectively till 1050 min (Fig. 1). 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 the 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 stages 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 the later stages of the Cr(VI) adsorption probably due to the slow pore diffusion of the solute ion into the bulk of the adsorbent.

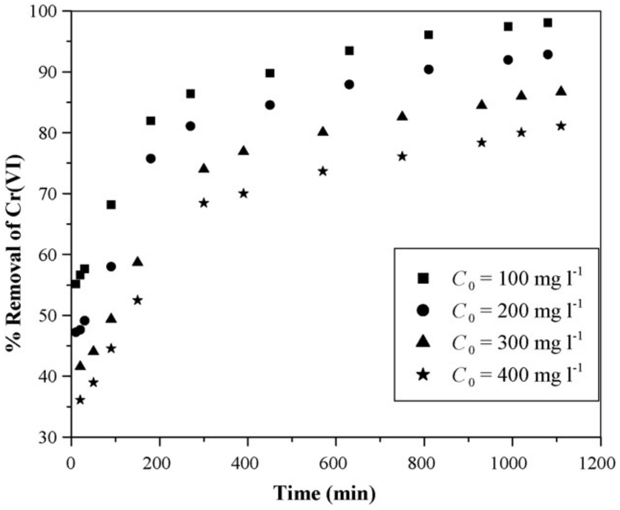

Fig. 1. Effect of contact time on the adsorption of Cr(VI) using sawdust at 30 °C and pH 1 for different initial Cr(VI) concentrations.

3.2. Effect of pH

It is well known that the initial pH of a system is an important parameter in the adsorption of Cr(VI) [90]. In the present work, the effect of initial 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 the percentage removal of Cr(VI) is shown in Fig. 2. The percentage removal of Cr(VI) is increased from 6.9% to 99.89% with decreasing the initial pH from 11 to 1. At an initial pH value of 1, the percentage removal of Cr(VI) from the aqueous Cr(VI) solution is 99.89% which shows almost the complete removal of Cr(VI). Hence, the further decrease in initial pH value does not have any significance. The following reaction (Eq. 24) and the subsequent reaction mechanism for adsorption of Cr(VI) at

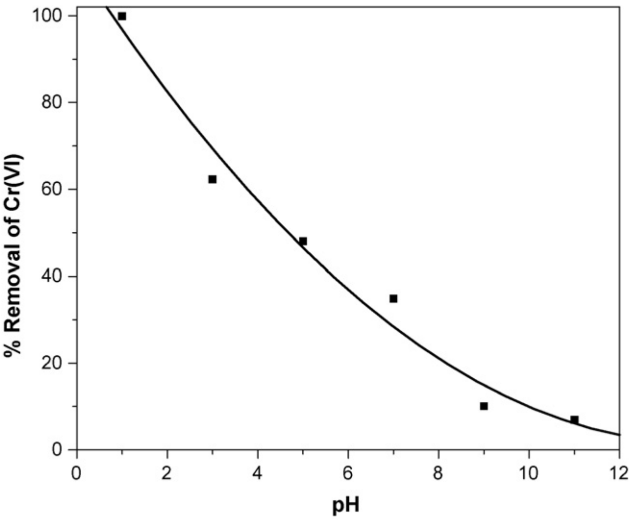

Fig. 2. Effect of pH on the adsorption of Cr(VI) using sawdust at 30 °C.

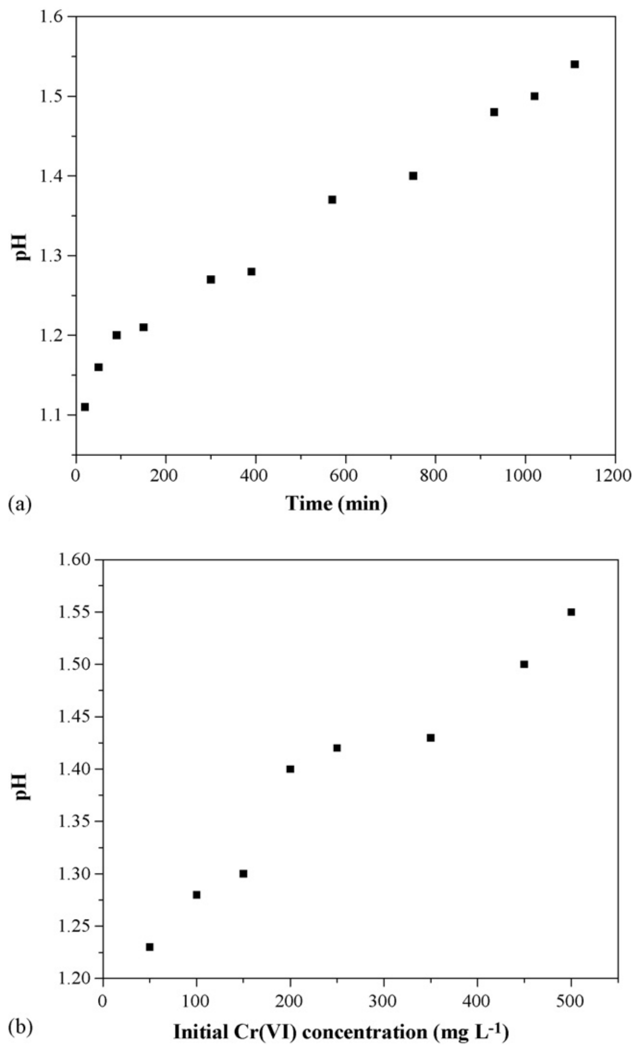

Fig. 3. (a) Change in pH of solution with time of adsorption at initial Cr(VI) concentration, 400 mg L^{-1}; and temperature, 30 °C. (b) Change in pH of solution with change in initial Cr(VI) concentration at initial pH 1; and temperature, 30 °C.

different pH values are used to explain the observed trend:

$$2H^+ + 2HCrO_4^- \xleftrightarrow{2H^+} 2H_2CrO_4 \leftrightarrow 2H_2O + Cr_2O_7^{2-} \xleftrightarrow{2H^+} 2CrO_3 + 2H_2O \qquad (24)$$

At a lower pH (pH 1) value, the dominant form of Cr(VI) is $HCrO_4^-$ while the surface of the adsorbent is charged positively. The stable forms of chromium such as H_2CrO_4 and CrO_3 exist as polynuclear species at a high chromium concentration [91] and hence the low pH value of 1 results in a higher percentage removal of Cr(VI) using sawdust. In addition, for the pH values above 1, the adsorption capacity decreases with increasing pH. Increasing the pH value will shift the concentration of $HCrO_4^-$ to other forms (CrO_4^{2-} and $Cr_2O_7^{2-}$). The decrease in adsorption of Cr(VI) by increasing the value of pH may be due to the dual competition of both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent of which OH^- predominates.

The change in solution pH is observed with time at initial Cr(VI) concentration of 400 mg L^{-1} by keeping the sawdust amount constant (10 g L^{-1}) and shown in Fig. 3(a). It is observed that the value of pH is increasing from 1.11 to 1.54 with the increase in adsorption time from 20 to 1110 min. Equilibrium solution pH value is also obtained at different initial Cr(VI) concentration ranging from 50 to 500 mg L^{-1} and is plotted in Fig. 3(b). The equilibrium pH is found increasing from 1.23 to 1.55 with increase in initial Cr(VI) concentration from 50 to 500 mg L^{-1}. The obtained results indicate that with increase in the adsorption of Cr(VI) on sawdust, the solution pH is found increasing. This may be due to the fact that sawdust is the carbonaceous material. Generally, oxo groups (C_xO and C_xO_2) are present on the surface of carbonaceous material which when come in contact with water, hydrolyze water molecules as shown in Eq. (25) [4]:

$$2H_2O + C_xO_2 \Leftrightarrow C_xOH_2^{2+} + 2OH^- \qquad (25)$$

Thus the equilibrium pH of solution is increased in the presence of hydroxyl ions. When Cr(VI) ions are introduced into the system, they are adsorbed onto the positively charged surface as given in the following Eq. (26):

$$C_xOH_2^{2+} + HCrO_4^- \Leftrightarrow C_xO_2H_3CrO_3^- \qquad (26)$$

Combining Eq. (25) and (26) gives Eq. (27):

$$C_xO + 2H_2O + HCrO_4^- \Leftrightarrow C_xO_2H_3CrO_3^- + 2OH^- \qquad (27)$$

Hence every mole of $HCrO_4^-$ adsorbed results in the release of two moles of hydroxyl ions into the solution which increases the solution pH.

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 the percentage removal of Cr(VI) resulting in an optimum sawdust amount. The influence of sawdust amount, varying from 4 to 24 g L^{-1} onto the Cr(VI) adsorption is shown in Fig. 4. The adsorption amount of Cr(VI) will not indicate the optimum amount of adsorbent used because both the percentage removal and the amount of Cr(VI) adsorbed show an increasing trend. So in the present study the adsorption capacity is used for the discussion of results obtained. Earlier studies have also reported in terms of the adsorption capacity [3,16]. The percentage of Cr(VI) removal increases from 98.30% to 99.66% with an increase in the sawdust amount from 4 to 24 g L^{-1} respectively. However, the adsorption capacity decreases from 12.29 to 2.08 mg g^{-1} by increasing the adsorbent amount from 4 to 24 g L^{-1}. It may be noted that though the increase in percentage removal is only from 98.30% to 99.66% (from 4 to 24 g/L for the above percentage removal range) which appears to be out of control, in order to find out the optimum amount of adsorbent (from

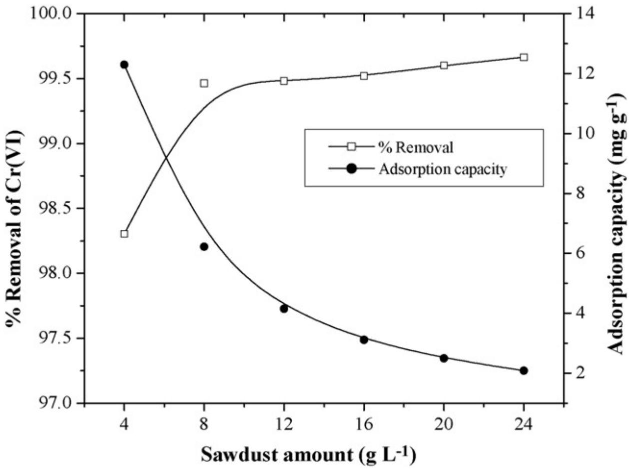

Fig. 4. Effect of amount of sawdust on the adsorption of Cr(VI) at initial Cr(VI) concentration, 50 mg L^{-1}; temperature, 30 °C; and initial pH, 1.

4 to 24 g/L for the above percentage removal range), the trade-off between the adsorption capacity (12.29–2.08 mg g^{-1}) and the percentage removal has to be studied. The increase in Cr(VI) removal with an increase in the sawdust amount is due to the increase in surface area and adsorption sites available for adsorption. The drop in adsorption capacity is basically due to the sites remaining unsaturated during the adsorption process. For the adsorbent amount of 5.4 g L^{-1}, the optimum values of Cr(VI) removal and the adsorption capacity are found to be 99.0% and 8.7 mg g^{-1}, respectively.

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} at an initial pH value of 1 while maintaining the sawdust amount of 10 g L^{-1} and obtained results are presented in Fig. 5. Once the equilibrium is reached between the solid phase Cr(VI) concentration and the aqueous phase Cr(VI) concentration, the pH value of solutions are measured. The equilibrium values of pH and final solution concentration are shown in Fig. 3(b). It is found that the final value of solution pH increases from 1.23 to 1.55 with an increase in the initial Cr(VI) concentration from 50 to 500 mg L^{-1}. This indicates that there is not a significant change in the final value of solution pH which confirms the higher acidic medium in solution after the adsorption of Cr(VI). The results show that with an increase in the Cr(VI) concentration from 50 to 500 mg L^{-1}, the percentage removal decreases from 99.9% to 89.9% and the adsorption capacity increases from 4.98 to 41.45 mg g^{-1}. The decrease in the percentage removal of Cr(VI) can be explained with 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 an increase in the Cr(VI) concentration may be due to the higher adsorption rate and the utilization of all the active sites available for the adsorption at higher concentration. For an initial Cr(VI) concentration of the 216 mg L^{-1}, the optimum values of Cr(VI) removal and the adsorption capacity are found to be 93.5% and 28 mg g^{-1} respectively.

3.5. Adsorption isotherm study

Adsorption isotherms are important to describe the adsorption mechanism for the interaction of Cr(VI) on the adsorbent surface. The equilibrium studies are useful to obtain the adsorption capacity of sawdust for Cr(VI) removal. An adsorption isotherm is characterized by certain constants that express the surface properties and the affinity of the adsorbent towards Cr(VI). The equilibrium data for the adsorption of Cr(VI) using sawdust fits into various isotherm models which results in a suitable model that can be used for the design of an adsorption process. In the present study, seven equilibrium models are analyzed to investigate the suitable adsorption isotherm, as the adsorbent developed is new.

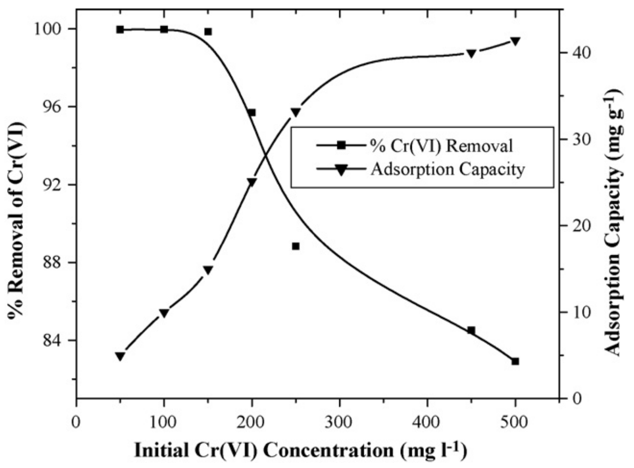

Fig. 5. Effect of initial Cr(VI) concentration on adsorption of Cr(VI) using sawdust at 30 °C and initial pH 1.

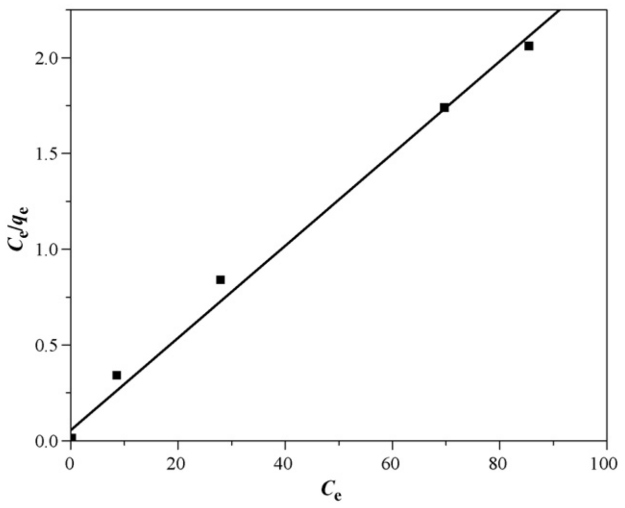

Fig. 6. Langmuir isotherm model for the Cr(VI) adsorption onto sawdust.

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 which is shown in Fig. 6. 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 equilibrium pH value range of 1.23–1.55. The Langmuir constant, b, which denotes adsorption energy, is found to be 0.4388 L mg^{-1}. The high value of coefficient of determination ($R^2 = 0.993$) obtained 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. The values of R_L are near to zero which favors the irreversible adsorption. Though the R^2 value obtained is reasonably high (0.993), in order to find out if a better fit is possible with other isotherms, the results are analyzed with other six isotherms available in the literature.

3.5.2. Freundlich isotherm

The Freundlich constants, K_f and n are obtained by plotting the graph between $\log q_e$ versus $\log C_e$ as shown in Fig. 7. The values of K_f and n_F are 16.66 and 0.2095 respectively. It is found that the coefficient of determination obtained from the 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.

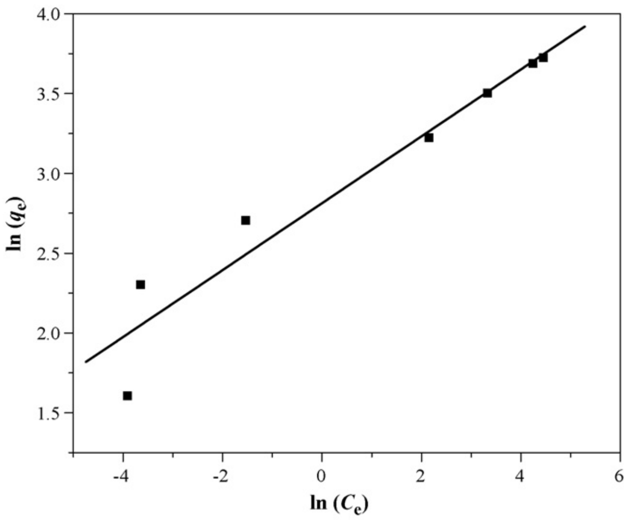

Fig. 7. Freundlich isotherm model for the Cr(VI) adsorption onto sawdust.

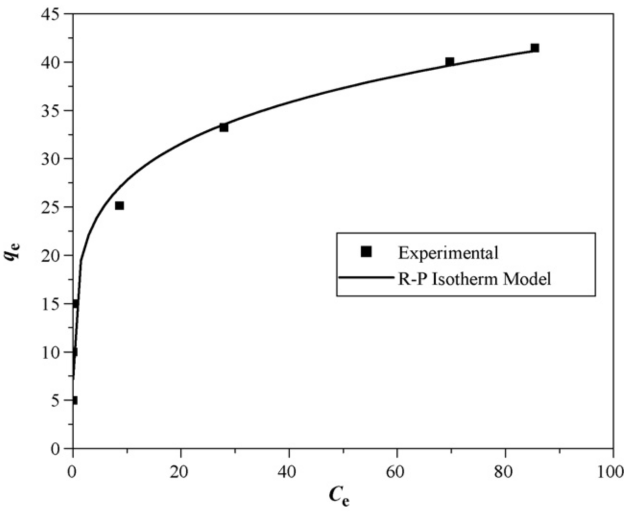

Fig. 8. Plot of equilibrium experimental data and calculated equilibrium data using Redlich–Peterson isotherm model for the adsorption of Cr(VI) onto sawdust.

So the three isotherm constants are obtained using a professional graphics software package ORIGIN (version 6) and are listed in Table 3. The experimental equilibrium data and the obtained equilibrium data using Redlich–Peterson model is plotted in Fig. 8. The coefficient of determination 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 coefficient of determination 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. Fig. 9 shows the comparison between the data predicted by Koble–Corrigan isotherm model and the equilibrium experimental data obtained for the adsorption of Cr(VI) at different initial Cr(VI) concentration. The coefficient of determination 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. The coefficient of determination obtained for Koble–Corrigan isotherm model is greater than that of Freundlich isotherm model but less than that of Langmuir isotherm and Redlich–Peterson isotherm models.

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	

3.5.5. *Tempkin isotherm*

A plot of q_e versus $\ln C_e$ at a constant temperature is used to calculate the Tempkin isotherm constants, A_T and b_T which is shown in Fig. 10. The constants A_T and b_T, obtained for Tempkin isotherm model are 235.49 L min^{-1} and 642.485 and also tabulated in Table 3. The obtained coefficient of determination (R^2) 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 coefficient of determination (R^2) in Table 3.

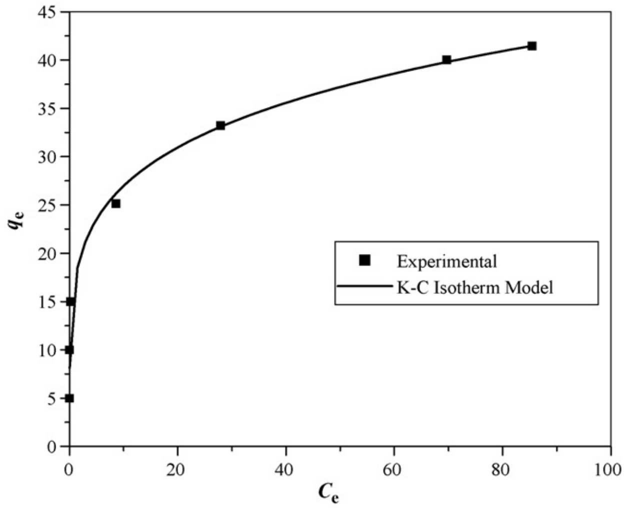

Fig. 9. Plot of equilibrium experimental data and calculated equilibrium data using Koble–Corrigan isotherm model for the adsorption of Cr(VI) onto sawdust.

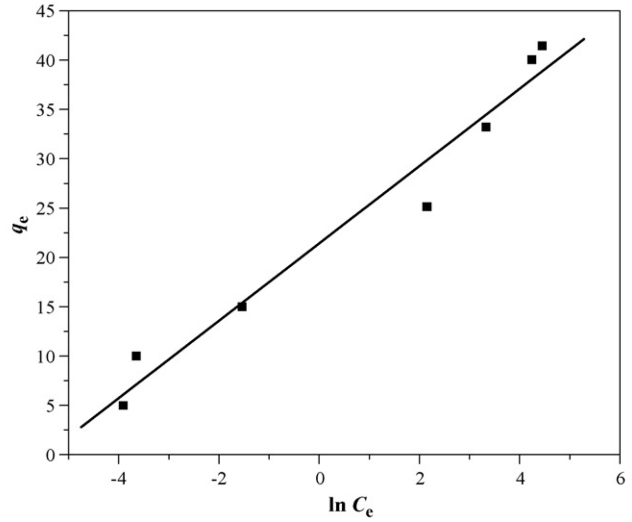

Fig. 10. Tempkin isotherm model for the Cr(VI) adsorption onto sawdust.

3.5.6. Dubinin–Radushkevich isotherm

Fig. 11 shows the plot between $\ln q_e$ and ε^2 at a constant temperature of 30 °C. The constants, Q_m and K obtained for Dubinin–Radushkevich isotherm model are 31.79 mg g^{-1} and 1.73×10^{-8} mol^2 kJ^{-2}. The value of coefficient of determination ($R^2 = 0.872$) 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 the adsorption of Cr(VI) by sawdust which is less than the value of Q_m obtained using the Langmuir isotherm model (41.5 mg g^{-1}). The mean free energy of adsorption, E, is obtained as 5.37 kJ mol^{-1}. The typical E values for ion-exchange mechanisms are ranged between 1 and 16 kJ mol^{-1}, indicating that the adsorption of Cr(VI) using sawdust is physical adsorption.

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 $\log C_e$ as shown in Fig. 12. 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 mg L^{-1}. The coefficient of determination obtained for the generalized isotherm model is 0.737 which is very much less than that obtained with the other isotherm models as given in Table 3. This shows that the equilibrium experimental data for adsorption of Cr(VI) on sawdust cannot be represented by the generalized isotherm model.

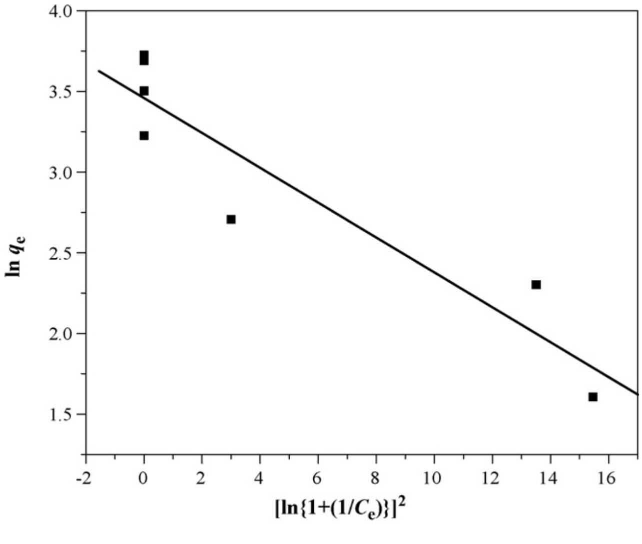

Fig. 11. Dubinin–Radushkevich isotherm model for the Cr(VI) adsorption onto sawdust.

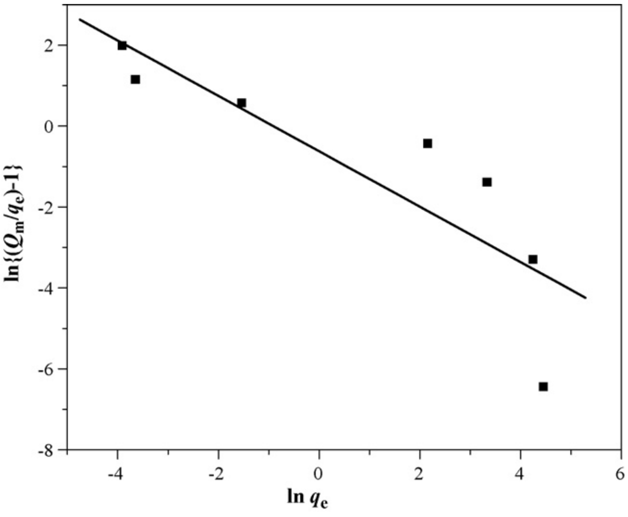

Fig. 12. Generalized isotherm model for the Cr(VI) adsorption onto sawdust.

3.5.8. Final remarks on isotherm study

The experimental equilibrium data are found to be fitted well with the Langmuir isotherm model which indicates the monomolecular adsorption of Cr(VI) onto sawdust. It is also fitting with Redlich–Peterson and Koble–Corrigan isotherm model as both these models are derived from Langmuir and Freundlich isotherm. Freundlich, Tempkin, Dubinin–Radushkevich, and Generalized isotherms cannot be used for explaining the equilibrium relationship of Cr(VI) adsorption onto sawdust.

Equilibrium relationship is required in designing of fixed-bed adsorption column which yields the difference in liquid-phase concentration and equilibrium solid phase concentration (driving force). This driving force is required to evaluate the amount of Cr(VI) accumulated on solid surface which is needed to obtain the liquid-phase concentration of Cr(VI) at any given height and time. Adsorption isotherm also characterizes the shape of the breakthrough curve which is dominant design parameter in designing of fixed-bed adsorption column. If the isotherm is favorable, the breakthrough curve becomes steeper which results decrease in the length of unused bed and higher percentage removal of Cr(VI) of the fixed-bed adsorption column.

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 as shown in Fig. 13 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 constant (10 g L^{-1}), are calculated and listed in Table 4. The coefficient of determination (R^2) 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

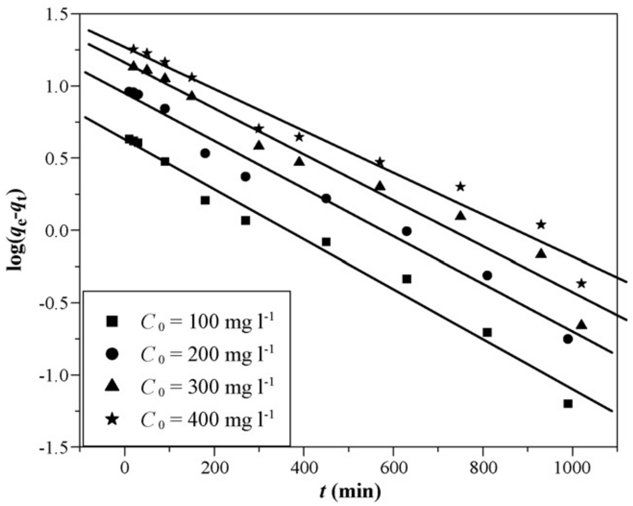

Fig. 13. Lagergren plot for the adsorption of Cr(VI) using sawdust for adsorbent amount, 10 g L^{-1}; initial pH, 1.0; and temperature, 30 °C.

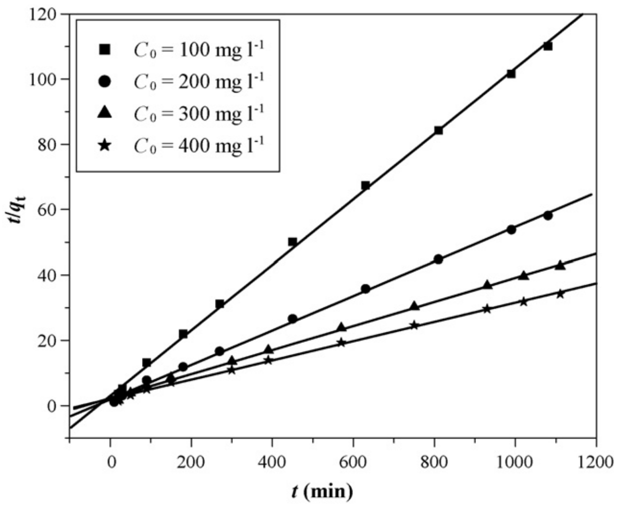

Fig. 14. Second-order plot for the adsorption of Cr(VI) using sawdust for adsorbent amount, 10 g L^{-1}; initial pH, 1.0; and temperature, 30 °C.

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 as expected (as discussed in Section 2.6.1) with the pseudo first-order model predicted values as given in Table 4.

3.6.2. Second-order kinetics

As a result of the non-applicability of pseudo first-order model, the kinetics for the adsorption of Cr(VI) on sawdust is tested with the second-order kinetic model. The application of the second-order kinetics by plotting t/q_t versus t as shown in Fig. 14, yielded the second-order rate constant, k_2, estimated equilibrium capacity q_e, and the coefficient of determination (R^2) for the initial Cr(VI) concentration ranging from 100 to 400 mg L^{-1}, which are reported in Table 4. The calculated q_e values show a good agreement with the experimental values and the obtained values for coefficient of determination (R^2) are more than 0.997 which indicates that the second-order kinetic model describes well the removal of Cr(VI) using sawdust as an adsorbent.

3.6.3. Elovich kinetic equation

Fig. 15 represents the application of linear form of Elovich kinetic equation which is a plot between q_t and $\ln t$. The Elovich kinetic constants α and β are obtained from the intercept and the slope respectively. The coefficient of determination (R^2) are obtained in the range of 0.962–0.976 for all the 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.

3.6.4. Final remarks on kinetic studies

The value of coefficient of determination (R^2) for the second-order kinetic model is more than that obtained using the pseudo first-order and Elovich kinetic models for all the values of the initial Cr(VI) concentration. Thus the kinetics of Cr(VI) adsorption using sawdust as an adsorbent can be better explained by the second-order kinetic model. It is important to get the rate at which Cr(VI) is adsorbed on to the solid surface of sawdust which is important in designing of fixed-bed adsorption column. With the use of adsorption rate kinetic constants, the mass transfer coefficient and equilibrium capacity of adsorbent at different fluid phase concentration can be obtained. Amount of Cr(VI) adsorbed in solid surface is estimated using the kinetic equation which is required to estimate the fluid phase concentration in fixed-bed column operation. The dominant design parameters of fixed-bed adsorption column, the breakthrough time and shape of the breakthrough curve are

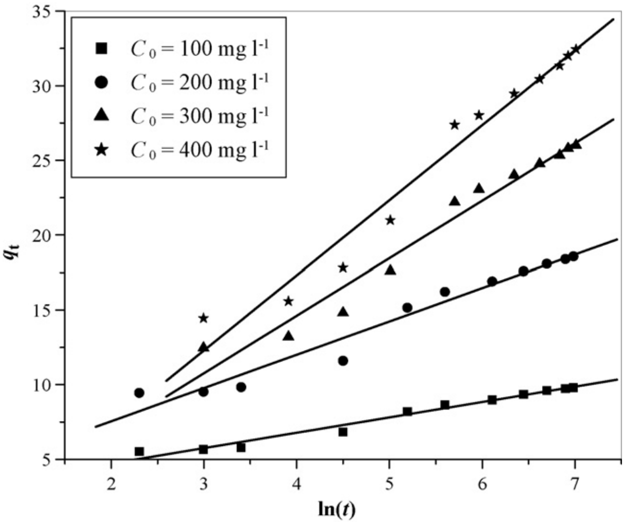

Fig. 15. Elovich kinetic model plot for the adsorption of Cr(VI) using sawdust for adsorbent amount, 10 g L^{-1}; initial pH, 1.0; and temperature, 30 °C.

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		
			$k_1 \times 10^3$	q_e	R^2	$k_2 \times 10^3$	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

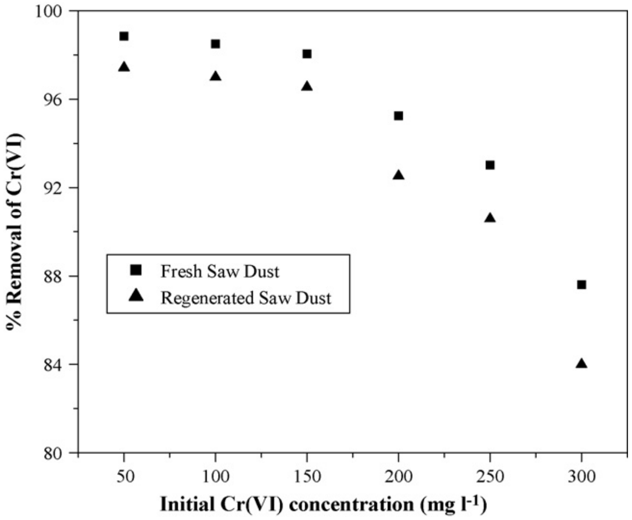

Fig. 16. Comparison for the percentage removal of Cr(VI) using fresh and regenerated sawdust.

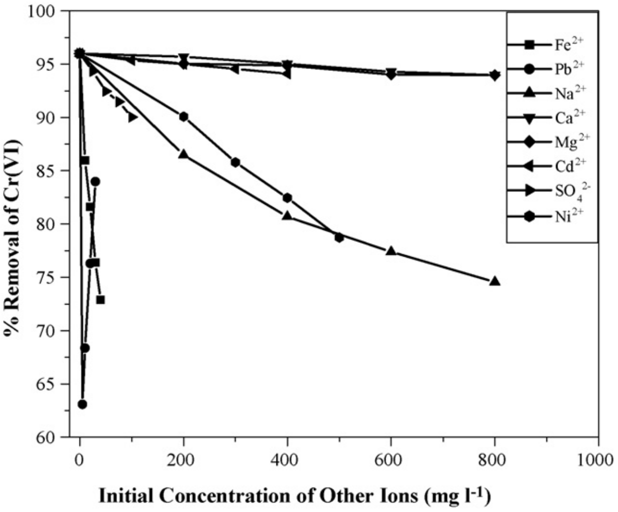

Fig. 17. Effect of other ions on the removal of Cr(VI) using sawdust.

dependent on rate of adsorption. For the faster rate of adsorption, breakpoint time is obtained earlier, and shape of the breakthrough curve is steeper.

3.7. Regeneration studies

The saturated adsorbent which contains Cr(VI) is not safe for the disposal due to the stringent environmental constraints. It is important and appropriate to propose a method for the 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. 16 shows the comparison of the percentage removal of Cr(VI) using fresh and regenerated sawdust. The regenerated sawdust is again used for the adsorption of Cr(VI) using the same initial Cr(VI) concentration ranging between 50 and 500 mg L^{-1} as used for fresh saw dust. The percentage removal of Cr(VI) obtained found to decrease from 97.42% to 83.99% respectively as compared to the corresponding values for fresh adsorbent ranging from 98.85% to 87.59%. These results using regenerated sawdust exhibit higher desorption efficiency by more than 95% of the fresh sawdust 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 as indicated by the results obtained in this study. The adsorption of Cr(VI) onto the sawdust is highly pH dependent. Hence, desorption of Cr(VI) is accomplished by increasing the solution pH.

3.8. Disposal of contaminated solution

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 Cr(VI) solution precipitates a bright yellow barium chromate, as given by the following reaction (Eq. (28))

$$Ba^{2+}(aq) + CrO_4{}^{2-}(aq) \rightarrow BaCrO_4(s) \qquad (28)$$

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.

3.9. Interference of other ions

In the present study, the interference of other ions such as Fe^{2+}, Pb^{2+}, Na^{+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, $SO_4{}^{-2}$, and Ni^{2+} present in the electroplating industrial effluent [9] and tannery effluent [71] wastewater streams is studied for the Cr(VI) removal. The effect of co-existed ions has not been determined in the present study. As per the results reported by Rajesh et al. [92], the other co-existed ions such as Cl^{-}, $NO_3{}^{-}$ have insignificant effect on the percentage removal of Cr(VI). The effect of initial concentration of each ion for varying ranges (Table 1) on the percentage removal of Cr(VI) is plotted in Fig. 17. The percentage removal of Cr(VI) is marginally decreased (94.1–89% as shown in Fig. 17) by the presence of Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} ions. Hence, it can be inferred 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 higher 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 the 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 the other ions such as Na^{+}, and $SO_4{}^{-2}$ as shown in Fig. 17. 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 an increase in the 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 the reaction below [Eq. (29)]:

$$Pb^{2+}(aq) + CrO_4{}^{2-}(aq) \rightarrow PbCrO_4(s) \qquad (29)$$

The synthetic solution for the electroplating industry and the tannery industry effluents (Table 1) are treated with the sawdust which resulted 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.

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 many other low cost and commercially available adsorbents. The maximum percentage removal of Cr(VI) is obtained at pH 1. The dominant form of Cr(VI) is $HCrO_4^-$ and the surface of adsorbent is charged positively at a lower pH values. It is found from the kinetic studies that the adsorption rate of Cr(VI) is faster for the 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 the availability of more unsaturated adsorption sites. The percentage removal decreases and the adsorption capacity increases with an increase in the initial Cr(VI) concentration. The equilibrium adsorption data are tested 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 $41.52\,\mathrm{mg\,g^{-1}}$, 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 saturated adsorption is regenerated by acid and base treatment. The adsorption efficiency of the regenerated sawdust is found to be more than 95% of fresh sawdust for the removal of Cr(VI). The possible solution for the major problem of desorption process [i.e. the disposal of the acid and base solution obtained that contains high concentration of Cr(VI)] is the precipitation of Cr(VI) as barium chromate. 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 amounts of Cr(VI).

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