

Adsorption of Hexavalent Chromium using Natural Goethite: Isotherm, Thermodynamic and Kinetic Study

Shanti Kar¹ and Sk. Md. Equeenuddin^{2*}

¹Department of Mining Engineering, National Institute of Technology, Rourkela - 769 008, India

²Department of Earth and Atmospheric Sciences, National Institute of Technology, Rourkela - 769 008, India

*E-mail: md_equeen@yahoo.co.in

ABSTRACT

This paper examines the potential of natural goethite as an adsorbent for removing Cr(VI) from the aqueous solution through adsorption isotherms, thermodynamics and kinetics study. The study is based on the batch experiments as a function of initial Cr(VI) concentrations, contact time, pH and temperature at fixed solid/solution ratio. The pH has pronounced effect on process of removal and removal is higher in lower pH range, maximum (99.14 %) being at pH 2. The adsorption of Cr(VI) onto goethite is endothermic in nature and therefore, higher temperature favours the uptake. The adsorbent capacity was determined using Langmuir, Freundlich, Dubinin-Radushkevich and Temkin adsorption isotherm models. The results showed that the adsorption fits best to the Langmuir isotherm model with the adsorption capacity 0.727 mg/g. Pseudo-first-order kinetic, pseudo-second-order kinetic and intraparticle diffusion were used to analyze the adsorption kinetic at different initial Cr(VI) concentrations. The kinetic study indicated that the pseudo-second order model explained the adsorption mechanism and intra-particle diffusion was found to be the rate-controlling step. The negative values of Gibb's free energy explained that the adsorption was feasible and spontaneous.

INTRODUCTION

The presence of Cr(VI) in wastewater is a major concern due to its high toxicity, carcinogenic and mutagenic properties (Buerge and Hug 1999). The Cr(VI) occurs in many industrial effluents like leather tanning, mining, electroplating, ceramic, textile industries and chromate preparation etc. (Hu et al. 2009; Anupam et al. 2011). The Cr(VI) is highly soluble in water, and thus, can move readily through soil and aquifer in different geological environment (Fendorf 1995; Dubey and Gopal 2007). Hence, proper treatment is required to reduce its concentration below the permissible limit before discharge the Cr(VI) containing wastewater. Based on its health effect and impact on the environment, the tolerance limit of Cr(VI) in potable water and discharge into inland surface water was set at 0.05 mg/L and 0.1 mg/L respectively (EPA 1990).

Various physico-chemical and biological techniques have been studied for the removal of Cr(VI) from waste water such as chemical precipitation (Yang and Kravets 2000), anion exchange resins (Shi et al. 2009), membrane processes (Kulkarni et al. 2007), reverse osmosis (Rad et al. 2009), ultrafiltration (Korus and Loska 2009), oxidation or reduction (Turan and Altundogan 2014), biosorption (Panda et al. 2011) and adsorption (Jung et al. 2013; Song and Wu 2014) etc. These methods have significant disadvantages like incomplete removal, high operation and maintenance cost, monitoring system, reagent, energy requirements, production of toxic sludge or other disposal waste product (Nemr et al. 2008). Adsorption has been proved to be one of the easily applicable and an

economically feasible method for the remediation of Cr(VI) (Choppala et al. 2013).

Several authors have used various natural and synthetic materials that are available in large quantities and also environmental friendly for removing Cr(VI). Among them, materials like limonite (Baig et al. 2013), akaganeite (Lazaridis et al. 2005), hematite, α -alumina (Ajouyed et al. 2010; Kim et al. 2007), kaolinite (Zachara et al. 1988; Rao et al. 2012), amorphous iron oxyhydroxide (Zachara et al. 1987), boehmite (Granados-Correa and Jiménez-Becerril 2009), calcined bauxite (Baral et al. 2007), mixed magnetite-maghemite nanoparticles (Chowdhury and Yanful 2010), micelle-clay (Qurie et al. 2013) have been extensively used for removal of Cr(VI) from wastewater. It has been found that iron and aluminium oxides have shown very high affinity towards Cr(VI) in an acidic medium (Ajouyed et al. 2010; Wu et al. 2016). An iron-aluminium-complex, rich laterite soil is naturally available material which can be used for removal of Cr(VI) ions was studied by many authors (Xiaohong et al. 2009; Mitra et al. 2016). Since, less work has been done on the removal of Cr(VI) using natural goethite, this paper aims to study the removal of Cr(VI) using natural goethite through the examination of adsorption isotherm, thermodynamics and kinetics study.

MATERIALS AND METHODS

Adsorbent

A natural goethite was collected from the Koira iron ore mines, which is located in the northern part of Odisha. The sample was crushed and sieved through 200 mesh size sieve (75 μ m) and stored for further use. The mineralogy of the sample was studied by X-ray diffraction (Ultima IV; Rigaku CBO technology) using Cu-K α radiation operating at 40kV and 40mA. XRD pattern obtained through the scanning rate of 2°/min and step size of 0.05%.

Mineral identification along with chemical composition and morphology of adsorbent was also carried out using high resolution transmission electron microscope (HRTEM) (FEI Tecnai G2 F30 S-TWIN) operated at 300 kV. The sample was dispersed in ethanol and drop casted on carbon-coated Cu grid which was used further for TEM analysis. The semi-quantitative elemental analysis was done through EDX equipped in HRTEM using Quantax 200 ESPRINT 1.9 version.

BATCH ADSORPTION EXPERIMENT

Batch adsorption experiments was carried out for removal of Cr(VI) ion using goethite by changing initial concentration, pH, contact time and temperature at a fix amount of adsorbent dosage of 10 g/L. A stock solution of Cr(VI) was prepared by dissolving 2.8287 g of K₂Cr₂O₇ (AR grade, Merck reagent) in 1 L of deionized water. The stock solution was diluted to obtain the standard solution of concentration 2, 4, 5, 10, 15, 20 and 25 mg/L. The adsorption studies were carried out by taking 1 g of goethite in 100 ml of Cr(VI) solution

and agitated in an orbital shaker at 150 rpm and 25 °C. The pH of the solution was adjusted in the range of 2-10 by drop wise addition of 0.1 N H₂SO₄ and NaOH solution wherever required. The contact time was studied in the range from 10 to 180 min to reach equilibrium. At timed interval, the contents were filtered through 0.22 µm sterile membrane filter paper using a vacuum pump to assure a very rapid and efficient separation of solid material. The concentration of remaining Cr(VI) ions in solution was determined by UV-Visible double beam spectrophotometer (2375 double beam spectrophotometer).

The adsorption isotherms were studied by varying the concentration (5-25 mg/L) of Cr(VI) at fixed equilibrium time of 120 minute. To investigate the kinetic during adsorption, the samples were agitated at different time periods (10, 30, 60, 90, 120 minute) with same dosage (10 g/L). The batch experiments were also conducted at different temperatures (298, 303, 308, and 313 K) to study the effect of temperature on adsorption.

The concentration of Cr(VI) ions in the solution after adsorption was determined by using diphenyl carbazide method (APHA 2012). The absorbance of the purple-violet colored solution developed in acidic solution was recorded within 10 min at 540 nm. All the tests were carried out in triplicate and the mean values were taken for calculation. The amount of Cr(VI) adsorbed at equilibrium (q_e , mg/g) and the percentage removal of Cr(VI) after adsorption by goethite was calculated by the following equation.

$$q_e = \frac{C_0 - C_e}{M} \times V \quad (1)$$

$$\% \text{ Removal of Cr(VI)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C_0 and C_e (mg/L) are the initial and final equilibrium concentrations of Cr(VI), respectively. M is the amount of goethite used (g) and V is the volume of the solution (L).

RESULTS AND DISCUSSION

Adsorbent Characterization

The XRD pattern of the adsorbent is shown in Fig. 1. The XRD pattern indicates that the adsorbent consists of pure goethite. The goethite is identified from its characteristics peak at 4.98, 4.18, 2.69, 2.45, 2.25 and 2.19 Å along with other lower order peaks. The sharp

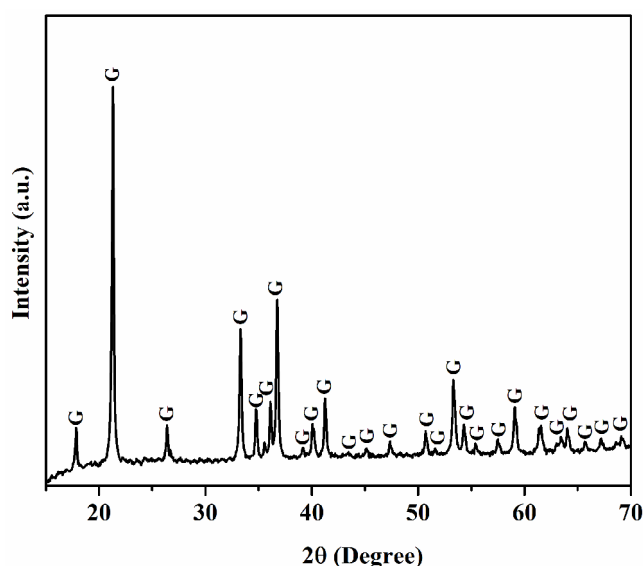


Fig. 1. X-ray diffraction pattern of goethite.

peaks indicate that it is in well crystalline form. The TEM image and EDX spectra of natural goethite is given in Fig. 2 that show the presence of acicular shaped goethite with subordinate quantity of Si, P and Al. The chemical analysis of goethite using EDX analysis shows concentration of Fe, Si, P and Al is 68.04, 0.81, 0.50 and 0.25 wt% respectively. Mohapatra et al (2008) reported the presence of Si, P and Al in minor quantity in goethite from the Banded Iron Formation of Orissa.

Effect of Initial Concentration

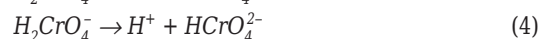
The removal of Cr(VI) ion was studied by varying the initial concentration from (2 to 25 mg/L) at pH 2 and 5 while keeping the rest of the parameters constant. It was observed that there was decrease in removal of Cr(VI) with increase in concentration (Fig. 3). The result showed that at 2 mg/L nearly 100% of Cr(VI) ions was removed at pH 2; but only 25 % was removed at the concentration of 25 mg/L. At pH 5, around 47% and 24% of Cr(VI) was removed at the concentration of 2 and 25 mg/L, respectively. This is due to the fixed number of available surface sites of goethite which become limited or saturated by Cr(VI) at certain concentration (Akar et al. 2009; Mor et al. 2007). Hence, more and more Cr(VI) ions compete for the same sites with the increase in concentration that causes decrease in removal percentage (Jung et al. 2013).

Effect of Contact Time

The adsorption of Cr(VI) ions as a function of time was studied to determine the equilibrium time onto goethite. These experiments were carried out at different Cr(VI) concentration such as 2, 5 and 20 mg/L at pH 2 and keeping other parameters constant (Fig. 4). The uptake of Cr(VI) was studied for 10, 30, 60, 90, 120 and 180 minute at 2, 5 and 20 mg/L concentrations. The results indicate that the adsorption of Cr(VI) increased gradually and after 120 minute there is hardly any change in adsorption as equilibrium is achieved. At the initial time of adsorption there are more vacant sites available in the adsorbent. Hence, faster rate of adsorption occurred with the increased concentration gradient between the adsorbate in solution and adsorbent (Acharya et al. 2009). After filling the vacant sites of adsorbent, the molecules also penetrate through the pores and again adsorbed inside the surface of the adsorbent at the slower rate, which is also known as intraparticle diffusion (Baral et al. 2009).

Effect of pH

The pH of the aqueous solution is one of the important controlling factors during adsorption process. This is mostly due to pH-dependant speciation of Cr(VI) ion and development of surface charge on the adsorbent (Weng et al., 2008). Hence, the removal of Cr(VI) ions by goethite was studied over a pH range of 2-10 with the initial concentration of 5 and 10 mg/L while keeping other parameters constant. Experimental results indicate that the removal efficiency decreases with increase in pH (Fig. 5). Maximum removal of 66% and 54% was observed at initial Cr(VI) concentration of 5 and 10 mg/L respectively at pH 2. However, removal was not much after pH 8. These result shows that goethite can adsorb Cr(VI) ions more readily in an acidic pH range. The Cr(VI) exists in the form of several species like $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{H}_2\text{Cr}_2\text{O}_7$, $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , HCrO_4^- , H_2CrO_4^- etc. depending on the solution pH (Zhao et al. 2013). Based on the Eh-pH diagram, among the Cr(VI) species, the HCrO_4^- and CrO_4^{2-} species are most dominant within pH range 1.0-6.5 and at pH > 6.5 respectively (Rai et al. 1989). With the increase in pH, HCrO_4^- is converted to CrO_4^{2-} and CrO_7^{2-} ions through Eqs (3) to (5)



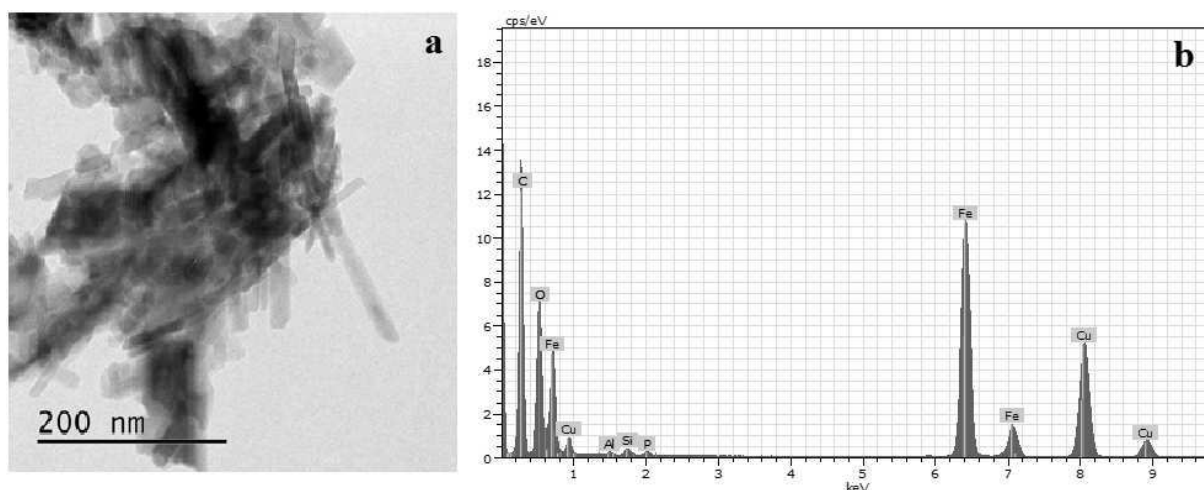


Fig.2. TEM image of goethite (a) and its EDX spectrum (b).

The highest adsorption removal efficiency was obtained at optimum pH 2, where HCrO_4^- ion was considered to be the dominant species. Adsorption free energy of various chromium species (CrO_4^{2-} , HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$) is one of the important factors affecting the adsorptive ability in different pH (Zhao et al. 2010). Among all the species, the adsorptions free energy of HCrO_4^- and CrO_4^{2-} are in the range of -2.26 to -0.52 kcal/mol and -2.13 to -0.34 kcal/mol, respectively (Weng et al. 1997). Hence, due to the lower value of the adsorption free energy of HCrO_4^- it is more favorably adsorbed than CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions at lower pH (Hyder et al. 2014).

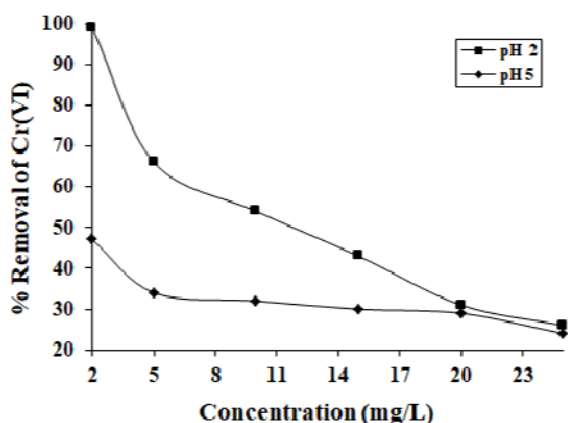


Fig. 3. Effect of concentration on removal of Cr(VI) by goethite at different pH 2 and 5, adsorbent dosage 10 g/L, contact time 2 h, temperature 25 °C and rotation speed 150 rpm.

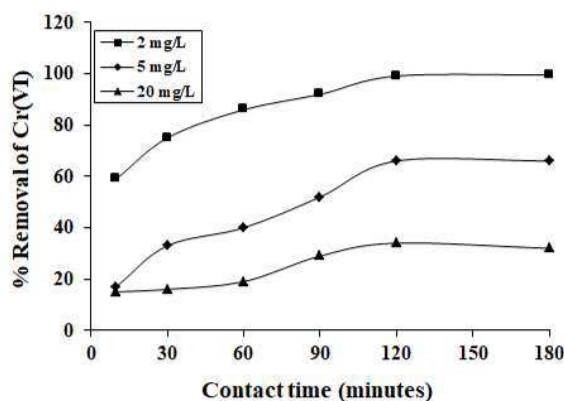
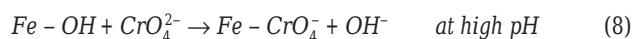


Fig. 4. Effect of contact time on removal of Cr(VI) by goethite at different concentration 2, 5 and 20 mg/L, adsorbent dosage 10 g/L, pH 2, temperature 25 °C and rotation speed 150 rpm.

Further, the goethite has the property to develop the variable surface charge based on the prevailing pH condition. At low pH, the surface is surrounded by hydronium ions (H^+) and thus, the hydroxyl goethite surface is protonated (Fe-OH_2^+) and become positively charged. Hence, the surface favors more adsorption of HCrO_4^- ions by the electrostatic force of attraction towards goethite as mentioned in Eq. (6) and leads to high percentage removal of Cr(VI). However, when the pH value increases the adsorption capacity decreases due to electrostatic repulsion between deprotonated surface (Fe-OH) and $\text{HCrO}_4^-/\text{Cr}_2\text{O}_7^{2-}$ ions lead to the gradual reduction in the adsorption of Cr(VI) species (Eq. 7) (Weng et al. 2008; Namasivayam and Yamuna, 1995).



From the above equations, it can be seen that at higher pH more OH^- ions are available which competes with HCrO_4^- and CrO_4^{2-} ions at adsorption sites. Hence, the formation of complexes through adsorbing Cr(VI) ions is ultimately decreasing (Namasivayam and Sureshkumar, 2008).

Effect of Temperature

Influence of temperature on the adsorption of Cr(VI) ions was conducted through series of experiments between 298 and 313 K temperature. The effect of this parameter for the Cr(VI) removal was

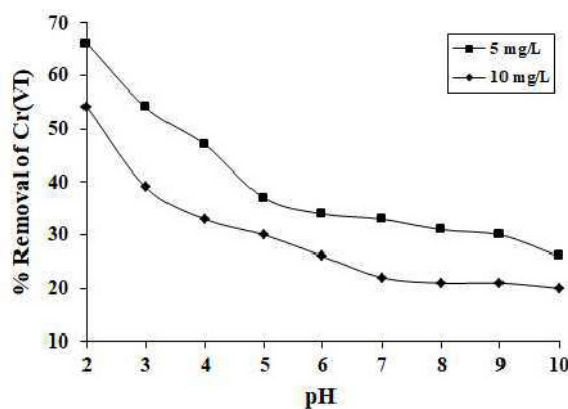


Fig. 5. Effect of pH on removal of Cr(VI) by goethite at different concentration 5 and 10 mg/L, adsorbent dosage 10 g/L, contact time 2 h, temperature 25 °C and rotation speed 150 rpm.

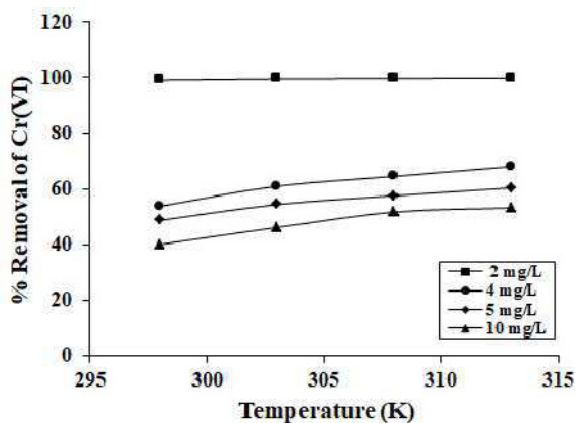


Fig. 6. Effect of temperature on removal of Cr(VI) by goethite at different concentration 2, 4, 5 and 10 mg/L, adsorbent dosage 10 g/L, pH 2, contact time 2 h and rotation speed 150 rpm.

Table 1. The percentage removal of Cr(VI) at different temperatures onto goethite

Temperature (K)	Percentage sorbed (%)			
	2 mg/L	4 mg/L	5 mg/L	10 mg/L
298	99.14	53.91	48.8	40.1
303	99.57	61	54.5	46.2
308	99.71	64.55	57.6	51.8
313	99.87	68.09	60.4	53.3

observed at different Cr(VI) concentration of 2, 4, 5, 10 mg/L at pH 2 with a constant adsorbent dose 10 g/L (Fig. 6). It is observed that the removal of Cr(VI) ions increases with increase in temperature which indicates that there is a better adsorption at higher temperature (Table 1). It was found that percentage removal of Cr(VI) increased from 53 to 68%, 48 to 60% and 40 to 53% at the concentration 4, 5, 10 mg/L respectively when the temperature increased from 298 to 313 K. Thus, the adsorption was found to be endothermic in nature (Selen et al. 2014). Moreover, the increase in sorption may be attributed to the increase in the number of the adsorption sites generated because of breaking of some internal bonds near the edge of active surface sites of adsorbent (Acharya et al. 2009).

Thermodynamic Studies

To determine the feasibility and the nature of the adsorption process various thermodynamic parameters such as Gibb's free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated at different temperatures between 298 and 313 K using the following equations.

$$K_c = \frac{q_e}{C_e} \quad (9)$$

$$\Delta G = -RT \ln K_c \quad (10)$$

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (11)$$

The equilibrium constant, K_c (L/g), of the adsorption process is calculated first (Khezami and Capart, 2005); where q_e is the amount of Cr(VI) adsorbed per unit mass of goethite (mg/g) and C_e is the equilibrium concentration in solution (mg/L), R is the ideal gas constant (8.314 J/mol K) and T is the absolute temperature in Kelvin (K). The enthalpy (ΔH°) and entropy (ΔS°) were calculated from the slope and intercept based on the Van't Hoff plot between $\log K_c$ and $1/T$ respectively (Fig. 7). It is observed that the value of standard free energy, ΔG° , is negative and it decreases with the increasing

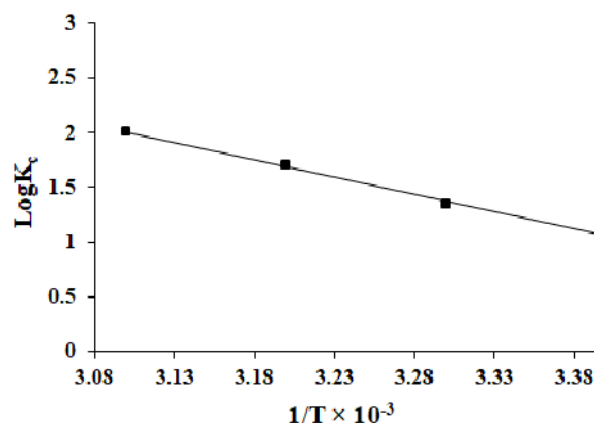


Fig. 7. A plot of $\log K_c$ and $1/T$ of Cr(VI) adsorption by goethite at concentration of 2 mg/L, adsorbent dosage 10 g/L and pH 2.

Table 2. Thermodynamic parameters of Cr(VI) adsorption at different temperatures by goethite

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol /K)	R^2
298	-6087.39			
303	-7930.52	60.29	225.19	0.9981
308	-10009.82			
313	-11978.3			

temperature (Table 2). It indicates that the adsorption of Cr(VI) onto goethite is feasible and spontaneous even at high temperature (Selen et al. 2014). The enthalpy change during the adsorption process is 60.29 kJ/mol. The positive value of ΔH° confirmed the endothermic nature of the adsorption. Additionally, the positive value of ΔS° reveals the increased randomness at the solid-solution interface during the adsorption process (Malkoc and Nuhoglu, 2007).

Adsorption Isotherm Models

The adsorption isotherms are used to obtain the adsorption capacity and affinity of adsorbent. The amount of Cr(VI) ion adsorbed per unit of adsorbent and remaining in solution at equilibrium can be obtained through isotherm study. The batch experimental data were analyzed using various isotherm models such as Langmuir, Freundlich, Dubinin-Radushkevich and Temkin with initial concentrations of Cr(VI) varied from 5 to 25 mg/L at pH 2.

The Langmuir isotherm is applied to the monolayer adsorption sites on an energetically homogenous surface with a finite number of identical sites (Nemr et al. 2008). Once a site is occupied by Cr(VI), no further adsorption can take place (Ramos-Ramírez et al. 2009). The linear form of the Langmuir model is described by the Eq. (12).

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_0 b} \right) + \left(\frac{1}{Q_0} \right) C_e \quad (12)$$

where C_e and q_e are the equilibrium concentration (mg/L) and the amount of Cr(VI) adsorbed per gram of goethite (mg/g), respectively. The Q_0 and b are the adsorption capacity of the goethite (mg/g) and the Langmuir affinity constant (L/mg) of the binding sites, respectively. The values of Langmuir constants Q_0 and b were determined from the slope and intercept respectively using the plot between C_e/q_e and C_e (Fig. 8a). The results reveal that the Langmuir isotherm has a maximum correlation coefficient ($R^2 = 0.994$) which indicated that the uptake occurred on a homogenous surface through monolayer adsorption. The maximum adsorption capacity of goethite was found to be 0.727 mg/g. Table 3 summaries the comparison of the maximum adsorption capacities of various natural adsorbent including goethite.

Table 3. Comparison of the maximum adsorption capacity of various adsorbents for the removal of Cr(VI) during adsorption.

Adsorbent	pH	Q _o (mg/g)	Reference
Dolomite	2	10.1	Albadarin et al. (2012)
Bentonite	2	0.57	Khan et al. (1995)
Kaolinite	4	0.447	Fritzen et al. (2006)
Montmorillonite	2	0.167	Fritzen et al. (2006)
Feldspar	2.5	0.091	Singh et al. (1992)
Siderite	2	17	Erdem et al. (2004)
Limonite	3	10.03	Baig et al. (2013)
Wollastonite	2.5	0.686	Sharma (2001)
Goethite	2	0.727	Present study

Table 4. Separation factor (R_L) of Cr (VI) adsorption at different concentration onto goethite

C _o (mg/L)	R _L
5	0.251
10	0.144
15	0.100
20	0.077
25	0.063

The result shows that goethite has the reasonable better adsorption capacity and affinity compared with other natural adsorbents. The essential features of Langmuir isotherm can be expressed in terms of dimensionless constant known as separation factor or equilibrium parameter (R_L) using Eq. (13). It is used to predict whether the adsorption is favorable or unfavorable. When the value of R_L lies between 0 and 1 indicates favorable adsorption; R_L > 1 indicates unfavorable adsorption; R_L = 1 represents the linear adsorption, and the adsorption operation is irreversible if R_L = 0 (Hyder et al. 2014).

$$R_L = \frac{1}{1 + bC_o} \quad (13)$$

where b (L/mg) and C_o (mg/L) are the Langmuir affinity constant and initial concentration of Cr(VI). Table 4 indicates the positive values of R_L for different initial Cr(VI) concentrations, and it is within 0 and 1. Thus, it indicates the adsorption is favorable and also feasible onto goethite.

The Freundlich isotherm is an empirical equation employed to describe a heterogeneous system. It can be used to describe the adsorption intensity of the goethite towards Cr(VI) and is expressed as follows (Qiu et al. 2015).

$$\log q_e = \log K_f + (1/n) \log C_e \quad (14)$$

where K_f (mg/g) and n (g/L) are the empirical Freundlich constants which represent the bond strength and the adsorption intensity of the heterogeneous surface. These parameters were determined from the intercept and slope using Eq. (14) and shown in (Fig. 8b). The result from the Table 5 indicates that the adsorption reaction is favourable as the magnitude of n is 3.48, which lies between 1 and 10 (Zhao et al. 2013). In addition to the above finding, the experimental R² value of this model is very less. Thus, it can be concluded that the adsorption of Cr(VI) onto goethite is not a multi-molecular adsorption process (Wang et al. 2012).

The Dubinin-Radushkevich isotherm is applied to estimate the nature of adsorption processes, whether physical or chemical, based

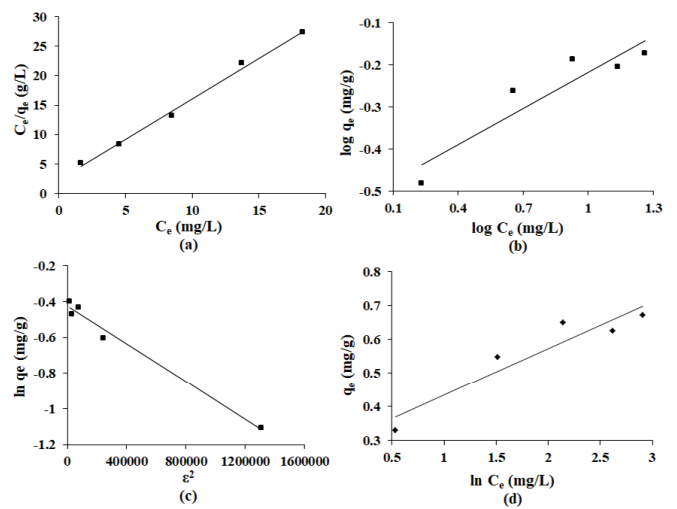


Fig. 8. (a) Langmuir, (b) Freundlich, (c) Dubinin-Radushkevich, (d) Temkin adsorption isotherms obtained from various concentrations at fixed temperature 25°C by goethite.

on the free energy of adsorption (E). This isotherm does not assume a homogeneous surface or constant sorption potential (Singha et al. 2011; Akçay 2006). The linear form of this model is represented in Eq. (15).

$$\ln q_e = \ln q_m - K_{DR} \varepsilon^2 \quad (15)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (16)$$

$$E = \frac{1}{\sqrt{-2K_{DR}}} \quad (17)$$

where q_m (mg/g) is the isotherm constant represents the maximum adsorption capacity of goethite. K_{DR} (mol²/kJ²) is a constant related to mean adsorption energy. The ε is Polanyi potential and the magnitude of E represents the mean free energy of adsorption. The plot of ln q_e versus ε² gives the values of K_{DR} and q_m from the slope and intercept respectively using Eq. (15). The straight line with a correlation coefficient (R² = 0.982) indicates that the D-R model was well fit to the adsorption of Cr(VI) ions. Again the positive value of free energy (E) proves the endothermic nature of adsorption.

The Temkin model assumes that the heat of sorption decreases linearly with the surface coverage due to interaction of adsorbent and adsorbate (Brdar et al. 2012). The linear form of Temkin isotherm is represented as follows:

$$q_e = \frac{RT}{b_T} \ln a_T + \frac{RT}{b_T} \ln C_e \quad (18)$$

where b_T (kJ/mol) is the Temkin isotherm constant related to the heat of adsorption and a_T (L/g) is the equilibrium binding constant corresponding to the maximum binding energy. R (8.314 x 10⁻³ kJ/mol K) is the Universal gas constant and T is the temperature in Kelvin (K). The constants b_T and a_T were obtained from the slope and intercept respectively from of linear plot between q_e and ln C_e using Eq. (18) (Fig. 8d).

Table 5. Comparison of isotherm models of Cr(VI) adsorption by goethite at different concentration

Langmuir			Freundlich			Dubinin-Radushkevich				Temkin		
Q _o (mg/g)	b (L/mg)	R ²	K _f (mg/g)	n (L/mg)	R ²	q _m (mg/g)	K _{DR} (mol ² /kJ ²)	E (kJ/mol)	R ²	a _T (L/g)	b _T (KJ/mol)	R ²
0.727	0.594	0.994	0.313	3.484	0.862	0.653	5 x 10 ⁻⁷	1	0.982	8.449	17.90	0.891

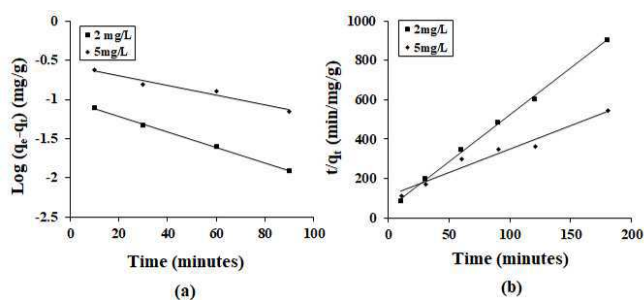


Fig. 9. (a) Pseudo first order kinetic model, (b) Pseudo second order kinetic model of Cr(VI) adsorption by goethite at different concentrations 2 and 5 mg/L, adsorbent dosage 10 g/L, contact time 2 h, pH 2 at 25°C.

Adsorption kinetic and modeling

To understand the different adsorption mechanism various kinetic models such as pseudo first order, pseudo second order and intraparticle diffusion models were used. The kinetic data were obtained from the plots of various models as given in Table 6 based on the adsorption experiment. Where q_e and q (mg/g) are the amounts of Cr(VI) adsorbed at equilibrium and at time t respectively. K_1 and K_2 are the rate constants of the Pseudo first and second order equations (19) and (20), K_d is the intraparticle diffusion coefficient of Eq. (21) and it was calculated from the slope of the graph; C_1 is the intercept called intraparticle diffusion constant. All the models of the kinetic sorption onto goethite were plotted (Fig. 9) and the graph of intraparticle diffusion was shown in Fig. 10. The $q_{e,cal}$ was determined from the slope for both Pseudo first and second order models; K_1 and K_2 were determined from the intercept of the graph. The experimental data of the models were compared with the parameters obtained from the graph of models shown in Table 7. It is observed that pseudo second order kinetic model is more suitable for the Cr(VI) adsorption onto goethite as the theoretical adsorption capacity values ($q_{e,cal}$) is more closer to that of experimentally derived parameter ($q_{e,exp}$).

The intraparticle diffusion model parameters were shown in Table 8 to determine whether bulk diffusion, film diffusion or intraparticle diffusion is the rate limiting step (Albadarin et al. 2012). The model suggested that if the sorption mechanism is only controlled by an intraparticle diffusion step, then a plot of q_t and $t^{1/2}$ gives a linear relationship and the line passes through the origin (Olu-Owolabi et al. 2014). The adsorption mechanism follows more than one diffusion mechanism when the plot do not passes in origin (Doke et al. 2013). In the present study, the plot shows linearity and not passing through the origin indicating Cr(VI) adsorption is controlled by more than

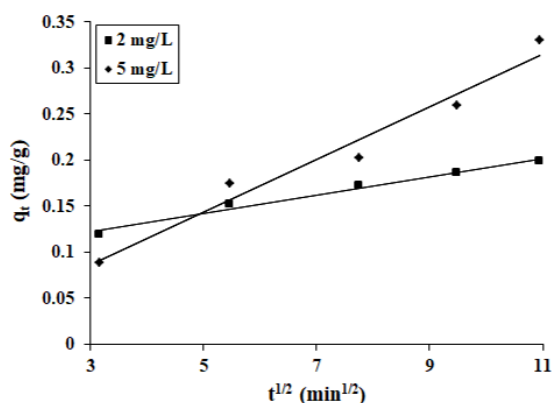


Fig. 10. Intraparticle diffusion model of Cr(VI) adsorption by goethite at different concentrations 2 and 5 mg/L, adsorbent dosage 10 g/L, contact time 2 h, pH 2 at 25 °C.

Table 6. The kinetic models of Cr(VI) adsorption can be expressed by the following equations

Kinetic models	Equation	Plots	Eq. no.
Pseudo-first order model	$\log(q_e - q_t) = \log q_e - K_1/2.303t$	$\log(q_e - q_t)$ vs t	(19)
Pseudo-second order model	$t/q_t = t/q_e + 1/K_2 q_e^2 t$	t/q_t vs t	(20)
Intra-particle diffusion	$q_t = K_d t^{1/2} + C_1$	q_t vs $t^{1/2}$	(21)

Table 7. Comparison of kinetic parameters of Cr(VI) adsorption at different concentration onto goethite

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo first order kinetic model			Pseudo second order kinetic model		
		$q_{e,cal}$ (mg/g)	K_1 (1/min)	R^2	$q_{e,cal}$ (mg/g)	K_2 (g/mg/min)	R^2
2	0.199	0.01	0.363	0.997	0.211	0.446	0.998
5	0.329	0.006	0.563	0.962	0.415	109.68	0.965

Table 8. Intraparticle diffusion model parameters of Cr(VI) adsorption at different concentration by goethite.

C_0 (mg/L)	Intraparticle coefficient (K_d) (mg/g min ^{1/2})	Intraparticle constant (C_1) (mg/g)	R^2
2	0.01	0.091	0.982
5	0.03	0.001	0.967

one mechanism. It indicates that there is some degree of boundary layer diffusion and film diffusion also plays an important role along with the intraparticle diffusion. In Table 8, it is seen that the rate constant K_d increases with increase in the Cr(VI) concentration, which may be due to the greater concentration driving force (Albadarin et al. 2012). The intercept C_1 represents the thickness of the boundary layer and it is found to be very small. It implies that the role of surface diffusion is very less as rate-limiting mechanism.

CONCLUSION

This study reveals that natural goethite can act as an effective and promising adsorbent to be utilized for the removal of Cr(VI) ions from aqueous solution. The feasibility of adsorption process was studied in batch scale with the different parameters. The Cr(VI) removal rate decreased with increasing pH and lowering with initial Cr(VI) concentration. The increase in temperature promotes more adsorption towards goethite due to endothermic nature. Thermodynamic study obtained that the adsorption of Cr(VI) is spontaneous and feasible. The comparison of the experimental values of different isotherms showed that Langmuir isotherm confirms well from its correlation coefficient value with maximum adsorption capacity 0.727 mg/g. This observation revealed that the adsorption of Cr(VI) onto goethite is a monolayer sorption. The kinetic studies of adsorption suggested that, the sorption followed pseudo-second-order kinetic model, where the Cr(VI) ions slowly diffuse inwards and adsorb to the inner site of adsorbent.

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References

- Acharya, J., Sahu, J.N., Sahoo, B.K., Mohanty, C.R. and Meikap, B.C. (2009) Removal of chromium(VI) from wastewater by activated carbon developed from Tamarind wood activated with zinc chloride. Chem. Engg. Jour.

- v.150, pp.25-39.
- Ajouyed, O., Hurel, C., Ammari, M., Allal, L. B. and Marmier, N. (2010) Sorption of Cr(VI) onto natural iron and aluminum (oxy)hydroxides: Effects of pH, ionic strength and initial concentration. *Jour. Hazard. Mater.*, v.174, pp.616-622.
- Akar, S.T., Yetimoglu, Y. and Gedikbey, T. (2009) Removal of chromium (VI) ions from aqueous solutions by using Turkish montmorillonite clay: effect of activation and modification. *Desalination*, v.244, pp.97-108.
- Akçay, M. (2006) Characterization and adsorption properties of tetrabutyl ammonium montmorillonite (TBAM) clay: Thermodynamic and kinetic calculations. *Jour. Colloid Interface Sci.*, v.296, pp.16-21.
- Albadarin, A. B., Mangwandi, C., Al-Muhtaseb, A., Walker, G.M., Allen, S.J. and Ahmad, M.N.M. (2012) Kinetic and thermodynamics of chromium ions adsorption onto low-cost dolomite adsorbent. *Chem. Engg. Jour.*, v.179, pp.193-202.
- Anupama, K., Dutta, S., Bhattacharjee, C. and Datta, S. (2011) Adsorptive removal of chromium (VI) from aqueous solution over powdered activated carbon: Optimisation through response surface methodology. *Chem. Engg. Jour.*, v.173, pp.135-143.
- APHA (2012) Standard Methods for Examination of water and wastewater. American Public Health Association, Washington, 22nd Edition, pp.1360.
- Baig, S.A., Wang, Q., Wang, Z., Zhu, J., Lou, Z., Sheng, T. and Xu, X. (2014) Hexavalent chromium removal from solutions: Surface efficacy and characterizations of three iron containing minerals. *Clean Soil Air Water*, v.42, pp.1409-1414.
- Baig, S.A., Wang, Q., Lv, X. and Xu, X. (2013) Removal of hexavalent chromium by limonite in aqueous solutions. *Hydrometallurgy*, v.138, pp.33-39.
- Baral, S. S., Das, N., Chaudhury, G.R. and Das, S.N. (2009) A preliminary study on the adsorptive removal of Cr(VI) using seaweed, *Hydrillaverticillata*. *Jour. Hazard. Mater.*, v.171, pp.358-369.
- Baral, S.S., Das, S.N., Rath, P. and Chaudhury, G.R. (2007) Chromium(VI) removal by calcined bauxite. *Biochem. Engg. Jour.*, v.34, pp.69-75.
- Brdar, M., Šeibani, M., Takaëi, A. and Došenović, T. (2012) Comparison of two and three parameters adsorption isotherm for Cr(VI) onto Kraft lignin. *Chem. Engg. Jour.*, v.183, pp.108-111.
- Buerge, I. J. and Hug, S. J. (1999) Influence of mineral surfaces on chromium (VI) reduction by iron(II). *Environ. Sci. Tech.*, v.33, pp.4285-4291.
- Choppala, G., Bolan, N. and Seshadri, B. (2013) Chemodynamics of chromium reduction in soils: Implications to bioavailability. *Jour. Hazard. Mater.*, v.261, pp.718-724.
- Chowdhury, S.R. and Yanful, E.K. (2010) Arsenic and chromium removal by mixed magnetite-maghemite nanoparticles and the effect of phosphate on removal. *Jour. Environ. Managmt.*, v.91, pp.2238-2247.
- Doke, K., Khan, E. and Gaikwad, V. (2013) Diffusion mechanisms of bioadsorption of Cr(VI) onto powdered cotton stalk. *Jour. Dispersion Sci. Technol.*, v.34, pp.1347-1355.
- Dubey, S.P. and Gopal, K. (2007) Adsorption of chromium(VI) on low cost adsorbents derived from agricultural waste material: A comparative study. *Jour. Hazard. Mater.*, v.145, pp.465-470.
- EPA (1990) Environmental pollution control alternatives: Drinking water treatment for small communities. *Technology Transfer, EPA/625/5-90/025*.
- Erdem M., Gur F. and Tümen F. (2004) Cr(VI) reduction in aqueous solutions by siderite. *Jour. Hazard. Mater.*, v.113, pp.217-222.
- Fendorf, S.E. (1995) Surface reactions of chromium in soils and waters. *Geoderma*, v.67, pp.55-71.
- Fritzen, M.B., Souza, A.J., Silva, T.A.G., Souza, L., Nome, R.A., Fiedler, H. D. and Nome, F. (2006) Distribution of hexavalent Cr species across the clay mineral surface-water interface. *Jour. Colloid Interface Sci.*, v.296, pp.465-471.
- Granados-Correa, F. and Jiménez-Becerril, J. (2009) Chromium (VI) adsorption on boehmite. *Jour. Hazard. Mater.*, v.162, pp.1178-1184.
- Hu, J., Chen, C., Zhu, X. and Wang, X. (2009) Removal of chromium from aqueous solution by using oxidized multiwalled carbon nanotubes. *Jour. Hazard. Mater.*, v.162, pp.1542-1550.
- Hyder, A.H.M.G., Begum, S.A. and Egiebor, N.O. (2014) Adsorption isotherm and kinetic studies of hexavalent chromium removal from aqueous solution onto bone char. *Jour. Environ. Chem. Engg.*, v.3, pp.1329-1336.
- Jung, C., Heo, J., Han, J., Her, N., Lee, S., Oh, J., Ryu, J. and Yoon, Y. (2013) Hexavalent chromium removal by various adsorbents: Powdered activated carbon, chitosan, and single/multi-walled carbon nanotubes. *Sep. Purif. Technol.*, v.106, pp.63-71.
- Khezami, L. and Capart, R. (2005) Removal of chromium(VI) from aqueous solution by activated carbons: Kinetic and equilibrium studies. *Jour. Hazard. Mater.*, v.123, pp.223-231.
- Kim, C., Lan, Y. and Deng, B. (2007) Kinetic study of hexavalent Cr(VI) reduction by hydrogen sulfide through goethite surface catalytic reaction. *Geochem. Jour.*, v.41, pp.397-405.
- Khan, S.A., Rehman, R.U. and Khan, M.A. (1995) Adsorption of chromium (III), chromium (VI) and silver (I) on bentonite. *Waste Managmt.*, v.15, pp.271-282.
- Korus, I. and Loska, K. (2009) Removal of Cr(III) and Cr(VI) ions from aqueous solutions by means of polyelectrolyte-enhanced ultrafiltration. *Desalination*, v.247, pp.390-395.
- Kulkarni, P. S., Kalyani, V., and Mahajani, V. V. (2007) Removal of hexavalent chromium by membrane-based hybrid processes. *Ind. Engg. Chem. Res.*, v.46, pp.8176-8182.
- Lazaridis, N.K., Bakoyannakis, D.N. and Deliyanni, E.A. (2005) Chromium(VI) sorptive removal from aqueous solutions by nanocrystalline akaganéite. *Chemosphere*, v.58, pp.65-73.
- Malkoc, E. and Nuhoglu, Y. (2007) Determination of kinetic and equilibrium parameters of the batch adsorption of Cr(VI) onto waste acorn of *Quercus ithaburensis*. *Chem. Eng. Process.*, v.46, pp.1020-1029.
- Mitra, S., Thakur L.S., Rathore, V.K. and Mondal, P. (2016) Removal of Pb(II) and Cr(VI) by laterite soil from synthetic waste water: single and bi-component adsorption approach. *Desalination Water Treat.*, v.57, pp.18406-18416.
- Mohapatra, B.K., Jena, S., Mahanta, K. and Mishra, P. (2007) Goethite morphology and composition in Banded Iron Formation, Orissa, India. *Resour. Geol.*, v.58(3), pp.325-332.
- Mor, S., Ravindra, K. and Bishnoi, N.R. (2007) Adsorption of chromium from aqueous solution by activated alumina and activated charcoal. *Bioresour. Tech.*, v.98, pp.954-957.
- Namasivayam, C. and Sureshkumar, M.V. (2008) Removal of chromium(VI) from water and wastewater using surfactant modified coconut coir pith as a biosorbent. *Bioresour. Tech.*, v.99, pp.2218-2225.
- Namasivayam, C. and Yamuna, R.T. (1995) Adsorption of chromium (VI) by a low-cost adsorbent: biogas residual slurry. *Chemosphere*, v.30, pp.561-578.
- Nemr, A. E., Khaled, A., Abdelwahab, O. and El-Sikaily, A. (2008) Treatment of wastewater containing toxic chromium using new activated carbon developed from date palm seed. *Jour. Hazard. Mater.*, v.152, pp.263-275.
- Olu-Owolabi, B. I., Diagboya, P. N. and Adebowale, K. O. (2014) Evaluation of pyrene sorption-desorption on tropical soils. *Jour. Environ. Managmt.*, v.137, pp.1-9.
- Panda, M., Bhowal, A. and Datta, S. (2011) Removal of hexavalent chromium by biosorption process in rotating packed bed. *Environ. Sci. Tech.*, v.45, pp.8460-8466.
- Qiu, B., Xu, C., Sun, D., Wang, Q., Gu, H., Zhang, X., Weeks, B. L., Hopper, J., Ho, T. C., Guo, Z. and Wei, S. (2015) Polyaniline coating with various substrates for hexavalent chromium removal. *Appl. Surf. Sci.*, v.334, pp.7-14.
- Qurie, M., Khamis, M., Manassra, A., Ayyad, I., Nir, S., Scranio, L., Bufo, S.A. and Karaman, R. (2013) Removal of Cr(VI) from aqueous environments using micelle-clay. *Sci. World Jour.*, v.942703, pp.7.
- Rad, S.A.M., Mirbagheri, S.A. and Mohammadi, T. (2009) Using reverse osmosis membrane for chromium removal from aqueous solution. *Int. Jour. Chem. Mol. Nucl. Mater. Metall. Engg.*, v.3, pp.9.
- Rai, D., Eary, L.E. and Zachara, J.M. (1989) Environmental chemistry of chromium. *Sci. Total Environ.*, v.86, pp.15-23.
- Ramos-Ramírez, E., Ortega, N.L. G., Soto, C.A.C. and Gutiérrez, M.T.O. (2009) Adsorption isotherm studies of chromium (VI) from aqueous solutions using sol-gel hydroxalcite-like compounds. *Jour. Hazard. Mater.*, v.172, pp.1527-1531.
- Rao, F., Song, S. and Lopez-Valdivieso, A. (2012) Specific adsorption of chromium species on kaolinite surface. *Miner. Process. Extr. Metall. Rev.*, v.33, pp.180-189.
- Selen, V., Özer, D. and Özer, A. (2014) A study on the removal of Cr(VI) ions by sesame (*sesamumindicum*) stems dehydrated with sulfuric acid. *Arab. Jour. Sci. Engg.*, v.39, pp.5895-5904.
- Sharma, Y.C. (2001) Effect of temperature on interfacial adsorption of Cr(VI)

- on wollastonite. *Jour. Colloid Interface Sci.*, v.233, pp.265-270.
- Singh, D.B., Rupainwar, D.C. and Prasad, G. (1992) Studies on the removal of Cr(VI) from wastewater by feldspar. *Jour. Chem. Tech. Biotechnol.*, v.53, pp.127-131.
- Shi, T., Wang, Z., Liu, Y., Jia, S. and Changming, D. (2009) Removal of hexavalent chromium from aqueous solutions by D301, D314 and D354 anion-exchange resins. *Jour. Hazard. Mater.*, v.161, pp.900-906.
- Singha, B., Naiya, T. K., Bhattacharya, A. K. and Das, S.K. (2011) Cr(VI) ions removal from aqueous solutions using natural adsorbents—FTIR studies. *Jour. Environ. Prot.*, v.2, pp.729-735.
- Song, X. and Wu, Y. (2014) Simultaneous adsorption of chromium (VI) and phosphate by calcined Mg-Al-CO₃ layered double hydroxides. *Bull. Korean Chem. Soc.*, v.35, pp.1817-1824.
- Turan, M.D. and Altundogan, H.S. (2014) A study on Cr(VI) reduction from aqueous solutions from bauxite. *Jour. Cent. South Univ.*, v.21, pp.1961-1967.
- Wang, W., Li, M. and Zeng, Q. (2012) Thermodynamics of Cr(VI) adsorption on strong alkaline anion exchange fiber. *Trans. Nonferrous Met. Soc. China*, v.22, pp.2831-2839.
- Weng, C., Sharma, Y.C. and Chu, S. (2008) Adsorption of Cr(VI) from aqueous solutions by spent activated clay. *Jour. Hazard. Mater.*, v.155, pp.65-75.
- Weng, C.H., Wang, J.H. and Huang, C.P. (1997) Adsorption of Cr(VI) onto TiO₂ from dilute aqueous solutions. *Wat. Sci. Tech.*, v.35, pp.55-62.
- Wu, S., Lu, J., Ding, Z., Li, N., Fu, F. and Tang, B. (2016) Cr(VI) removal by mesoporous FeOOH polymorphs: performance and mechanism. *RSC Adv.*, v.6, pp.82118-82130.
- Xiaohong, Y., Lijun, Z., Baiwei, G. and Shouyang, H. (2009) A study on the adsorption of chromium on laterite from Guizhou Province, China. *Chin. Jour. Geochem.*, v.28, pp.220-226.
- Yang, C. and Kravets, G. (2000) Removal of chromium from abrasive blast media by leaching and electrochemical precipitation. *Jour. Air Waste Manage. Assoc.*, v.50, pp.536-542.
- Zachara, J.M., Cowan, C.E., Schmidt, R.L. and Ainsworth, C.C. (1988) Chromate adsorption by kaolinite. *Clays Clay Miner.*, v.36, pp.317-326.
- Zachara, J.M., Girvin, D.C., Schmidt, R.L. and Resch, C.T. (1987) Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions. *Environ. Sci. Tech.*, v.21, pp.589-594.
- Zhao, Y., Shen, H., Pan, S., Hu, M. and Xia, Q. (2010) Preparation and characterization of amino-functionalized nano-Fe₃O₄ magnetic polymer adsorbents for removal of chromium(VI) ions. *Jour. Mater. Sci.*, v.45, pp.5291-5301.
- Zhao, Y., Yang, S., Ding, D., Chen, J., Yang, Y., Lei, Z., Feng, C. and Zhang, Z. (2013) Effective adsorption of Cr (VI) from aqueous solution using natural Akadama clay. *Jour. Colloid Interface Sci.*, v.395, pp.198-204.

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