

Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents

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Abstract

The removal of Cr(VI) from aqueous solution by batch adsorption technique using different low-cost adsorbents was investigated. Adsorbents such as clarified sludge—a steel industry waste material, rice husk ash, activated alumina, fuller's earth, fly ash, saw dust and neem bark were used to determine the adsorption efficiency. The influence of pH, adsorbent type and concentration, initial Cr(VI) concentration and contact time on the selectivity and sensitivity of the removal process were investigated. Adsorption process was found to be highly pH dependent. The optimum pH range for adsorption of Cr(VI) was found to be between 2 and 3. Kinetics studies were performed to understand the mechanistic steps of the adsorption process and the rate kinetics for the adsorption of Cr(VI) was best fitted with the pseudo-2nd-order kinetic model. Langmuir and Freundlich adsorption isotherms were applicable to the adsorption process and their constants were evaluated. The thermodynamic equilibrium constant and the Gibbs free energy were determined for each system. The adsorption capacity (q_{\max}) calculated from Langmuir isotherm and the Gibbs free energy (ΔG°) value obtained for the different adsorbents showed that clarified sludge was the most effective among the selected adsorbents for the removal of Cr(VI) from aqueous solution. The adsorption efficiencies of rice husk ash and activated alumina were also equally comparable with that of clarified sludge.

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Keywords: Chromium(VI); Low-cost adsorbents; Clarified sludge; Langmuir isotherm; Gibbs free energy

1. Introduction

Chromium exists usually in both trivalent and hexavalent forms in aqueous systems. The two-oxidation states of chromium have different chemical, biological and environmental characteristics [1]. Cr(III) is relatively insoluble and required by microorganisms in small quantities as an essential trace metal nutrient [2], while Cr(VI) is a great concern because of its toxicity. Cr(VI) has been reported to be a primary contaminant to humans, animals, plants and microorganisms and it is known to be carcinogenic [3–5]. Chromium is used in a variety of industrial applications; hence, large quantities of chromium are discharged into the environment. Sources of chromium waste leading to water pollution includes electroplating, steel fab-

rication, paints and pigments, mining, leather tanning, textile dyeing, aluminum conversion coating operations, plants producing industrial inorganic chemicals and wood treatment units [6–8]. Due to environmental concern, discharge limits of both Cr(III) and Cr(VI) have been instituted by most industrial countries. Their concentration in industrial wastewaters ranges from 0.5 to 270 mg/L [7]. The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L [9,10]. The Ministry of Environment and Forest (MOEF); Government of India has set minimal national standards (MINAS) of 0.1 mg/L for safe discharge of effluent containing Cr(VI) in surface water [11]. In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr(VI) concentration in water and wastewater to acceptable levels before its transport and cycling into the natural environment.

Therefore, the level of chromium in final effluent has to be reduced by the application of appropriate technology. In

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Nomenclature

b	Langmuir constant (L/mg)
C	concentration of Cr(VI) after certain period of time (mg/L)
C_a	concentration of Cr(VI) on the adsorbent at equilibrium (mg/L)
C_e	concentration of Cr(VI) in solution at equilibrium (mg/L)
C_{final}	final concentration of Cr(VI) in solution (mg/L)
C_{initial}	initial concentration of Cr(VI) in solution (mg/L)
C_0	initial concentration of Cr(VI) in solution (mg/L)
C_t	concentration of Cr(VI) after time t (mg/L)
ΔG°	Gibbs free energy (kJ/mol)
K'	pseudo-2nd-order rate constant of adsorption [(mg/g) min]
K_{ad}	Lagergren rate constant (min^{-1})
K_c	thermodynamic equilibrium constant
K_f	measure of adsorption capacity (mg/g)
K_{id}	intra-particle rate constant [$\text{mg/g}/\text{min}^{1/2}$]
K_{bq}	the constant obtained by multiplying q_{max} and b
m	amount of adsorbent added (g)
M	mass of the adsorbent per unit volume (g/L)
n	Freundlich constants, intensity of adsorption
q	amount adsorb per gm of the adsorbent (mg/g)
q_e	amount adsorb per gram of the adsorbent at equilibrium
q_{max}	maximum adsorption capacity (mg/g)
q_t	amount adsorb per gm of adsorbent at time t (min)
r^2	correlation coefficient
R_L	separation factor
S_s	external surface area of the adsorbent per unit volume (m^{-1})
t	time (min)
V	volume of the solution in (mL)
<i>Greek letter</i>	
β	mass transfer coefficient (m/s)

wastewater treatment, various methods are utilized to remove chromium. These include reduction followed by chemical precipitation [12], ion exchange [13], electrochemical precipitation [14], reduction [15], adsorption [16], solvent extraction [17], membrane separation [18], concentration [19], evaporation, reverse osmosis and bio-sorption [20,21] and emulsion pertraction technology [22].

Adsorption is by far most versatile and effective method for removing any contaminants like heavy metal, especially, if combined with appropriate regeneration steps. This solves the problem of sludge disposal and renders the system more economically viable, especially if low-cost adsorbents are used [23]. In the last few years, several approaches have been reported in this direction utilizing inexpensive and effective adsorbent for removal of Cr(VI) from aqueous solutions. The advantages of the low-cost adsorbents over the conventional adsorbents are as follows:

- (1) The efficiencies of various non-conventional adsorbents towards adsorbate removal vary generally between 50% and 90% depending on the characteristics and particle size of the adsorbent, and the characteristics and concentration of the adsorbate, etc. Hence, low-cost adsorbents can be employed efficiently in removal of heavy metals.
- (2) Non-conventional adsorbents are much cheaper relative to conventional adsorbents, and when readily available locally lead to much reduced transportation costs.
- (3) Non-conventional adsorbents require simple alkali/and or acid treatment for the removal of lignin before application in order to increase their efficiency.
- (4) Non-conventional adsorbents require less maintenance and supervision.

The materials developed for this purpose range from industrial wastes to agricultural waste products, biomass and various solid substances. Some examples are hydrous concrete particles [24], paper mill sludge [16], seaweed biosorbent [25], tannin gel particles [26], sugar beet pulp [27], wheat bran [28], leaf mould [29], coniferous leaves [30], activated groundnut husk carbon [31], coconut husk and palm pressed fibers [32], coconut shell, wood and dust coal activated carbons [33], coconut tree sawdust carbon [34], used tyres carbon [35], cactus, olive stone/cake, wool, charcoal, and pine needles [36], rice husk carbon [37], moss [38], sphagnum moss peat [39], hazelnut shell carbon [40,41], almond shell carbon [42], corncob [43], cow dung carbon [44], agricultural wastes [45], waste slurry [46], carbon slurry [47], lignocellulosic solid wastes [48], charred rice husk and activated charcoal and eucalyptus bark [49] have been reported in literature.

However, to cover this problem, more work and investigations are needed to deal with other locally available and economically viable adsorbents to eliminate Cr(VI) from aqueous solutions having different composition and characteristics. In this paper, the use of seven different inexpensive and readily available adsorbents was reported to determine their efficiency on removing Cr(VI) from aqueous solution. The effects of adsorbent concentration, pH, contact time and initial metal ion concentration on the adsorption capacity were investigated. The rate kinetics and equilibrium parameters were determined. Adsorption isotherm models and thermodynamic parameters were also investigated to know the adsorption behavior.

2. Materials and methods

2.1. Adsorbents used and its sources

The adsorbent used for the experiments are clarified sludge—a steel industry waste material, rice husk ash, activated alumina, fuller's earth, coal fly ash, sawdust of teak wood origin and neem bark.

Clarified sludge was collected from sludge thickener of Basic Oxygen Furnace of Steel Industry. The huge quantity of sludge generated per day has got a severe disposal problem from pollution control point of view. It is collected from Rourkela Steel

Plant, Rourkela, India. After collection, the material was ground and homogenized.

Rice husk is widely used as fuel source in rice mill boiler. After burning the husk the ash generated is called rice husk ash. The sample of rice husk ash was collected from a local rice mill, ground and homogenized.

Coal fly ash was collected from Bandel Thermal Power Station; Bandel, West Benagal, India. After collection, the material was ground and homogenized.

Sawdust was collected from a local sawmill. It was of teakwood origin. After collection it was washed thoroughly with double distilled water and then with 0.1 N NaOH to remove lignin based color materials followed by 0.1 N H₂SO₄. Finally, it was again washed with double distilled water several times and dried in an oven at 105 ± 5 °C for 6 h.

Neem bark was collected from a local source. After collection it washed thoroughly with double distilled water to remove muddy materials and then sun dried. Then it was cut into small pieces and ground to pass through –44 + 52 mesh screen. After screening it again washed with double distilled water several times to remove dust and color. Finally it was dried in an oven at 105 ± 5 °C for 6 h.

Activated alumina was procured from M/S Titan Biotech, New Delhi, India. After procurement the material was ground and homogenized.

Fuller's earth was procured M/S Loba Chemie Pvt. Limited; Mumbai, India.

All the adsorbents after drying at 105 ± 5 °C to constant weight were cooled in desiccators, homogenized and finally sieved to obtain particle size of –44 + 52 mesh prior to use for adsorption studies.

2.2. Reagents

All the primary chemicals used were of analytical grade. Potassium dichromate, caustic soda, hydrochloric acid solution and other necessary chemicals were purchased from E. Merck India Limited, Mumbai, India. The stock solution containing 1000 ppm of Cr(VI) was prepared by dissolving 1.4143 g quantity of AR grade K₂Cr₂O₇ in 500 mL of de-ionized, double distilled water. Required initial concentration of Cr(VI) standards were prepared by appropriate dilution of the above stock Cr(VI) standard solution.

2.3. Equipment

The surface area of the adsorbents was determined by BET method using a surface area analyzer (Model 1750 SORPTY, Carlo Erba, Italy). The densities of the adsorbents were determined using specific gravity bottles. X-ray diffraction studies were carried out with an X-ray diffractometer (Model No. XRD 3000P, Seifert, Germany) employing nickel filtered Cu K α radiations. The particle size distributions analysis was carried out with the different adsorbents of mesh size –44 + 52 using a Particle Size Distribution analyzer (Model 117.08, MALVERN instruments, USA). The chemical analysis of clarified sludge, rice husk ash and fly ash was carried out by standard meth-

ods of chemical analysis [50]. HACH-DR-4000 UV Visible Spectrophotometer was used for determination of chromium content in standard and treated solutions. The pH of the solution was measured with a EUTECH make digital microprocessor based pH meter previously calibrated with standard buffer solutions.

2.4. Batch adsorption experiments

All experiments were carried out at room temperature, i.e., 30 ± 2 °C. Using the necessary adsorbents in a 250 mL stopper conical flask containing 100 mL of test solution batch adsorption studies were carried out at the desired pH value, contact time and adsorbent dosage level. Different initial concentration of Cr(VI) solutions was prepared by proper dilution from stock 1000-ppm Cr(VI) standard. pH of the solution was monitored by adding 0.1 M HCl and 0.1 M NaOH solution as required. Necessary amount of adsorbent material was then added and contents in the flask were shaken for the desired contact time in an electrically thermo stated reciprocating shaker @ 110–125 strokes/min. The time required for reaching the equilibrium condition estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through filter paper and the filtrate was analyzed for remaining Cr(VI) concentration in the sample using HACH-DR-4000 UV visible spectrophotometer with 1,5-diphenylcarbazide in acid medium by following APHA, AWWA standard methods for examination of water and wastewater [51]. The amount of Cr(VI) adsorbed per unit mass of the adsorbent was evaluated by using the following mass balance equation,

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

The percent removal of Cr(VI) was calculated as follows:

$$\% \text{Removal of Cr(VI)} = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100 \quad (2)$$

The effect of adsorbent dosage level on percent removal of chromium was studied using Cr(VI) concentration of 50 mg/L having pH adjusted to 3. The selected adsorbents were used at concentration ranging from 2.5 g/L to 30 g/L.

Adsorption experiments for the effect of pH were conducted by using a solution having 50 mg/L of Cr(VI) concentration with an adsorbent dosage of 10 g/L and stirring the same for a contact time of 4 h.

Effect on variation of initial concentration was studied using Cr(VI) solution of concentration 3 mg/L to 50 mg/L at pH 3, contact time of 4 h and adsorbent dosage level of 10 g/L.

The kinetic parameters for the adsorption process were studied on the batch adsorption of 50 ppm of Cr(VI) at pH 3. The contact time was varied from 0.25 h to 5 h and the percent removal of Cr(VI) was monitored during the study.

Adsorption isotherm studies were carried out with eight different initial concentrations of Cr(VI) from 10 mg/L to 300 mg/L at pH 3, contact time 4 h and adsorbent dosage level of 10 g/L.

All the investigations were carried out in duplicate to confirm reproducibility of the experimental results. The reproducibility

Table 1
Bulk density and surface area of the adsorbents (–44 + 52 mesh size)

Material	Bulk density (g/cm ³)	Surface area (m ² /g)
Clarified sludge	1.98	78.54
Rice husk ash	0.96	57.5
Activated alumina	0.83	126
Fuller's earth	0.78	38.5
Fly ash	1.76	6.42
Neem bark	0.56	3.47
Saw dust	0.53	3.85

and relative deviation are of the order of $\pm 0.5\%$ and $\pm 2.5\%$, respectively.

3. Results and discussion

3.1. Characterization of the adsorbent materials

The surface area and density of the adsorbents of –44 + 52 mesh are given in Table 1. The X-ray diffraction studies were carried out for clarified sludge, rice husk ash, fly ash, activated alumina and fuller's earth samples and the obtained spectra of the samples are shown in Fig. 1(a)–(e). The spectra of clarified sludge as shown in Fig. 1(a) indicate the presence of iron oxide, silica and calcium as major constituents with other metal oxides as trace or minor constituents. XRD spectra of rice husk ash (Fig. 1(b)) indicate the presence of silica as major constituents with calcium, iron, aluminum and sodium as minor constituents. The spectra of activated alumina as shown in Fig. 1(c) indicate that it is an alumina-based material with silica as extremely minor constituents. Fuller's earth is an alumina and magnesium silicate based material (Fig. 1(d)). The XRD spectra pattern (Fig. 1(e)) of fly ash indicates the presence of silica, iron oxide, calcium oxide with alumina and other metal oxides as trace and minor constituents.

The Particle size distribution analysis was carried out with the different adsorbents of mesh size –44 + 52 using a Particle Size Distribution analyzer (Model 117.08, MALVERN instruments, USA). The results obtained are presented in Table 2.

Saw dust and neem bark are cellulose-based material containing tannin and lignin based organic compounds. The chemical analysis of clarified sludge, rice husk ash and fly ash was carried out by standard methods of chemical analysis [50]. The

Table 2
Particle size distribution of the different adsorbents (–44 + 52 mesh: 250–350 μm)

Adsorbents	Size distribution (μm)							
	250–275	275–285	285–295	295–305	305–315	315–325	325–335	335–350
Clarified sludge (%)	0.9	18.3	25.1	10.7	16.5	17.2	8.7	2.6
Rice husk ash (%)	3.5	17.3	20.1	13.2	10.1	25.3	10.1	0.4
Activated alumina (%)	2.0	40.4	30.5	9.2	7.8	6.5	2.2	1.4
Fuller's earth (%)	0.8	17.9	6.8	35.2	20.1	15.5	3.7	–
Fly ash (%)	3.8	15.9	16.7	19.2	30.1	6.3	6.1	1.9
Saw dust (%)	5.2	29.7	18.3	17.1	15.6	3.2	9.1	1.8
Neem bark (%)	1.1	25.7	15.4	23.5	20.2	10.5	3.6	–

Table 3
Chemical composition and characteristics of clarified sludge, rice husk ash, fly ash and activated alumina

Constituent	Percent by weight (%)			
	Clarified sludge	Rice husk ash	Fly ash	Activated alumina
Loss on ignition	12	12.2	12	6.7
Fe ₂ O ₃	48	0.6	8.33	0.03
Al ₂ O ₃	–	0.3	22.01	93.1
CaO	23.4	1.4	2.57	–
MgO	2.5	0.5	0.91	–
MnO	0.2	–	–	–
SiO ₂	12.6	84.3	57.82	0.03
Na ₂ O	0.7	0.4	–	0.1
K ₂ O	0.5	0.2	0.45	–

chemical composition of clarified sludge, rice husk ash, fly ash and activated alumina used for adsorption studies is shown in Table 3.

3.2. Effect of pH

The uptake of Cr(VI) as a function of hydrogen ion concentration was examined over a pH range of 2–11 and shown in Fig. 2. From the figure, it is evident that the adsorption characteristics of the adsorbents are highly pH dependent. The optimum pH range for removal of Cr(VI) was found to be between 2 and 3. For clarified sludge, at pH 3 maximum 97.4% Cr(VI) removal was observed. In case of rice husk ash and sawdust removal efficiency of Cr(VI) at pH 3 was 94.8% and 86.5%, respectively. For fly ash and neem bark, the maximum removal of Cr(VI) was achieved at pH 2, and the removal efficiency was 89.2% and 84.5%, respectively. Activated alumina and fuller's earth showed maximum removal efficiency at pH 3 for adsorption of Cr(VI). Therefore, maximum removal of Cr(VI) from aqueous solution was achieved at pH 2–3 and all the further studies on comparative adsorption of Cr(VI) by the selected adsorbents were carried out by maintaining the solution at pH 3.

Chromium exists mostly in two oxidation states which are Cr(VI) and Cr(III) and the stability of these forms is dependent on the pH of the system [33,40]. It is well known [36,52] that the dominant form of Cr(VI) at aforesaid pH is HCrO_4^- which arises from the hydrolysis reaction of the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$)

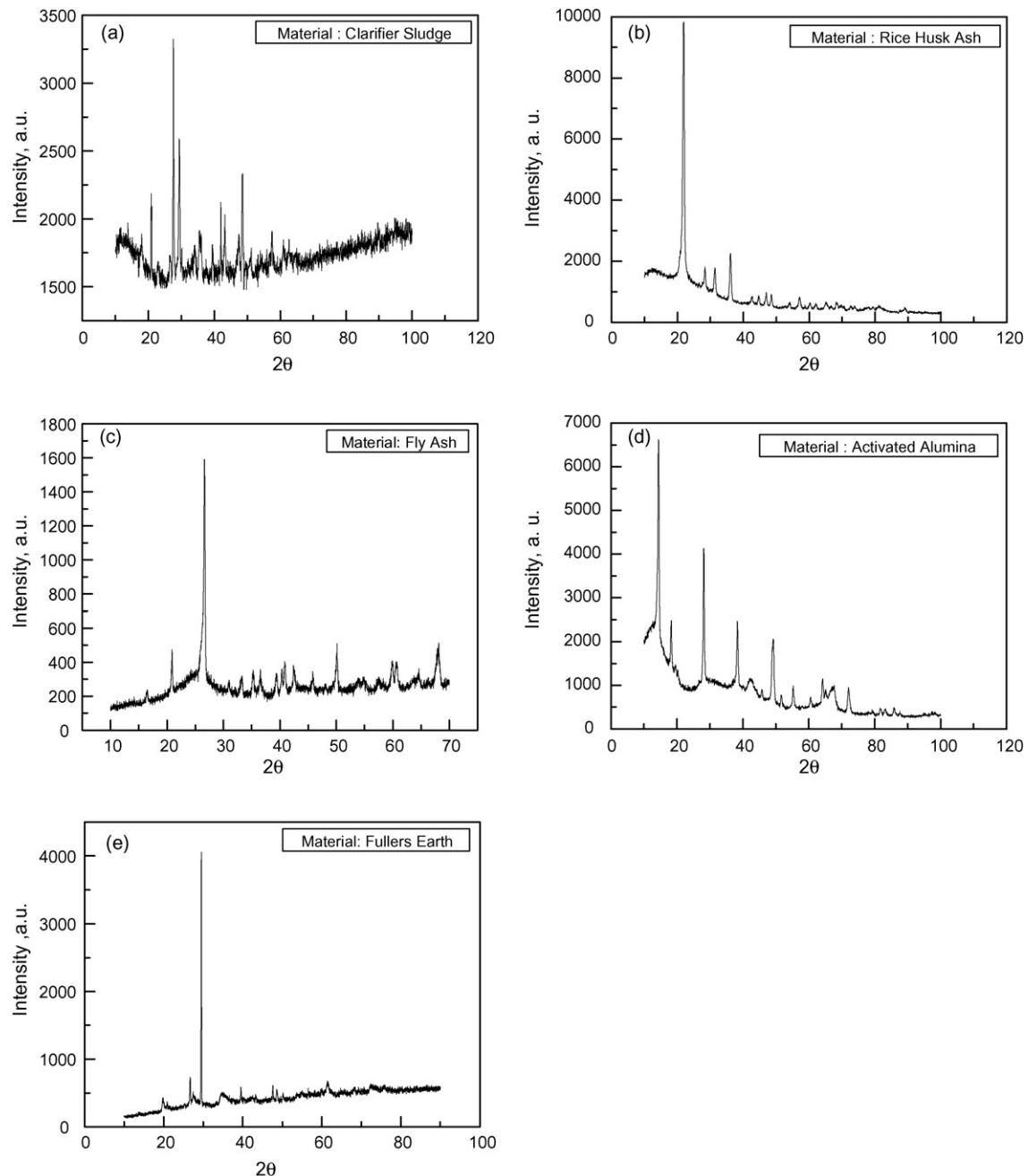


Fig. 1. (a)–(e) XRD spectra of clarified sludge, rice husk ash, fly ash, activated alumina and fuller's earth.

according to the equation



Increasing the pH will shift the concentration of HCrO_4^- to $\text{Cr}_2\text{O}_7^{2-}$ and other forms as CrO_4^{2-} . Maximum adsorption at pH 2 and 3 indicates that it was the HCrO_4^- form of Cr(VI), which was the predominant species at this pH range and adsorbed preferentially on the adsorbents. Better adsorption capacity observed at low pH values with optimum range of pH between 2 and 3 may be attributed to the large number of H^+ ions present at these pH values, which in turn neutralize the negatively charged hydroxyl group ($-\text{OH}$) on adsorbed surface thereby reducing

the hindrance to the diffusion of dichromate ions. At higher pH values, the reduction in adsorption may be possible due to abundance of OH^- ions causing increased hindrance to diffusion of dichromate ions.

3.3. Effect of initial metal ion concentration

The efficiency of Cr(VI) removal was affected by the initial metal ion concentration, with decreasing removal percentages as concentration increases from 3 mg/L to 50 mg/L at constant pH 3, adsorbent dosage level 10 g/L and contact time of 4 h duration as shown in Fig. 3. At low metal ion/adsorbent ratios, metal ion adsorption involves higher energy sites. As the metal

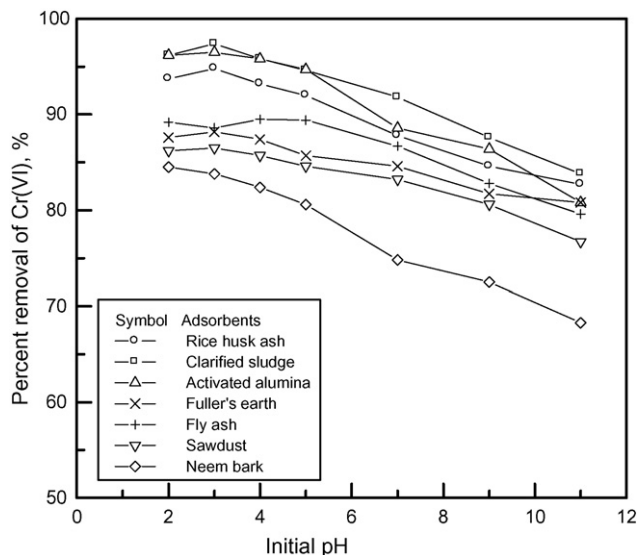


Fig. 2. Effect of pH on the adsorption of Cr(VI) by selected adsorbents, Initial Cr(VI) concentration 50 mg/L, adsorbent dosage 10 g/L, contact time 4 h.

ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decreases in the adsorption efficiency [53,54].

3.4. Effect of adsorbent type and concentration

The effect of adsorbent type and its concentration is depicted in Fig. 4. The selected adsorbents (clarified sludge, rice husk ash, activated alumina, fuller's earth, coal fly ash, sawdust and neem bark) were used at concentration ranging from 2.5 g/L to 30 g/L in a batch adsorption technique. In each case increase in adsorbent concentration resulted in an increase in percent removal of Cr(VI). After certain adsorbent dosage the removal efficiency is not increased so significantly. At 5 g/L of adsorbent

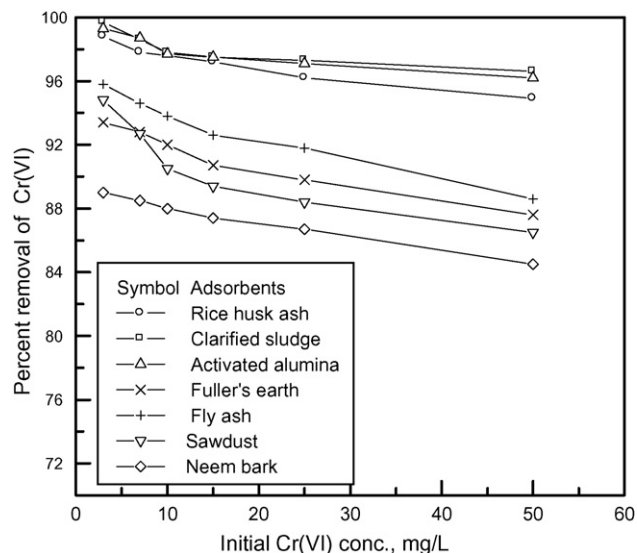


Fig. 3. Effect of initial concentration on the adsorption of Cr(VI) by selected adsorbents: pH 3, adsorbent concentration 10 g/L, contact time 4 h.

dosage level, the removal of Cr(VI) was found to be between 95.6% for clarified sludge and 80.7% for sawdust. At 10 g/L of clarified sludge the Cr(VI) removal was 96.6%. In case of rice husk ash, Cr(VI) removal efficiency of 95.2% was achieved at an adsorbent dosage level of 10 g/L and for activated alumina under same condition the removal efficiency was 96.5%. Fly ash and fuller's earth showed the removal efficiency of 89.7% and 87.7%, respectively at the same dosage level (10 g/L). For neem bark at 10 g/L adsorbent dosage level, maximum 84.3% Cr(VI) removal was obtained under the same experimental conditions. It is evident that for all the adsorbents maximum removal efficiency was achieved at an adsorbent dosage level of 10 g/L. Therefore, the following experiments were carried out at adsorbent concentration of 10 g/L. The variation in sorption capacities between the various adsorbents could be related to the type and concentration of surface group responsible for adsorption of metal ions from solution. With increasing adsorbent dosage more surface area is available for adsorption due to increase in active sites on the adsorbent. Rice husk ash contains carbon and silica based material that binds the metal ion from aqueous solution. Activate Alumina is an alumina based material with trace amounts of metal oxides and silica which act as an adsorbent sites. Adsorption Cr(VI) by clarified sludge may be attributed due to the combined effect of silica, metal oxides and carbon present in it as major constituents. Fuller's earth contains hydrous alumina-silicate based substances that makes it a useful adsorbent. Fly ash is an amorphous ferroaluminosilicate. Silica and alumina are the major constituents of fly ash. Adsorption of metals by fly ash may be due to silica, metal oxides and carbon present in it. Sawdust and Neem bark contains ligno-cellulose based plant materials with many nitrogenous, hydroxyl and carboxylic groups that are responsible for binding Cr(VI) ion from aqueous solution. The availability of a particular functional group or binding site does not necessarily guarantee its accessibility as a sorption site for a metal ion, due to steric, conformational or other types of

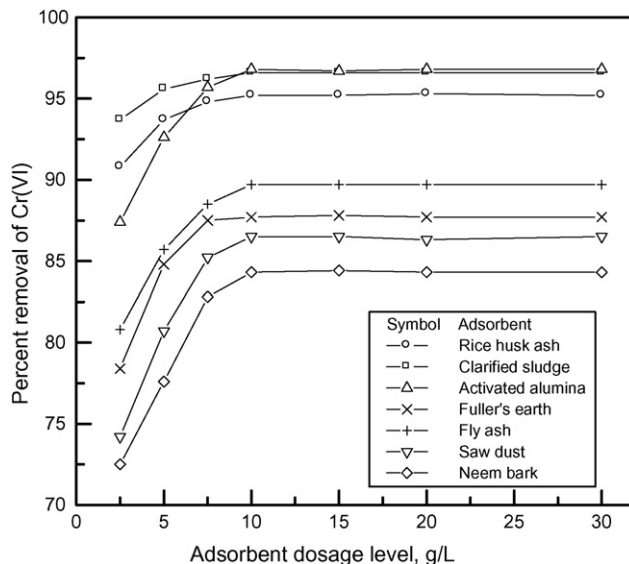


Fig. 4. Effect of adsorbent dosage level on adsorption of Cr(VI) by selected adsorbents: pH 3, initial Cr(VI) concentration 50 mg/L, contact time 4 h.

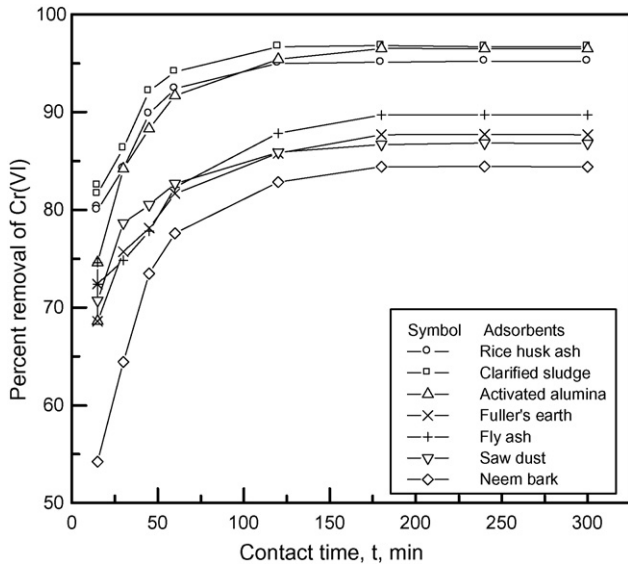


Fig. 5. Effect of contact time on the adsorption of Cr(VI) by selected adsorbents: initial Cr(VI) concentration 50 mg/L, adsorbent dosage 10 g/L and pH 3.

barriers [36]. The advantage of clarified sludge for the removal of Cr(VI) from aqueous solution over the other adsorbents may arise due to the availability of high concentration of active sorption sites per unit weight of the material, making the penetration of Cr(VI) to the sorption sites easier.

3.5. Effect of contact time

The experimental runs measuring the effect of contact time on the batch adsorption of Cr(VI) and at initial pH value 3 and initial Cr(VI) concentration of 50 mg/L is shown in Fig. 5.

It is obvious that increase in contact time from 0.5 to 2.0 h enhanced the percent removal of Cr(VI) significantly. The initial rapid adsorption gives away a very slow approach to equilibrium. The nature of adsorbent and its available sorption sites affected the time needed to reach the equilibrium. For clarified sludge and rice husk ash this time was 2 h. In case of other adsorbents, a contact time of 3 h was needed for equilibrium to be established. According to these results, the rest of the batch experiments on the physical properties of adsorption were conducted after 4 h of contact time to make sure that equilibrium was reached.

The optimum conditions (pH, adsorbent concentration and contact time) for adsorption of Cr(VI) by different adsorbents are shown in Table 4.

3.6. Kinetics study

The kinetics of Cr(VI) adsorption was studied from the time versus %removal curves. The rate kinetics of Cr(VI) adsorption on the different adsorbents was analyzed using the 1st-order rate kinetic model proposed by Lagergren [55] and generally expressed as

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

Table 4

The optimum conditions for adsorption of Cr(VI) by different adsorbents initial Cr(VI) concentration 50 g/L

Adsorbents	pH	Equilibrium contact time (h)	Adsorbent dosage level (g/L)
Clarified sludge	3	2	10
Rice husk ash	3	2	10
Activated alumina	3	3	10
Fuller's earth	3	3	10
Fly ash	2	3	10
Saw dust	3	3	10
Neem bark	2	3	10

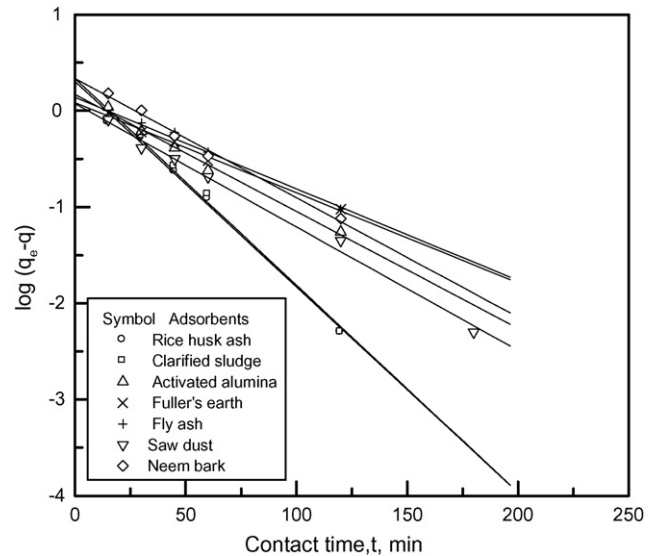


Fig. 6. Lagergren plot for the adsorption of Cr(VI) by selected adsorbents: pH 3, initial concentration 50 mg/L, and adsorbent dosage 10 g/L.

Fig. 6 shows the Lagergren plot of $\log(q_e - q)$ versus t (min) for adsorption of Cr(VI) by different adsorbents. The linearity of these plots indicates that a 1st-order mechanism is indeed followed in this process. The rate constants (K_{ad}) for each system were calculated from the linear least square method and are given in Table 5 along with the correlation coefficient (r^2). However in many cases, it has also been found that a pseudo-2nd-order model can provides a better relationship for kinetics of adsorption process. The pseudo-2nd-order equation is expressed

Table 5

Lagergren rate constants for adsorption of Cr(VI) by the selected adsorbents with removal efficiency

Adsorbents	Lagergren rate constants $K_{ad} \times 10^{-2}$ (min ⁻¹)	Correlation coefficient (r^2)
Clarified sludge	4.95	0.9901
Rice husk ash	4.90	0.9930
Activated alumina	2.78	0.9923
Fuller's earth	2.07	0.9925
Fly ash	2.18	0.9862
Saw dust	2.94	0.9926
Neem bark	2.76	0.9916

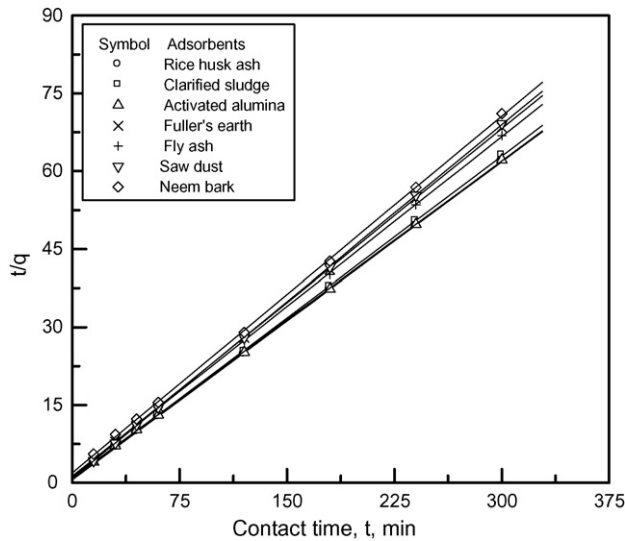


Fig. 7. Pseudo-2nd-order plot for the adsorption of Cr(VI) by selected adsorbents: pH 3, initial concentration 50 mg/L, and adsorbent dosage 10 g/L.

as [56]

$$\frac{t}{q_t} = \left[\frac{1}{2} K' q_c^2 \right] + \frac{t}{q_e} \quad (5)$$

Linear plots of (t/q) versus t curves (Fig. 7) were used to determine the rate constants and correlation coefficients. Table 6 shows the pseudo-2nd-order rate constants and correlation coefficients for removal of Cr(VI) from aqueous solutions. The values of correlation coefficients indicated a better fit of pseudo-2nd-order model with the experimental data compared to the Lagergren 1st-order model. The results of pseudo-2nd-order kinetics found in this study are supported by the findings of many earlier works [31,42,48,57]. Sometimes there is a possibility that intra particle diffusion will be the rate-limiting step and this was determined by using the rate equation expressed Weber and Morris [58]

$$K_{id} = \frac{q}{t^{1/2}} \quad (6)$$

Fig. 8 shows that the adsorption process for Cr(VI) by different adsorbents at a particular pH and adsorbent dosage of 10 g/L are not linear over the entire time range indicating that more than one phenomenon is governing the adsorption process of Cr(VI).

Table 6
Pseudo-2nd-order rate constants for adsorption of Cr(VI) by the selected adsorbents with removal efficiency

Adsorbents	Pseudo-2nd-order rate constants K_2 (mg/g/min)	Correlation coefficient (r^2)
Clarified sludge	0.0534	0.9994
Rice husk ash	0.0504	0.9994
Activated alumina	0.0787	0.9995
Fuller's earth	0.1245	0.9993
Fly ash	0.1301	0.9998
Saw dust	0.0877	0.9997
Neem bark	0.2176	0.9997

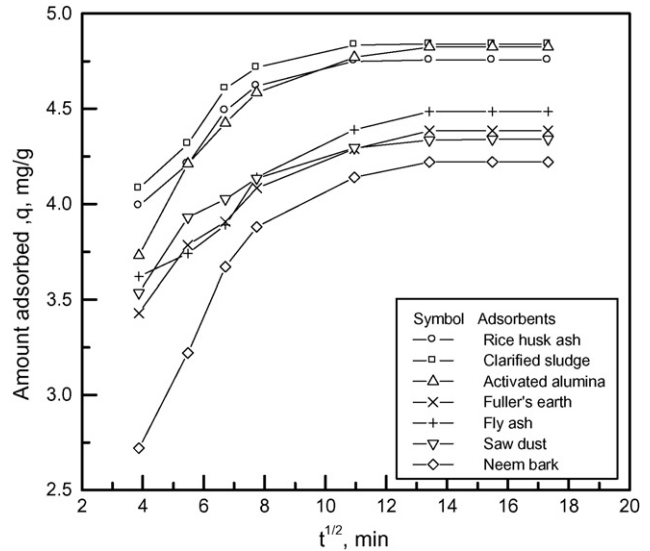


Fig. 8. Weber and Morris (intraparticle diffusion) plot for the adsorption of Cr(VI) by selected adsorbents: pH 3, initial concentration 50 mg/L, and adsorbent dosage 10 g/L.

This type of non-linearity has also been reported by earlier researchers [57,59]. The slope of the initial linear portion of the curve was used to derive the intra particle rate constant K_{id} . The values of K_{id} for different adsorbents are presented in Table 7. The linear portions of the curves do not pass through the origin (Fig. 10). This indicates that mechanism of Cr(VI) adsorption is complex and both the surface adsorption as well as intra-particle diffusion contribute to the rate determining step [57,59].

3.7. Mass transfer analysis

Mass transfer analysis for adsorption of Cr(VI) was carried out using the McKay et al. equation [60],

$$\ln \left(\frac{C_t}{C_0} - \frac{1}{1 + MK_{bq}} \right) = \ln \left(\frac{MK_{bq}}{1 + MK_{bq}} \right) - \left(\frac{1 + MK_{bq}}{MK_{bq}} \right) \beta S_s t \quad (7)$$

The plot of $\ln(C_t/C_0 - 1/1 + MK_{bq})$ versus t resulted a straight line (Fig. 9) indicating the applicability of the model.

Table 7
Intra particle diffusion for adsorption of Cr(VI) by the selected adsorbents with removal efficiency

Adsorbents	Intra particle diffusion constant K_{id} (mg/g/min ^{1/2})	Correlation coefficient (r^2)
Clarified sludge	0.1684	0.9847
Rice husk ash	0.1709	0.9879
Activated alumina	0.2198	0.9732
Fuller's earth	0.1636	0.9773
Fly ash	0.129	0.9299
Saw dust	0.1511	0.9301
Neem bark	0.3075	0.9919

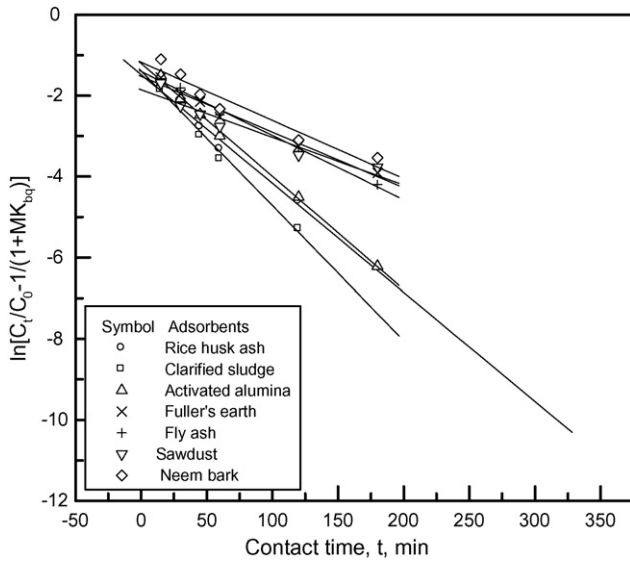


Fig. 9. Mass transfer plot for the adsorption of Cr(VI) by selected adsorbents: pH 3, initial concentration 50 mg/L, and adsorbent dosage 10 g/L.

The values of mass transfer coefficient (β) were determined graphically from the slope $\{(1 + MK_{bq}/MK_{bq}) \beta S_s\}$ of the individual plots and presented in Table 8. The values obtained from the study indicated that the velocity of the adsorbate Cr(VI) for transporting from bulk i.e. solution phase to solid phase was quite rapid.

3.8. The adsorption isotherms

The adsorption isotherms for the Cr(VI) removal were studied using initial concentration of Cr(VI) between 10 mg/L and 300 mg/L at an adsorbent dosage level of 10 g/L. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e . The experimental data obtained were fitted to the Langmuir adsorption isotherm [61] applied to equilibrium adsorption assuming mono-layer adsorption onto a surface with a finite number of identical sites and is represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \quad (8)$$

Table 8
Mass transfer analysis for adsorption of Cr(VI) by the selected adsorbents with removal efficiency

Adsorbents	Mass transfer constants β_s (cm/s)	Correlation coefficient (r^2)
Clarified sludge	1.72×10^{-4}	0.9844
Rice husk ash	2.47×10^{-4}	0.9797
Activated alumina	0.92×10^{-4}	0.9805
Fuller's earth	3.56×10^{-4}	0.9838
Fly ash	2.01×10^{-4}	0.9917
Saw dust	4.28×10^{-3}	0.9179
Neem bark	2.96×10^{-3}	0.9318

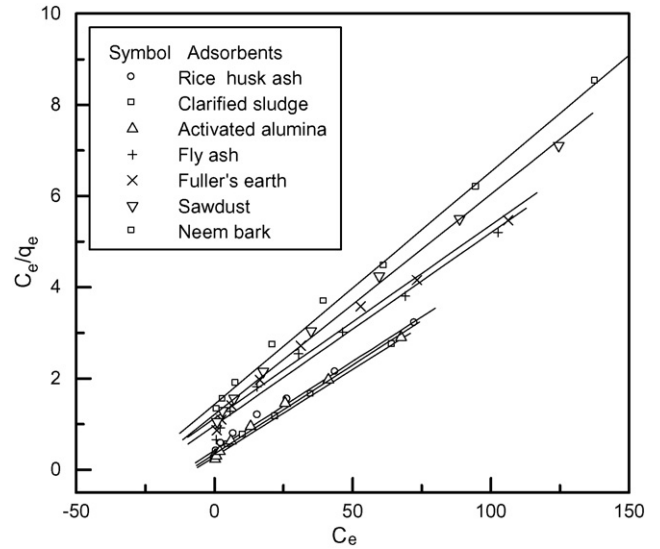


Fig. 10. Langmuir plot for the adsorption of Cr(VI) by selected adsorbents: pH 3; adsorbent dosage 10 g/L; contact time 4 h.

Fig. 10 shows the linear plots of C_e/q_e versus C_e and is used to determine the value of q_{max} (mg/g) and b (L/mg). The data obtained were listed in Table 9 for all adsorbents. The Langmuir constants q_{max} and b are related to the adsorption capacity (amount of adsorbate adsorbed per unit mass of the adsorbent to complete monolayer coverage) and energy of adsorption, respectively. The highest and lowest values of adsorption capacity q_{max} (maximum uptake) are for clarified sludge (26.31 mg/g) and neem bark (19.5 mg/g), respectively. The essential characteristics of the Langmuir isotherm may be expressed in terms of a dimensionless constant separation factor or equilibrium parameter [62], R_L , which is defined as,

$$R_L = \frac{1}{(1 + bC_0)} \quad (9)$$

The R_L value lying between 0 and 1 indicate favorable adsorption [63]. The R_L value for the adsorption of Cr(VI) on different adsorbents at initial concentration of 10 mg/L (lowest concentration studied) and 300 mg/L (highest concentration studied) are listed in Table 10. The data represented a favorable adsorption for all the adsorbents used in the study.

The experimental data on adsorption were fitted to the Freundlich adsorption isotherm [64], which is the earliest rela-

Table 9
The Langmuir adsorption isotherm constants for adsorption of Cr(VI) by the selected adsorbents

Adsorbents	q_{max} (mg/g)	b (L/mg)	Correlation coefficient (r^2)
Clarified sludge	26.31	0.133	0.9972
Rice husk ash	25.64	0.093	0.9901
Activated alumina	25.57	0.114	0.9916
Fuller's earth	23.58	0.037	0.9925
Fly ash	23.86	0.043	0.9917
Saw dust	20.70	0.039	0.9967
Neem bark	19.60	0.035	0.9966

Table 10

The separation factor or equilibrium parameter R_L for adsorption of Cr(VI) by the selected adsorbents

Adsorbents	Separation factor or equilibrium parameter R_L	
	Initial Cr(VI) concentration 10 mg/L	Initial Cr(VI) concentration 100 mg/L
Clarified sludge	0.424	0.024
Rice husk ash	0.518	0.034
Activated alumina	0.467	0.028
Fuller's earth	0.729	0.083
Fly ash	0.699	0.072
Saw dust	0.719	0.078
Neem bark	0.746	0.087

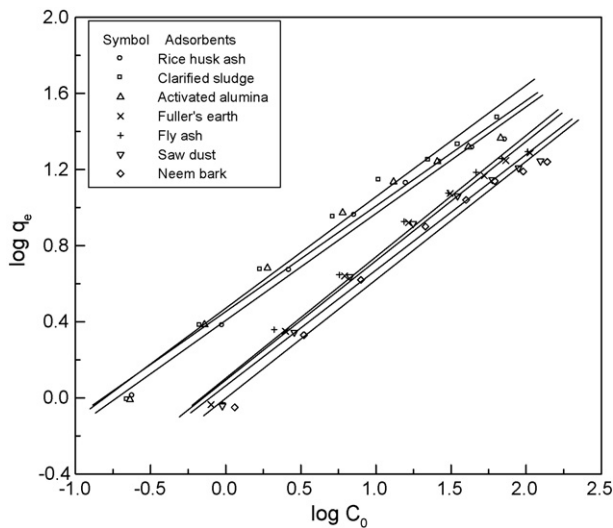


Fig. 11. Freundlich plot for the adsorption of Cr(VI) by selected adsorbents: pH 3; adsorbent dosage 10 g/L; contact time 4 h.

relationship known describing the adsorption equilibrium and is expressed by the following equation,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (10)$$

The Freundlich isotherm described as a fairly satisfactory empirical isotherm used for non-ideal adsorption is related to heterogeneous process. Fig. 11 shows the Freundlich plots for different adsorbents and the constants K_f and n were calculated from Eq. (9), and tabulated in Table 11. The value of n lies

Table 11

The Freundlich adsorption isotherm constants for adsorption of Cr(VI) by the selected adsorbents

Adsorbents	Adsorption capacity (K_f)	Intensity of adsorption (n)	Correlation coefficient (r^2)
Clarified sludge	2.96	1.71	0.9922
Rice husk ash	2.55	1.76	0.9936
Activated alumina	2.84	1.80	0.9880
Fuller's earth	1.24	1.59	0.9938
Fly ash	1.26	1.56	0.9892
Saw dust	1.16	1.65	0.9881
Neem bark	1.01	1.62	0.9902

Table 12

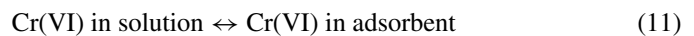
Thermodynamic equilibrium constants and Gibbs free energy (ΔG°) for adsorption of Cr(VI) by the selected adsorbents

Adsorbents	Equilibrium constant (K_c)	Gibbs free energy ($-\Delta G^\circ$)
Clarified sludge	52.50	9.98
Rice husk ash	49.92	9.85
Activated alumina	48.52	9.78
Fuller's earth	13.22	6.50
Fly ash	18.05	7.28
Saw dust	10.77	5.98
Neem bark	10.48	5.76

between 1 and 10 for all adsorbents, which represents a favorable adsorption [16,53,65]. The adsorption capacity K_f was highest for clarified sludge and the lowest for saw dust.

3.9. Thermodynamics for adsorption

The process of Cr(VI) adsorption can be represented by the following reversible process, which represents a heterogeneous equilibrium,



The thermodynamic equilibrium constant (K'_C) for each adsorbent was calculated by determining the apparent equilibrium constant K'_c at different initial concentration of Cr(VI) and extrapolating to zero.

$$K'_C = \frac{C_a}{C_e} \quad (12)$$

The Gibbs free energy (ΔG°) for the adsorption process was obtained using the formula,

$$\Delta G^\circ = -RT \ln K'_C \quad (13)$$

Table 12 represents the Gibbs free energy for the adsorption process of Cr(VI) by different adsorbents. The Gibbs free energy indicates the degree of spontaneity of the adsorption process, where more negative values reflect a more energetically favorable adsorption process. The ΔG° values obtained in this study for the adsorbents confirm the feasibility of all the adsorbents and spontaneity of the adsorption process. The ΔG° for the clarified sludge shows that it has got the largest capacity and affinity for the selective removal of Cr(VI) from aqueous solution over the other adsorbents used in this study.

3.10. Comparison of Cr(VI) removal with different adsorbents reported in literature

The adsorption capacities of the adsorbents for the removal of Cr(VI) have been compared with those of other adsorbents reported in literature and the values of adsorption capacities have been presented in Table 13. The values are reported in the form of monolayer adsorption capacity. The experimental data of the present investigations are comparable with the reported values in some cases. The adsorption capacity varies and it depends on the characteristics of the individual adsorbent, the extent of

Table 13
Comparison of adsorption capacities of the adsorbents for the removal of Cr(VI) with those of other adsorbents

Sl. no.	Adsorbent	Adsorption capacities (mg/g)	Reference
1	Almond	10.62	[36]
2	Cactus	7.08	[36]
3	Carbon slurry	25.60	[47]
4	Chitosan-cross linked and non cross linked	78.00, 50.00	[67]
5	Coal	6.78	[36]
6	Coconut husk fibres	29.0	[35]
7	Coniferous leaves	83.30	[30]
8	Eucalyptus bark	45.00	[49]
9	Hazelnut shell	17.70	[40]
10	Hazel nut shell activated carbon	170	[41]
11	Olive cake	33.44	[36]
12	Paper mill sludge	7.4	[16]
13	Pine needles Almond	21.50	[36]
14	Red mud	75	[66]
15	Sago waste activated carbon	5.78	[68]
16	Saw dust	15.82	[36]
17	Sphagnum moss peat	119.0	[39]
18	Tyre activated carbon	58.5	[35]
19	Wood activated carbon	87.6	[33]
20	Wool	41.15	[36]
21	Clarified sludge	26.31	Present work
22	Rice husk ash	25.64	Present work
23	Activated alumina	25.57	Present work
24	Fuller's earth	23.58	Present work
25	Fly ash	23.86	Present work
26	Saw dust	20.70	Present work
27	Neem bark	19.60	Present work

surface/surface modification and the initial concentration of the adsorbate. However, the present experiments are conducted to find the technical applicability of the low-cost adsorbents to treat Cr(VI).

4. Conclusions

Batch adsorption studies for the removal of Cr(VI) from aqueous solutions have been carried out using seven different adsorbents. The study indicated the suitability of the adsorbents used for removal of Cr(VI) aqueous solution. The selected adsorbents may be viewed as a useful material while considering the economic aspects of wastewater treatment. The obtained results may be summarized as follows:

- (1) The pH variation studies showed that the adsorption process for the all the adsorbents is highly pH dependent. The optimum pH range for the removal was found to be 2–3.
- (2) Increase in adsorbent dosage leads to increase in Cr(VI) adsorption due to increased number of adsorption sites. Maximum uptake of Cr(VI) was obtained at adsorbent dosage of 10 g/L.
- (3) Adsorption equilibrium attained with in 2 h time for clarified sludge and rice husk ash. For other adsorbents 3 h time was needed to reach the equilibrium. The adsorption process found to follow Lagergren-1st-order kinetics model. However, the rate kinetics for adsorption of Cr(VI)

by the different adsorbents was best described by pseudo-2nd-order model.

- (4) The results suggests that adsorption of Cr(VI) on the selected adsorbents involves a complex mechanism and in the adsorption process there are two distinct stages—the initial stages of boundary layer diffusion due to external mass transfer effects and the later stages it was due to intra-particle diffusion which contributes to the rate determining step.
- (5) The adsorption isotherm studies showed that both Langmuir and Freundlich adsorption isotherm model fits well with the experimental data. The maximum adsorption capacity (q_{\max}) was obtained for clarified sludge (26.31 mg/g). For neem bark adsorption capacity (q_{\max}) was minimum (19.60 mg/g).
- (6) Thermodynamic studies indicated the spontaneous nature of adsorption process and it increases with increase in temperature showing endothermic nature of the adsorption process.
- (7) The clarified sludge—a steel industry waste was found to be the most effective one, for which the removal efficiency reached to 99.8% of Cr(VI) at $30 \pm 2^\circ\text{C}$. Adsorbents like rice husk ash and activated alumina were also found to be almost equally effective under identical conditions for removal of Cr(VI) from aqueous solutions.
- (8) The adsorption capacities of the adsorbents for the removal of Cr(VI) have been compared with those of other adsorbents reported in literature. The values reported in the form of monolayer adsorption capacity.

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