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Studies on sorption of Cd(II) on Tata chromite mine overburden

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Abstract

Chromite mine overburden containing iron as oxide/hydroxide, a waste material generated in chromite mines was used as sorbent for cadmium. The iron content of material was 43.75% with a specific surface area of 50.8 m²/g. Batch experiments were conducted to study the sorption behavior of Cd(II) on this material. The variable experimental parameters were: time, pH, temperature, Cd(II) and sample concentration. The point of zero charge (PZC) of the overburden sample was experimentally determined as 6.48 which shifted to a pH of 7.8 when the sample was equilibrated with 100 mg/L Cd(II) solution. Maximum loading capacity of the overburden sample was found to be ∼19 mg Cd/g of material. It was observed that within 30 min the sorption attains equilibrium. Hence, the sorption data generated at 30 min with various initial Cd(II) concentrations and temperatures were taken to evaluate the thermodynamic parameters, i.e., $\Delta G°$, $\Delta H°$ and $\Delta S°$. The $\Delta G°$ values reflect the feasibility of the metal removal from aqueous solution. The negative values of $\Delta H°$ confirmed the exothermic sorption of cadmium and the positive $\Delta S°$ values suggested the increased randomness at the solid–solution interface. The sorption data fitted well to both the Langmuir and Freundlich isotherm models indicating a monolayer sorption. The value of Freundlich parameter 'n' (n is indicative of sorption intensity) lying between 1.46 and 1.59 shows that the surface of the sorbent is heterogeneous in nature.

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Keywords: Chromite mine overburden; Cadmium; Thermodynamics; Langmuir isotherm; Freundlich isotherm

1. Introduction

Cadmium is a naturally occurring, potentially toxic and mobile element present in most soil environments. Effluents of metallurgical, chemical, ceramics, electrogalvanization and textile industries are potential sources of water pollution by cadmium ions. It has been reported that chronic exposure of humans through ingestion and/or inhalation to Cd may cause severe damage to kidney and lungs, and can lead to other pathological symptoms [1,2]. Due to toxicity of metals, the Ministry of Environment and Forests (MOEF), Government of India, has set Minimal National Standards (MINAS) of 0.2 mg/L for Cd(II) for safe discharge of the effluents containing this metal ion into surface waters [3]. Naturally occurring materials such as zeolites, apatite, bentonite or diatomite, kaolin and natural iron oxides are commonly used as sorbent. Many of them have been used to eliminate heavy metals from wastewater [4,5]. Studies have also been reported on possibilities of utilization of industrial

wastes such as red mud, fly ash [6], blast furnace slag [7], and manganese nodule leach residue [8] as sorbents for elimination of heavy metals. For each ton of mining the chromite ore, 10 tonnes of overburden needs to be removed resulting in piling up of chromite mine overburden containing 30–40% iron as oxide/hydroxide. It is a waste material generated in chromite mines. In India, large quantities of such overburden have accumulated over the years. In view of high iron content, this material may be a potential sorbent for heavy metals. Keeping this in view, the present work on Cd(II) sorption was carried out on a typical chromite mine overburden sample from Overburden Dumps of Tata Iron and Steel Company (TISCO), Sukinda region, Orissa, India.

2. Experimental

2.1. Materials and methods

A typical TISCO overburden sample was ground and sieved to obtain 100% to 150 mesh British Standard Sieves (BSS) corresponding to <100 μm fraction. A weighed amount of sample was subjected to tri-acid digestion for wet chemical analysis.

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Nomenclature

b	Langmuir's constant related to the energy of the sorption (L/mg)
C_A	is the adsorbed amount of sorbate at equilibrium (mg/L)
C_e	is the equilibrium concentration in solution (mg/L)
$\Delta G°$	change in standard free energy (kJ/mol)
$\Delta H°$	change in standard enthalpy (kJ/mol)
K_d	is equilibrium constant
K_F	a constant related to the sorption capacity
n	an empirical parameter related to the intensity of sorption, which varies with the heterogeneity of the sorbent. For values in the range $1 < n < 10$, sorption is favorable.
q_m	Langmuir's constants related to the capacity of sorption (mg/g)
Q_e	(X/M) sorbate: sorbent ratio (mg/g)
R	universal gas constant (J/K/mol)
$\Delta S°$	change in standard entropy (J/mol/K)
T	absolute temperature (K)
r^2	regression coefficient

Iron was analysed volumetrically by taking a known aliquot and first reducing it with stannous chloride followed by addition of saturated mercurous chloride, 10% H_2SO_4 and phosphoric acid. The contents were titrated against standard potassium dichromate in presence of barium diphenyl ammine sulphonate (BDAS) as an indicator [9]. The concentrations of other metal ions were determined by atomic absorption spectrophotometer (Perkin-Elmer 2380) after proper dilutions. The X-ray diffraction (XRD) measurements were done over a range of 20–70° using Phillips Powder Diffractometer Model PW3710 with Co Kα radiation at a scan speed of $1.2°\,min^{-1}$. The specific surface area of the sample was measured according to N$_2$-BET method.

The pH$_{pzc}$ of prepared sample was determined by method adopted by Balistrieri and Murray [10]. Accordingly, to a series of well-stoppered 125 mL polyethylene bottles containing 40 mL of 0.01 M KNO$_3$ electrolyte solution, different volumes of either 0.1 M HCl or 0.1 M NaOH solution were added to obtain wide-ranging pH values from 2 to 8. The total volume of solution in each bottle was made up to 50 mL by addition of distilled water. After 2 h of equilibration the pH values (pH$_i$) were noted and known amounts of overburden samples were added. After 72 h of equilibration at room temperature (305 + 3 K) with intermittent shaking, the pH value of the supernatant liquid in each bottle was noted (pH$_f$). The difference between pH$_i$ and pH$_f$ (ΔpH) were then plotted against pH$_i$. The solution pH at which ΔpH 0 is "the pH$_{pzc}$ of the sample. Similarly, the PZC of the material in presence of Cd(II) ions was determined by equilibrating the samples with 100 mg/L Cd(II) solution.

2.2. Cadmium sorption experiment

To carry out sorption experiments a known weight of chromite mine overburden sample was taken in 250 mL conical flasks and predetermined volume of Cd(II) stock solution was added at required pH. The contents were agitated in a horizontal shaker (160 rpm) for desired time period. The contents were filtered using a 0.45 μm membrane filter paper and the filtrate was analyzed for residual Cd(II) by a Perkin-Elmer 2380 atomic absorption spectrophotometer (AAS).

3. Results and discussions

3.1. Chemical analysis and characterization

Chemical analysis of a typical ground and sieved TISCO chromite overburden sample (100% to 150 BSS mesh) used for the present study was: 43.75% Fe, 0.79% Ni, 0.60% Mn, 0.08% Co, 0.02% Zn, Cr$_2$O$_3$, 2.5%, Al$_2$O$_3$, 7% and acid insolubles 20%. The specific surface area of the sample was 50.8 m^2/g as measured by the N$_2$-BET method. The XRD pattern (Fig. 1) shows goethite and hematite as the two major crystalline phases. The presence of relatively flat background indicates that the sample was predominantly crystalline with minimal amorphous material.

3.2. Effect of contact time

Effect of contact time was studied under the following conditions: sorbate concentrations 100 mg/L, sorbent concentrations 5 and 10 g/L, temperature 308 K and pH 4.0 (Fig. 2). There is no increase of Cd sorption after 30 min of contact time indicating attainment of quasi-equilibrium state. Accordingly all the experiments were conducted with a contact time of 30 min.

3.3. Effect of pH

The experiments for observing pH effect in the range 2–8 were carried out at 308 K using sorbate and sorbent con-
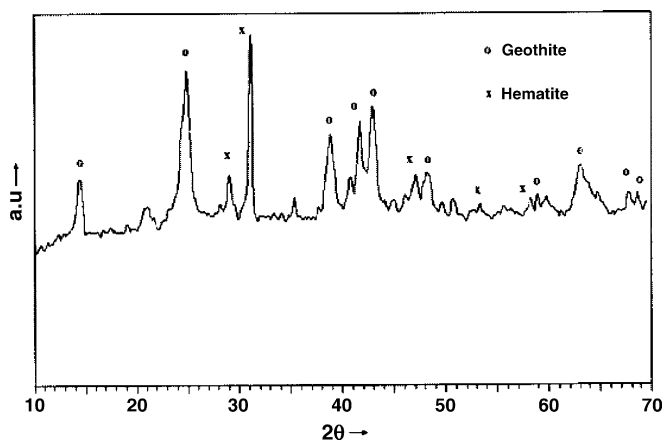

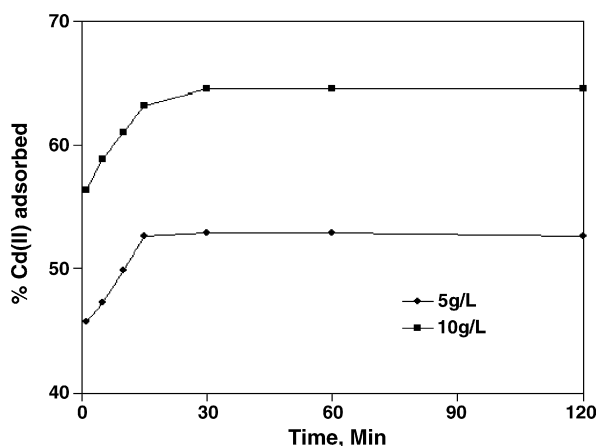Fig. 1. XRD pattern of the TISCO chromite mine overburden sample.

Fig. 2. Effect of contact time on sorption of Cd(II). Conditions: sorbate concentration 100 mg/L, sorbent concentration 5 and 10 g/L, temperature 308 K and pH 4.0.

centrations as 100 mg/L and 5 g/L, respectively. During these experiments no background electrolyte was used to maintain the pH as the study aims at using this material for the effluent treatment as such without addition of any external chemical. Fig. 3 shows that Cd(II) sorption increased from 9.63 to 69.9% with the increase of pH from 2.0 to 8.0. Such pH effects on Cd(II) sorption on other oxide surfaces has been reported [11–13]. It has been proposed that increasing solution pH leads to an increase in net negative surface charge on samples where Cd(II) is adsorbed by a simple binding mechanism as given below:

The increase of pH decreases the positive charge of material by the reaction:

$$SOH_2^+ + OH^- \rightarrow SOH + H_2O \qquad (1)$$
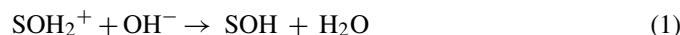
This enables surface reactions (by physisorption and/or chemisorption).

$$SOH + Cd^{2+}$$
$$\rightarrow SO^- \cdots Cd^{2+} + H^+ \quad \text{(surface reaction of physisorption)} \qquad (2)$$
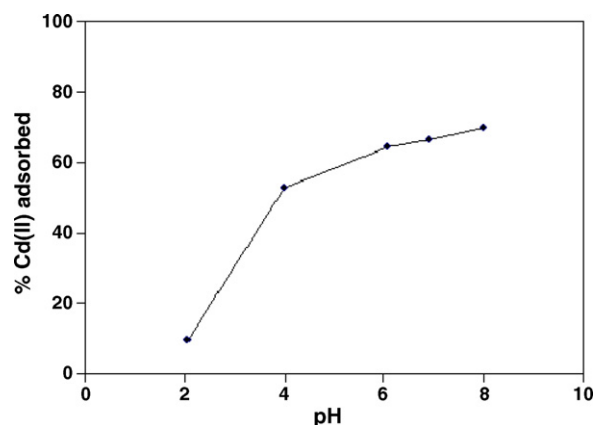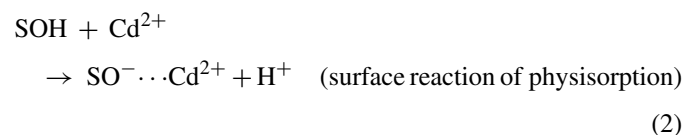

Fig. 3. Effect of pH on Cd(II) sorption. Conditions: sorbate concentration 100 mg/L, sorbent concentration 5 g/L, temperature 308 K and time 30 min.
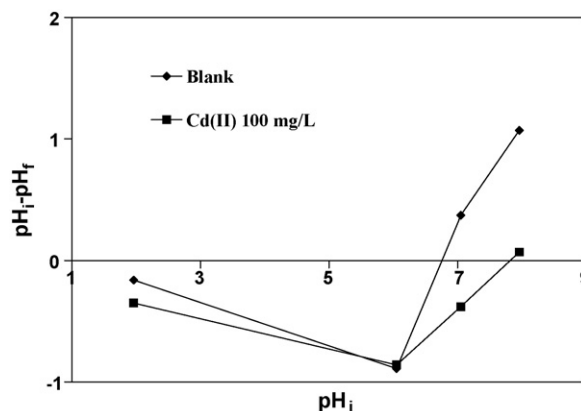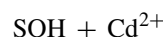

Fig. 4. PZC measurements of the chromite overburden sample with and without Cd(II) solution.

$$SOH + Cd^{2+}$$
$$\rightarrow SOCd^+ + H^+ \quad \text{(surface reaction of chemisorption)} \qquad (3)$$

Experimentally determined PZC of the sample was at a pH of 6.48 which shifted to a pH of 7.8 (Fig. 4) when the sample was equilibrated with 100 mg/L Cd(II) solution. The shift in the pH may indicate that the sorption of Cd(II) is taking place by chemisorption [14]. It may be mentioned here that at pH 2, wherein there is a possibility of dissolution of other metal ions from the TISCO Overburden, the chemical analysis of the solution after Cd(II) sorption showed Fe 0.11 mg/L, Ni 0.06 mg/L, Zn 0.04 mg/L, Cu nil, Cr nil and Mn nil. At pH of ≥4 all the metal ions were found to be nil except 0.04 mg/L Fe at a pH of 4.

3.4. Effect of Cd(II) concentration

Fifty milliliters of Cd(II) solution of different concentrations ranging from 50 to 500 mg/L with 5 g/L of sorbent at a pH of 4.0 was stirred in a horizontal shaker at ambient temperature (308 K) for a contact period of 30 min. The results were given in Fig. 5 showing that cadmium sorption decreased from 59.6 to 19.2% with increase in initial cadmium concentration from 50 to 500 mg/L. At higher initial concentrations the ratio of initial number of moles of Cd(II) to the available surface area is high, hence fractional sorption becomes lower. To quantitatively estimate the amount of Cd(II) adsorbed, the loading capacities were calculated at all initial Cd(II) concentrations and given in Fig. 6. It shows that the amount of Cd(II) adsorbed per gram of material remains as ~19 mg when the initial Cd concentration increased from 350 to 500 mg/L. It shows the limitation of active sorption sites per gram of material.

3.5. Effect of amount of sorbent

Another variable chosen for studying Cd(II) sorption was the amount of sorbent which was varied from 2 to 15 g/L while keeping the Cd concentration as 100 mg/L (Fig. 7). The results show that the percent sorption of cadmium increased from 47.35
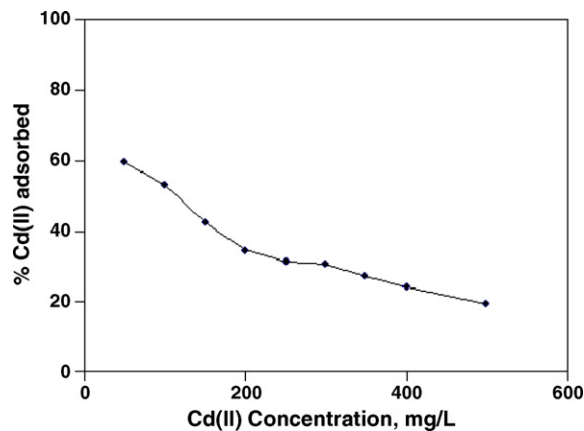
Fig. 5. Effect of initial Cd(II) concentration on the amount of Cd(II) sorption. Conditions: sorbent concentration 5 g/L, temperature 308 K, time 30 min and pH 4.0.
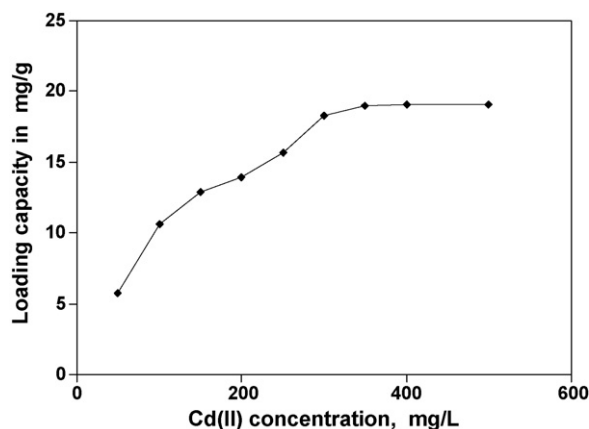

Fig. 6. Loading capacity of chromite overburden sample. Conditions: sorbent concentration 5 g/L, temperature 308 K, time 30 min and pH 4.0.

to 74% with the increase in the concentration of the sorbent from 2 to 15 g/L. According to Fig. 7, with increasing the sorbent concentration the absolute amount of Cd retained by the solid phase increased but the amount of Cd sorbed per unit mass of the sorbent decreased. It is probably because of dilu-
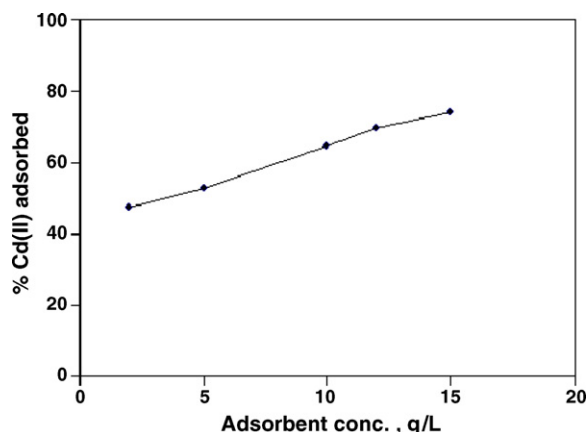

Fig. 7. Effect of sorbent concentration on Cd(II) sorption. Conditons: sorbate concentration 100 mg/L, temperature 308 K, time 30 min and pH 4.0.
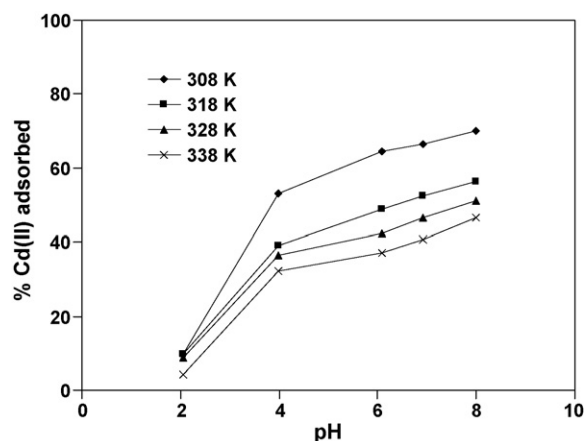

Fig. 8. Effect of temperature on Cd(II) sorption at various pH. Conditions: sorbent concentration 5g/L, sorbate concentration 100 mg/L and time 30 min.

tion of Cd(II) in the solid phase at higher solid/solution ratios [15,16].

3.6. Effect of temperature

Two series of experiments were conducted at different temperatures (308, 318, 328 and 338 K) (a) by varying the initial pH from 2 to 8.0 (Fig. 8) while keeping rest of parameters constant: sorbent concentration 5 g/L, sorbate concentration 100 mg/L, and (b) by varying sorbate concentration (Fig. 9) from 50 to 200 mg/L at 308 K while maintaining sorbent concentration as 5 g/L, time 30 min and pH 4.0. Figs. 8 and 9 show that irrespective of sorption conditions, sorption efficiency decreases with temperature. For example, it is apparent from Fig. 8 that the percent sorption of Cd(II) decreased from 69.88 to 46.63% when the temperature increased from 308 to 338 K at a pH of 8.0. This may be attributed to a relative increase in the escaping tendency of the solute from the solid phase to the bulk phase with the rise in temperature of the solution [17].
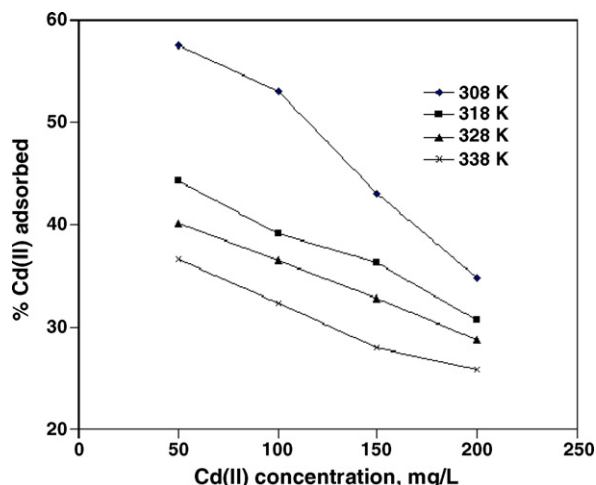

Fig. 9. Effect of temperature on Cd(II) sorption at various sorbate concentration. Conditions: sorbent concentration 5 g/L. pH 4 and time 30 min.

3.7. Thermodynamic parameters

The mechanism of sorption may be determined through the thermodynamic quantities such as change in free energy (ΔG°), change in enthalpy of sorption (ΔH°) and change in entropy (ΔS°). For determination of thermodynamic parameters, sorption data at various temperatures and initial Cd(II) concentrations in the range of 50–200 mg/L were considered, as the sorption approaches quasi-equilibrium at 30 min.

The free energy of a sorption reaction is given by the following equation:

$$\Delta G^\circ = -RT \ln K_d \qquad (4)$$

where R is the gas constant, T the temperature (in Kelvin) and K_d is equilibrium constant which is determined as:

$$K_d = \frac{C_A}{C_e} \qquad (5)$$

where C_e is the equilibrium concentration in solution (mg/L) and C_A is the adsorbed amount of sorbate at equilibrium (mg/L) [18].

The negative value of Gibbs free energy indicates the spontaneity of the sorption process, which is thermodynamically favorable. The higher negative values reflect a more energetically favorable sorption process. The increasing value of ΔG° with temperature indicates less driving force of the sorption reaction and therefore less sorption capacity of overburden samples at higher temperatures. Plots of Gibbs free energy change, ΔG°, versus T (kelvin), were found to be almost linear (Fig. 10) and the negative values of ΔG° increased with the increase of initial Cd(II) concentrations.

The values of ΔH° and ΔS° were determined from the Van't Hoff equation as given below:

$$\log K_d = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \qquad (6)$$

From the slopes and intercepts of the plots (Fig. 11) ΔH° and ΔS° were calculated and are given in Table 1. The negative value of ΔH° confirms the exothermic sorption of cadmium. The positive ΔS° suggested the increased randomness at the solid–solution interface during the sorption of cadmium on the
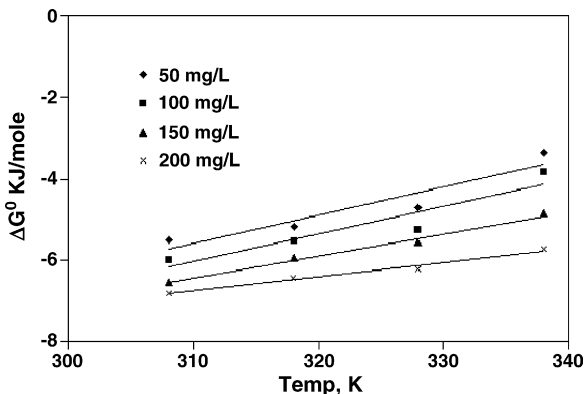

Fig. 10. ΔG° vs. temperature for different initial concentrations of Cd(II). Conditions: sorbent concentration 5 g/L, pH 4 and time 30 min.
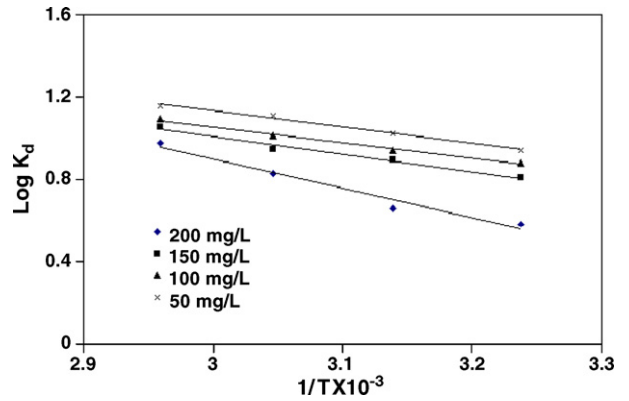

Fig. 11. Van't Hoff plots for different initial concentrations of Cd(II). Conditions: sorbent concentration 5 g/L, pH 4 and time 30 min.

sample [17]. The enthalpy value (14.55–27.5 kJ/mol) suggested that the physisorption (<41.8 kJ/mol) is predominant as in case of chemisorption ΔH° values are reported to be in the range of 41.8–125.4 kJ/mol [19]. Based on the above, it could be inferred that physisorption possibly takes place on TISCO overburden sample.

3.8. Sorption isotherms

The sorption data was fitted to well know Langmuir and Freundlich models. A familiar form of Langmuir equation for dilute solutions is given below:

$$\frac{C_e}{Q_e} = \frac{1}{bq_m} + C_e \left(\frac{1}{q_m} \right) \qquad (7)$$

where C_e is the equilibrium concentration (mg/L); Q_e (X/M) the amount of metal ion sorbed (mg/g); q_m is Q_e for a complete monolayer (mg/g) and b is an energy term which varies as a function of surface coverage strictly due to variations in the heat of sorption.

Freundlich isotherm constants were calculated by the equation

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \qquad (8)$$

where Q_e and C_e have been defined earlier and K_F and $1/n$ are constants indicating the sorption capacity and the sorption intensity, respectively ($1/n < 1$). The Freundlich constant, 'n' indicates the degree of favorability of sorption [20]. The 'n' should have values lying in the range of 1–10 for classification as favorable sorption [21]. A smaller value of "n" indicates a weaker bond between sorbate and sorbent and also it indicates the sorbent

Table 1
Thermodynamic parameters calculated from the data corresponding to Fig. 9

Initial Cd(II) concentration (mg/L)	ΔH° (kJ/mol)	ΔS° (J/mol/K)
50	−14.55	63.87
100	−15.09	66.99
150	−16.32	68.26
200	−27.5	99.68

Conditions: sorbent concentration 5 g/L, pH 4 and time 30 min.

Table 2
Isotherm parameters for various samples calculated from data corresponding to Figs. 12 and 13

Temp. (K)	Langmuir isotherm parameters			Freundlich isotherm parameters		
	b	q_m (mg/g)	r^2	n	K_f	r^2
308	0.312	22.47	0.92	1.59	13.612	0.90
318	0.201	22.83	0.98	1.53	16.612	0.98
328	0.166	22.62	0.99	1.50	19.612	0.99
338	0.140	19.88	0.99	1.46	48.11	0.99

Conditions: adsorbent concentration 5 g/L, time 30 min and pH 4.0.
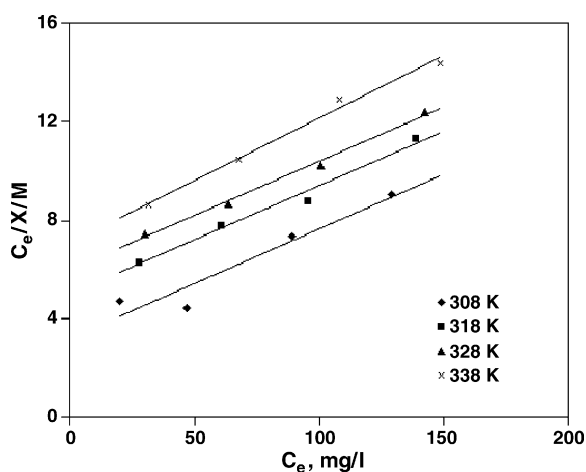

Fig. 12. Langmuir sorption isotherm at various temperature. Conditions: sorbent concentration 5 g/L, time 30 min and pH 4.0.

surface is of heterogeneous nature [18,22], while a higher value for K_F indicates that the rate of sorbate removal is high [23]. The experimental data of Fig. 9 was treated for both the isotherms and the plots are shown in Figs. 12 and 13. The isothermic parameters are given in Table 2. From the correlation coefficient given in Table 2, it is seen that the sorption data gives good fits for both Langmuir and Freundlich models. Since the sorption data fits for both the isotherm models suggesting that the binding of the cadmium ions occurs as a monolayer on the surface of the samples [24]. The calculated sorption capacity, q_m, from
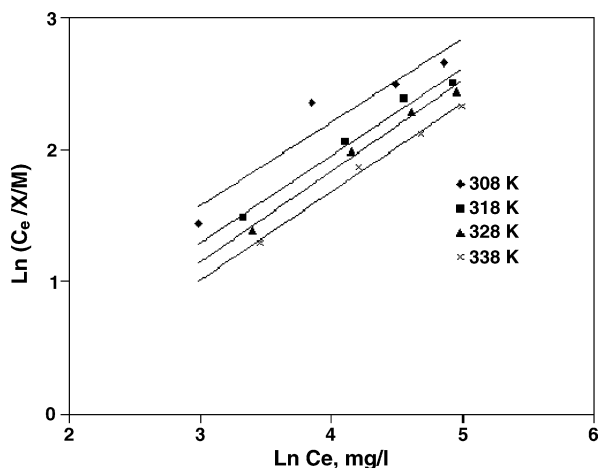

Fig. 13. Freundlich sorption isotherms at various temperature. Conditions: sorbent concentration 5 g/L, time 30 min and pH 4.0.

the Langmuir equation was found to be 22.47 mg/g at 308 K (Table 2). The measured q_m, value was 19.18 mg/g which is comparable to the calculated value. The relatively low Langmuir b constants (0.147–0.312 L/mg) may indicate a low heat of sorption [25,26]. The values of n were varied from 1.59 to 1.46 in the temperature range of 308–338 K confirming the existence of weaker bonds between Cd(II) and chromite overburden samples at higher temperatures and also indicating the heterogeneous nature of the surface [18,22].

3.9. Conclusions

1. Chromite mine overburden is found to be a very effective sorbent for the removal of Cd(II) in a concentration range of 50–500 mg/L from aqueous solution.
2. Under the present experimental conditions, at pH 4.0, the maximum loading capacity was 19.2 mg of Cd(II)/g of TISCO overburden. However, the maximum loading capacity would vary with pH.
3. The thermodynamic parameters ($\Delta G°$) reflect the feasibility of the metal removal from aqueous solution using chromite mine overburden. The negative values of $\Delta H°$ confirm the exothermic sorption of cadmium and the positive $\Delta S°$ values suggest the increased randomness at the solid–solution interface during the sorption of cadmium on the sample.
4. The sorption data were fitted well to the Langmuir and Freundlich sorption isotherms for these systems. The decrease in the value of q_m (maximum loading capacity) with the increase in temperature indicates the exothermic nature of this process. The Langmuir constant b values were relatively small indicated a low heat of sorption. The low value of 'n' (intensity of sorption) may indicate that weak chemisorption took place between Cd(II) and chromite overburden samples and also indicate the heterogeneous nature of the surface.

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