ADSORPTIVE REMOVAL OF Pb(II) AND Cr(VI) IONS ON NATROLITE

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Natrolite proved to be an effective adsorbent for the adsorptive removal of lead and chromium ions from aqueous solutions. Adsorption parameters such as pH, adsorbent dose, temperature, and contact time were optimized. For the determination of rate of metal adsorption by natrolite from 50 mL (20 mg L^{-1}), the supernatant was analyzed for residual metals after the contact period of 10-120 min. The effect of pH on metal adsorption by natrolite was determined at values pH 2-8 and the effect of different doses of natrolite from 0.1 to 0.6 was determined, as well as to what extent the adsorption data obey Langmuir and Freundlich adsorption isotherms were also investigated. Thermodynamic studies shows the negative values of ΔG^0 at all the temperature indicates the spontaneous nature of Pb(II) and Cr(VI) ions on natural mineral natrolite. Natrolite has shown good results ans exhibits that the pH plays an important role in adsorption of metal ions.

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Introduction

Heavy metals are common pollutant found in various industrial effluents. The stricter environment regulation on the discharge of heavy metals makes it necessary to develop various technologies for the removal. Waste streams containing low to medium level of heavy metals are often encountered in metal plating facilities, electroplating, mining operations, fertilizer battery manufacture, dyestuffs, chemical pharmaceutical, electronic device manufactures and many others. Most of the heavy metals are highly toxic and are not biodegradable; therefore they must be removed from the polluted streams in order to meet increasingly stringent environmental quality standards. Many methods including chemical precipitation, electro-deposition, ion exchange, membrane separation, and adsorption have been used to treat such streams of these methods, traditional chemical precipitation is the most economic but is inefficient for dilute solution. Ion exchange and reverse osmosis are generally affective but have rather high maintenance and operation costs and subject to fouling. Adsorption is one of the few promising alternatives for this purpose, especially using sorbents such as agricultural wastes, clay materials, zeolites, biomass and sea food processing waste.[1,2]

In the present work, the adsorption behaviour of natural zeolite (natrolite) with respect to Pb(II) and Cr(VI) has been studied in order to consider the application to purify metal containing wastewater. Adsorption parameter such as pH, adsorbent dose, contact time and temperature were optimized in order to explore zeolites application in removal of metals from wastewater. The adsorption equilibrium data were compared to the Langmuir and Freundlich adsorption models. Thermodynamic studies were also performed to evaluate the nature of the adsorption process.

Experimental

Adsorbent

Naturally occurring zeolite (natrolite as a geological specimen, collected from Sinner, Nasik (Maharashtra) and was powdered after cleaning, washing and grinding to very fine white particles and sieved through 100 mesh and then stored in air tight container.

Chemical composition of natural natrolite is given in Table 1.[3] The specimen was further characterized by XRD (X-ray diffraction) and it was established that sample was natrolite.

Table 1. Chemical composition of natural natrolite

Chemical composition	Composition, in %
SiO_2	48.41
Al_2O_3	26.82
Na_2O	16.30
Fe_2O_3	1.12
K_2O	0.20
CaO	0.52
MgO	0.20
H_2O	6.43

Preparation of stock solution

An aqueous solution (1000 mg L^{-1}) of Pb(II) and Cr(VI) was prepared and pH of solution was adjusted using 0.1 M HCl or NaOH. Fresh dilutions were used for each study.

Batch adsorption experiments

The adsorption experiments were carried out in batches of 50 mL of 20 mg L^{-1} metal solution with known amount of natrolite. The solutions were shaken in orbital shaker (Shivam ISO 900/2000) at 120 rpm, at 30 °C for a definite period of time, followed by centrifugation.

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The supernatant containing the residual concentration of metals was determined using atomic absorption spectrophotometer (AAS, ECIL-4141). Adsorption parameters such as pH, adsorbent dose, temperature, and contact time were optimized by the method of trial and error. For the determination of rate of metal adsorption by natrolite from 50 mL (20 mg L^{-1}), the supernatant was analyzed for residual metals after the contact period of 10, 20, 30, 60, 90 and 120 min. The effect of pH on metal adsorption by natrolite was determined at values pH 2-8 and the effect of different doses of natrolite from 0.1 to 0.6 was determined. For the adsorption isotherm studies optimized parameters were determined to reach equilibrium for 20 mg L^{-1}, Pb(II) and Cr(VI) ion concentration.

Calculations

The percent removal of metal ions was calculated by using the Equation 1.

$$R(\%) = \frac{C_i\text{-}C_f}{C_i} \times 100 \qquad (1)$$

where

R is the removal,

C_i is the initial metal concentration and

C_f is the final concentration of the metal ion in mg L^{-1}.

The sorption capacity was calculated from Eqn. 2

$$Q_e = \frac{V(C_i - C_e)}{1000W} \qquad (2)$$

where

Q_e is the adsorption capacity (mg g^{-1}),

C_i is the initial metal concentration (mg L^{-1}),

C_e is the equilibrium concentration of metal (mg L^{-1}),

W is the adsorbent dose (g) and

V is the solution volume (mL).

Results and discussion

Effect of pH

pH is an important parameter for adsorption of metal ions because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction.

The removal of metal ions from wastewater sample by adsorption is related to the pH of the sample, as the latter affects the surface charge of adsorbents, the degree of ionization, and the species of adsorbate. Adsorption of heavy metals from aqueous solutions depends on properties of adsorbent and molecules of adsorbate transfer from the solution to the solid phase.
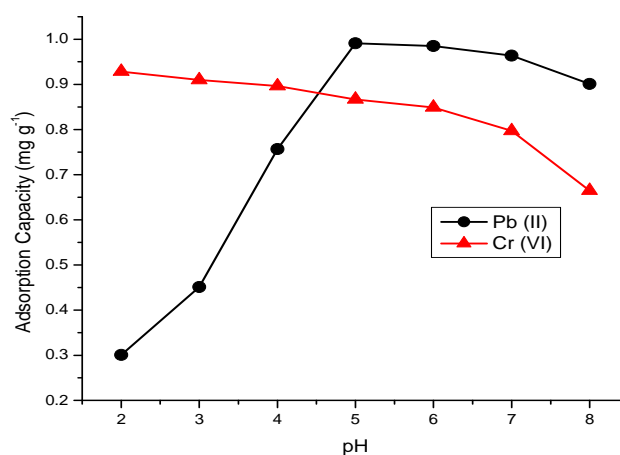

Figure 1. Effect of pH on adsorption capacities of Pb(II) and Cr(VI) ions.

It has been also reported that adsorption capacities for heavy metals are strongly pH sensitive and that adsorption increases as solution pH increases.[4,5] Initial investigation of adsorption capabilities of natrolite for Pb(II) and Cr(VI) ions with the adsorbent dose 0.5 g, per 50 mL of 20 mg L^{-1} metals solution and the role of H$^+$ concentration was examined at different values of pH 2-8 and Figure 1, showed maximum adsorption capacity for Pb(II) at pH value 5 and whereas Cr(VI) ions shows maximum adsorption capacity at pH value 2.

Zeolites in general, are weakly acidic in nature and sodium form exchanges are selective for hydrogen (R-Na + H$_2$O↔RH +Na$^+$ OH$^-$), which leads to high pH values when the exchanger is equilibrated with relatively dilute electrolyte solutions.[6] When the pH of aqueous solution of Pb(II) ion increases, the adsorption capacity increases (Figure 1) sharply up to pH 5. The increase in Pb(II) ion adsorption as pH increases can be explained on the basis of a decrease in competition between proton (H$^+$) and metal ions on the surface of adsorbent. As pH increased, more adsorbent surface would be exposed and carried negative charges with subsequent attraction of metal ions.[7] However, at pH 4.5 and 5 the hydrolysis of Pb(II) ion starts.[8] The stepwise hydrolysis process could be shown to take place as below.

$$Pb^{2+} + OH^- \rightarrow Pb(OH)^+ \rightarrow Pb(OH)_2$$

The formation of Pb(OH)$^+$ ion makes not only the ion heavier but also reduced charged by one on the ion therefore, the attraction of the ion towards site is not to that extent which explains the slow increase in removal of ions. At a pH where, Pb(OH)$_2$ come out of the solution the removal of lead become difficult. That explains the decrease in adsorption capacity.

At lower pH (pH = 2), dominant form of Cr(VI) is HCrO$_4^-$ while the surface of adsorbent is charged positively. The stable forms of chromium such as H$_2$CrO$_4$ and CrO$_3$ exist as polynuclear species at high chromium concentration and hence the low pH value of 2 results in a higher percentage removal of Cr(VI).[9] Cr(VI) is present in solution as CrO$_4^{-2}$ and Cr$_2$O$_7^{-2}$ at normal pH values but when pH values are

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reduced below 3 then chromium exists in the form of $HCrO_4^-$.[10,11] When adsorbent mixed with chromium solution at low pH values then OH^- group present in adsorbent are replaced by chromate ions in the solution. Since the charge of chromates are negative and the charge of lead ion is positive, it can explain the different trend in adsorption of Cr(VI) ions and Pb(II) at at different pH values. On increase in the pH of the metal solution the acidic sites decreases and increases the Na^+ sites on the natrolite surface. This results into increase in the anionic (alkaline) OH^- sites on Al atoms and increase in the negative charge along with decrease in the positive partial charge on the surface of the adsorbent. When the pH decreases the acidic sites of Si (OHs at Si) increases. This result into decrease in the Na^+ sites and decrease in the Al-OH sites along with increase in the positive charges with decrease in the negative charge on the natrolite cage.

According to Low et al,[12] at low pH values the surface of the adsorbent would be closely associated with hydroxonium ions (H_3O^+), by repulsive force, to the surface functional groups, consequently decreasing the percentage removal of metals. The pH of the aqueous solution is an important controlling parameter in the adsorption process. As the solution pH increase, the onset of the metal hydrolysis and precipitation began at pH >8 and the onset of adsorption therefore occurs before the beginning of hydrolysis.[13] When the pH of the adsorbing medium was increased from 2-8, there was a corresponding increase in de-protonation of the adsorbent surface, leading to decrease in H^+ ion on the adsorbent surface, which favours adsorption of positively charge species and the positive sites on the adsorbent surface.[14-16]
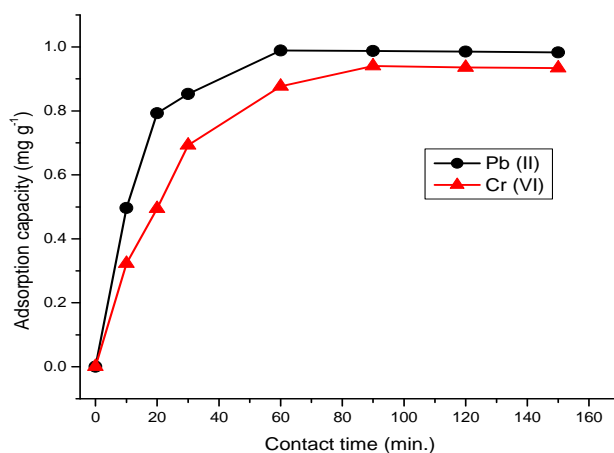
Effect of adsorbent dose

It is important to fix the amount of adsorbent to design the optimum treatment systems and for a quick response of the analysis. To achieve this aim batch experiments were conducted with the adsorbent dose 0.1-0.6 g per 50 mL 20 mg L-1 of metal solution. Figure 2 shows the adsorption of Pb(II) and Cr(VI) with varying weight of the adsorbent. It indicates that the uptake of Pb(II) and Cr(VI) ions increases as the adsorbent dose increases from 0.1 0.6 g per 50 mL of 20 mg L^{-1} metals solution.
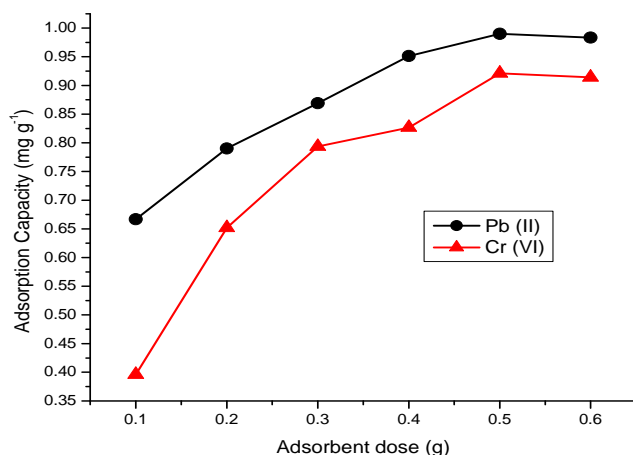
Figure 2. Effect of adsorbent dose on adsorption capacities of Pb(II) and Cr(VI) ions.

Beyond 0.5 g of adsorbent the Pb (II) and Cr(VI) ions removal decreased. According to Shukla et al,[17] the decrease in adsorption with increase in adsorbent dose is due to the high number of unsaturated sites. Based on Figure 2 , an amount of 0.5 g of adsorbent was found to be sufficient to remove Pb (II) and Cr (VI) ions from aqueous solution.

Figure 3. Effect of contact time on adsorption capacities of Pb(II) and Cr(VI) ions.

Effect of contact time

Batch experiments were conducted with the adsorbent dose 0.5 g, per 50 mL of 20 mg L^{-1} of metal solution to study the effect of contact time. Shaking time was varied from 5 minute to 120 min. The Figure 3 shows that the adsorption capacity of natrolite for of Pb(II) and Cr(VI) ions by natrolite was increased with the time of shaking. A sharp increase was observed at 60 min for Pb (II) ions and 90 min for Cr (VI) ions. Hence the contact time of 60 min for Pb (II) ion and 90 min for Cr (VI) ion was set for adsorption isotherm studies.

According to Bhattacharya and Gupta,[18] the initial high rate of metal uptake may be attributed to the existence of the base surface. However the number of available adsorption sites decreased as the number of metal ions adsorbed increases. The enhanced adsorption of metal ion with in agitation time may also in boundary resistance to mass transfer in the bulk solution and an increase in the kinetic energy of hydrated ion.[19] By increasing the agitation time, the boundary layer resistance will be reduced and there will be an increase in the mobility of ions in the solution.
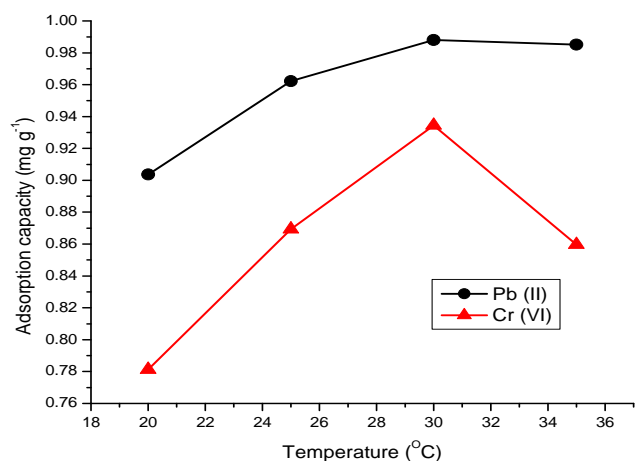
Effect of temperature

Temperature is one of the most important factors in the process of sorption used for wastewater treatment. The net increase or decrease of sorption however, depends upon the nature of the sorbate as well as sorbent. The adsorption process may be either exothermic or endothermic. Temperature increases the rate of removal indicating the process to be endothermic and decrease in the removal indicates exothermic process

Batch experiments were conducted with the adsorbent dose 0.5 g, per 50 mL of 20 mg L^{-1} of metal solution to study the effect of temperature. The effect of temperature on

the adsorption capacity of the Pb(II) and Cr(VI) by the natrolite is shown in Figure 4. It is clear that the uptake of Pb(II) and Cr(VI) ions increased with in an increase in temperature from 20-30 °C.

The adsorption of Pb(II) and Cr(VI) ions may involves chemical bond formation and ion-exchange since the temperature is the main parameter affecting the above two process.[20]

The increase in amount of Pb(II) and Cr(VI) ions adsorbed at equilibrium with increases in temperature may be due to the acceleration of some originally slow adsorption steps or to the creation of some active sites on the adsorbent surface.[21] The increase in uptake of metals with temperature may also due to the change in pore size.[22]

Figure 4. Effect of temperature on adsorption capacities of Pb (II) and Cr(VI) ions.

The amount of Pb(II) and Cr(VI) metals sorbed on natrolite increases by temperature can be explained on the basis of hydrogen binding. In aqueous solutions of metals, there exists extensive hydrogen bonding between the metal molecules and water, resulting in appreciable solubility. This hydrogen bonding get broken at higher temperatures and, this cause metals to be less soluble and, therefore, exhibit a higher tendency to go to the adsorbent surface and adsorbed their rather remaining in the solution.[23]

Adsorption Isotherm Models

The adsorption of a substance from one phase to the surface of another in a specific system leads to a thermodynamically defined distribution of that substance between the phases as the system reaches equilibrium. This distribution can be expressed in terms of adsorption isotherms.[24] Adsorption of Pb(II) and Cr(VI) ions on natrolite was studied in the concentration range 5-20 mg L^{-1} with 0.5 g of adsorbent. The adsorption data were applied to the Langmuir and Freundlich isotherm models.[25, 26] The isotherm constants of Langmuir and Freundlich were calculated using normal linearization method.

Since, the adsorption isotherm is important to describe how adsorbate will interact with adsorbents and so is critical for design purpose, therefore, data using an equation is essential adsorption operation.[27] Modelling of equilibrium

data is fundamental for the industrial application of adsorption since it gives information for comparison among different adsorbent under different operational conditions, designing and optimizing operation procedure.[28]

The result of batch equilibrium was used to characterize the equilibrium between the amount of adsorbate that accumulated on the adsorbate and the concentration of dissolve adsorbate. The experimental isotherm data set obtained was fitted using adsorption models including the Langmuir and Freundlich isotherm.

The isotherm constants of Langmuir and Freundlich were calculated using normal linearization method.

Freundlich model

The adsorption data have been fitted to the Freundlich isotherm. Its linearised form is represented by Equation 3.

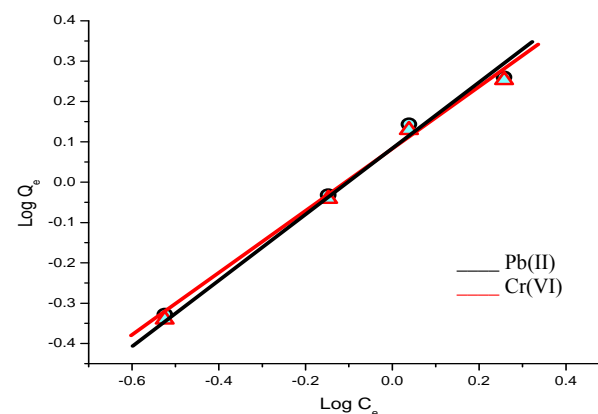$$\lg Q_e = \lg K + \frac{1}{n}\lg C_e \qquad (3)$$

where

C_e is the equilibrium concentration (mg L^{-1}),

Q_e is the amount adsorbed (mg g^{-1})

K is adsorption capacity and $1/n$ is adsorption intensity.

A plot of log Q_e versus log C_e (Figure 5) gives a straight line of slope n and intercepts K and the coefficient of determination (R^2).

Figure 5. The linearized plot for the Freundlich adsorption isotherm of Pb(II) and Cr (VI) using natrolite.

Langmuir model

The capacity of metal binding was determined by plotting C_e/Q_e against C_e, using the Langmuir equation. The plot of the specific sorption C_e/Q_e against equilibrium concentration C_e gave the linear isotherm parameters Q_{max}, b and the coefficient of determination (R^2).

The linear equation of Langmuir represented as Equation 4.

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}b} + \frac{C_e}{Q_{max}} \qquad (4)$$

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where

C_e is the metal concentration in the solution at equilibrium (mg L^{-1}),

Q_{max} (adsorption capacity) and b (energy of adsorption) are the Langmuir constants.

The essential characteristics of Langmuir equation can be described by dimensionless equilibrium parameter,[29] R_L which is defined as;

$$R_L = \frac{1}{1 + C_0}$$ (5)

where, b is the Langmuir constant C_0 is the initial metal concentration.

Table 2. Relationship between R_L and type of isotherm

R_L	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$R_L < 1$	Favourable
$R_L = 0$	Irreversible

The values of both Langmuir and Freundlich isotherm parameters were given in Table 3. Examination of correlation coefficient suggests that Freundlich isotherm is a better model for the sorption of Pb(II) and Cr(VI) ions. The values of n that vary between 1 and 10 indicate the favorable adsorption of heavy metals.[30] This isotherm does not predict any saturation of the sorbent by the sorbate; thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface.[31]

The plots of C_e/Q_e against C_e for adsorption of Pb(II) and Cr(VI) ions gave a straight line are shown in Figure 6. It has seen that the linear fit is fairly good and enables the applicability of the Langmuir model to the Pb(II) and Cr(VI) ions adsorption on the natrolite.

The Langmuir isotherm model effectively describes the sorption with R^2 values. The sorption capacity, Q_{max} which is a measure of maximum adsorption capacity corresponding to complete monolayer coverage showed that natrolite had a mass capacity for Pb(II) and Cr(VI) ions are 4.3956 and 7.0225 mg g^{-1}, respectively. The adsorption coefficient b which is related to the apparent energy of adsorption Pb(II) and Cr(VI) ions are 0.3969 and 0.1602 L mg^{-1} respectively. The high Si/Al ratio of natrolite results in typical low anionic field that gives rise to good selectivity.

The correlation coefficient of data for Langmuir and Freundlich plot give a value which is > 0.9 although this value for Freundlich isotherm is slightly higher than that of Langmuir isotherm since, the correlation coefficient for both are high, it reveals that besides monolayer adsorption there is multilayered adsorption and also suggests that adsorption reaction is physico-chemical type.

Table 3. Langmuir and Freundlich adsorption parameters for the adsorption of Pb(II) and Cr(VI) ions at 30 ^{o}C.

Freundlich Parameters	Pb(II)	Cr(VI)
K	0.8007	0.9519
n	1.1469	1.1555
R^2	0.9990	0.9978
Langmuir Parameters	**Pb(II)**	**Cr(VI)**
Q_{max} (mg g^{-1})	4.3956	7.0225
b (L mg^{-1})	0.3969	0.1602
R^2	0.9641	0.9469
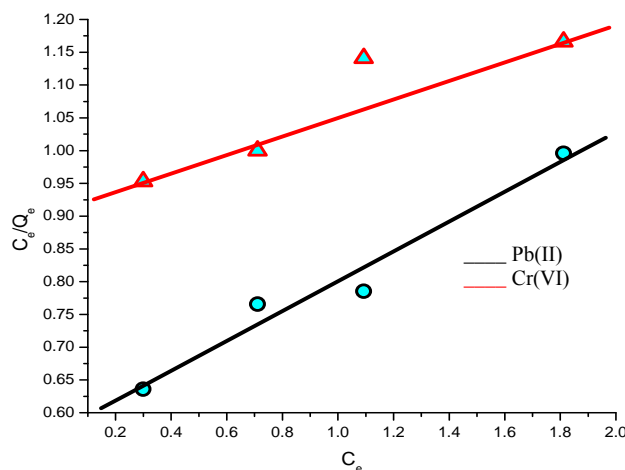
Figure 6. The linearized plot for the Langmuir adsorption isotherm of Pb(II) and Cr(VI) using natrolite
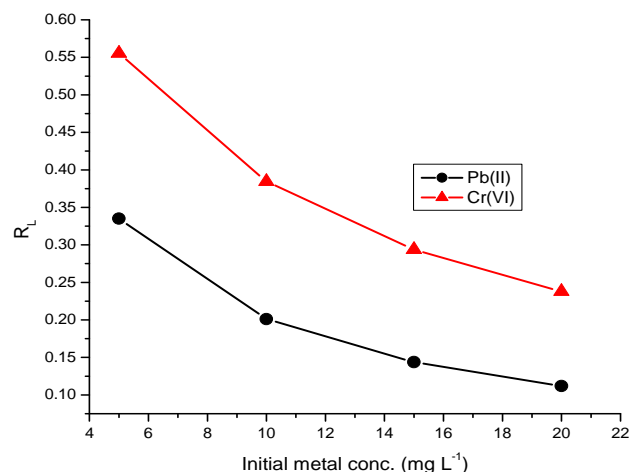
Figure 7. R_L vs initial concentration of metal ion

The R_L values between 0 and 1 indicate favorable adsorption.[32] In the present study the R_L for Pb(II) ions were found to be, 0.3351, 0.2012, 0.1438 and 0.1119 and the R_L for Cr (VI) ions were found to be 0.5552, 0.3843, 0.2938, and 0.2379 as shown in figure- 7, for the initial concentration of Pb (II) and Cr (VI) ions of 5-20 mg L^{-1} indicating that the adsorption of Pb (II) and Cr (VI) ions is favorable. The Langmuir model deals with monolayer coverage and constant adsorption energy while Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces.[33]

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In the present study the applicability of both these isotherms to the adsorption of Pb(II) and Cr(VI) adsorption, implies that monolayer adsorption and heterogeneous surfaces conditions exist under the experimental conditions used. The adsorption properties of the adsorbent are thus likely to be complex, involve more than one mechanism.

Zeolites in general, are weakly acidic in nature and sodium form exchanges are selective for hydrogen (R-Na + H₂O↔RH +Na⁺ OH⁻), which leads to high pH values when the exchanger is equilibrated with relatively dilute electrolyte solutions[6] making metal hydroxide precipitate feasible. In natural zeolites these metals seem to reach saturation, which means that the metal had filled possible available sites and adsorption could take place only at new surfaces.

The heavy metal cations are present as hexa aqua complex ions with six surrounding water molecules in the solution and they assed the channel of zeolite in this form.[34] Since the adsorption phenomena depend on the charge density of cations, the diameter of hydrate cations is very important.

It was found that the adsorption equilibrium data was better fitted by the Freundlich isotherm, although it can also be modeled by the Langmuir isotherm in the concentration range studied since it presented the greater coefficient of correlation.

Thermodynamic studies

Thermodynamic parameters such as change in Gibb's free energy ΔG^0, enthalpy ΔH^0 and entropy ΔS^0 were determined using the following Equation 6

$$K_d = \frac{Q_e}{C_e} \qquad (6)$$

where

K_d is the apparent equilibrium constant,

Q_e is the amount of metal adsorbed on the unitary sorbent mass (mmol g⁻¹) at equilibrium and

C_e equilibrium concentrations of metal ions in solution (mmol L⁻¹), when amount adsorbed is equals Q_e.

The thermodynamic equilibrium constants (K_d) of the Pb(II) and Cr(VI) ions adsorption on studied natrolite were calculated by the method suggested by Khan and Singh[35] from the intercept of the plots of ln (Q_e/C_e) vs. Q_e.

Then, the standard free energy change ΔG^0, enthalpy change ΔH^0 and entropy change ΔS^0 were calculated from the Van't-Hoff Equation 7.

$$\Delta G^0 = -RT \ln K_d \qquad 7$$

where

K_d is the apparent equilibrium constant;

T is the temperature in Kelvin and

R is the gas constant (8.314 Jmol⁻¹ K⁻¹)

The slope and intercept of the Van't-Hoff plot of ΔG^0 vs T were used to determine the values of ΔH^0 and ΔS^0. The influence of the temperature on the system entropy was evaluated using the equations-8.

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \qquad (8)$$

where

ΔH^0 is the enthalpy change (kJ mol⁻¹) and

ΔS^0 is the entropy change (kJ mol⁻¹ K⁻¹).

The values of standard Gibbs free energy change for the adsorption process gained from Equation 8 are listed in Table 4. The negative values of ΔG^0 at all the temperature indicates the spontaneous nature of Pb(II) and Cr(VI) ions on natural mineral natrolite. The negative value of ΔG^0 decrease with increase in temperature, suggests that a better adsorption is actually obtained at higher temperature.

Table 4. Thermodynamic parameters for the equilibrium sorption of Pb(II) and Cr(VI).

Parameters for Pb(II)	Temperature, K			
	295	300	305	310
ΔG^0 (kJ mol⁻¹)	-1.294	-1.936	-2.242	-2.433
ΔH^0 (kJ mol⁻¹)	20.54			
ΔS^0(kJ mol⁻¹ K⁻¹)	-0.074			
Parameters for Cr(VI)	Temperature, K			
	295	300	305	310
ΔG^0 (kJ mol⁻¹)	-5.022	-5.505	-6.334	-6.884
ΔH^0 (kJ mol⁻¹)	32.87			
ΔS^0(kJ mol⁻¹ K⁻¹)	-0.128			

The standard enthalpy changes of Pb(II) and Cr(VI) ions adsorption determine from the Equation 8, were 20.54 kJ mol⁻¹and 32.87 kJ mol⁻¹, respectively. The changes in entropy of Pb(II) and Cr(VI) ions adsorption were -0.074 kJ mol⁻¹ K⁻¹ and -0.128 kJ mol⁻¹ K⁻¹, respectively.

The negative ΔG^0 values indicates that the adsorption process is exothermic and the negative value of ΔS^0 for both Pb(II) and Cr(VI) ions shows that the exothermic adsorption process occurs with increase in disorder at solid-liquid interface, which suggests that the process is always spontaneous at all temperature.[36]

Conclusions

This work indicates that natrolite can be used for removal of Pb(II) and Cr(VI) ions from wastewater. Both Langmuir and Freundlich isotherm models can be used to estimate maximum metals uptake and the affinity parameter. It was found that the adsorption equilibrium data was better fitted by the Freundlich isotherm; although it can also be modeled by the Langmuir isotherm in the concentration range studied. The negative ΔG^0 values indicate the spontaneous nature of the adsorption and the process is exothermic and also suggests that a better adsorption is actually obtained at higher temperature. The removal of carcinogenic toxicant was found to depend on metal solution pH, adsorbent

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dosage, contact time and temperature. Solution pH is an important parameter affecting adsorption of Pb(II) and Cr(VI) ions and maximum removal for Pb(II) ions at pH value 5 and for Cr(VI) ions at pH value 2 was observed. The adsorption mechanism of Pb (II) and Cr (VI) ions on natrolite involves either cation exchange or complexation between the metal cation and the hydroxide ion in the solution. This study shows a new trend for using natrolite for the benefit of environmental pollution control

Acknowledgements

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