



Research Article

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Separation of lead (II) ions from aqueous solutions by adsorption on kaoline

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ABSTRACT

The presence of heavy metals in the environment has adverse effects on plants, animals and humans. Even a low concentration of lead in water is toxic to aquatic life. Lead affects the central nervous system, cardiovascular system and kidney function. The present study was aimed at the development of Kaoline, a carbonate mineral, as the adsorbent for the removal of lead(II) ions by adsorption. Separation of lead(II) ions from aqueous solutions containing 10 to 200 mg dm⁻³ of lead was studied. The effects of change in pH, adsorbent dosage, initial concentration of lead(II) ions, temperature and contact time were studied using batch method. The data were fed into various isotherm equations – Langmuir, Freundlich, Redlich Peterson and Dubinin- Radushkevich and the best fit was envisaged. Thermodynamic parameters like changes in enthalpy, entropy and Gibbs free energy for the adsorption process were evaluated. Kinetics of the adsorption process was studied using Lagergren's first order, pseudo-second order, Elovich and Inter particle diffusion model rate equations and the rate constants and other parameters were deduced. Spectral studies (FTIR, XRD and SEM) were conducted on the adsorbent before and after the adsorption process and the data were analysed. Results show that the adsorption of lead(II) ions on kaoline is a spontaneous, endothermic process proceeding with increase in entropy.

Keywords: Adsorption, lead(II) ion , kaoline, Environmental pollution, Isotherms, Kinetics

INTRODUCTION

Lead is widely used in storage batteries ,plumbing, soldering , ammunition ,bearings ,printing and in petroleum, chemical, electrochemical, textile ,paper and paint industries. It is estimated that about five million tons of the metal are produced all over the world annually contamination is a major environmental health hazard. The exhaust from automobiles contain oxides of lead which are potential air pollutants. These oxides are washed by rain and reach the soil. Tons and tons of effluents containing as much as 0.1 g dm⁻³ of lead are released into water sources from many industries. Lead accumulates in the blood and in the bones and affects the soft tissues. It is the culprit behind many health hazards such as anemia, and damage to kidney, lungs, brain and the central nervous system. For the separation of heavy metals like lead from aqueous solutions, several techniques are in use. Some of them are precipitation & filtering, chemical oxidation, membrane separation, adsorption, ion exchange, solvent extraction, reverse osmosis, complex formation and distillation. Many of these processes are associated with disadvantages like high cost, low selectivity, incomplete removal, high energy requirements and generation of toxic slurries Adsorption methods are preferred because of their ease of operation, low maintenance costs and high efficiency. The most efficient and widely used adsorbent is activated carbon but owing to its high cost, alternative cheap, readily available adsorbents are discovered through research. Clay minerals like Bentonite and Zeolite have been successfully used as adsorbents. The present study makes use of the mineral kaoline as the adsorbent.

EXPERIMENTAL SECTION

The kaoline used in this study was from M/s Loba Company, Mumbai. It has the composition .It was crushed to fine powder in a mortar and sieved to get particles with diameter 0.63 nm or less and then dried in an air oven at 110⁰ C.

Lead(II) ion Solutions:

A stock solution of lead(II) ions containing 1000 mg dm⁻³ of lead was prepared by dissolving accurate quantity of analar grade lead nitrate in deionized water. Solutions of desired concentrations were prepared by proper dilutions of this stock solution. The solution PH was adjusted to desired value with 0.1 M HCl and 0.1 M NaOH solutions.

Batch adsorption studies:

The batch experiments were carried out in 250 cm³ closed bottles kept in a mechanical shaker at 200 rpm. The effect of PH on the adsorption of lead(II) ions onto kaoline was studied by equilibrating the mixture containing 0.15 g of Kaoline and 50 cm³ of lead(II) ion solution containing 50 mg dm⁻³ of lead at different PH values between 1 and 6. The optimum PH was determined as 5.0 and used throughout all adsorption experiments. The effect of adsorbent dosage was studied using kaoline ranging from 50 to 250 mg with 50 cm³ lead(II) ion solution containing 50 mg dm⁻³ lead. The optimum value for adsorbent dosage was determined as 150 mg and this value was used in all batch experiments. After the adsorption has reached equilibrium the mixture was centrifuged at 3500 rpm for 5 min and the supernatant and solution subjected to quantitative analysis. For kinetic studies equilibrium concentrations were determined at 10,20,30,40,50 and 60 min intervals and the data fit into various kinetic models. Metal ion solutions ranging from 10 to 60 mg dm⁻³ were employed in the study of adsorption isotherms.

RESULTS AND DISCUSSION

Effect of PH:

The effect of PH on the adsorption of lead(II) ions on kaoline is given . It was observed that the absorption capacity initially increased with increasing PH but decreased after PH=5. Under highly acidic conditions metal binding sites in the adsorbent were associated with H₃O⁺ ions which restricted approach of Pb²⁺ ions due to electrostatic repulsion. With increasing PH, H₃O⁺ ions get replaced by neutral molecules or negative OH⁻ ions, thereby facilitating approach of metal ions. Metal precipitation was found to occur at higher PH values.

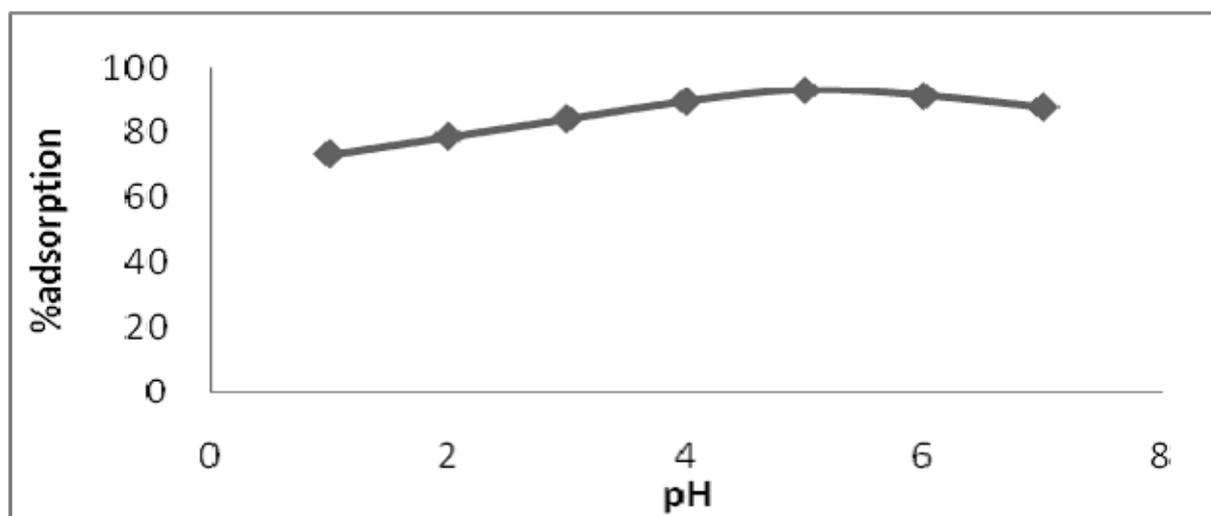


Fig.1. Percentage adsorption of Pb²⁺ on kaoline as a function of PH at 30^oc

Effect of adsorbent concentration on metal removal:

The results of the experiment with varying adsorbent dosages is given .Adsorption was found to increase with increasing dosage of adsorbent since the number of metal binding sites would be increased. Maximum adsorption was found to occur with an adsorbent dosage of 200 mg or above

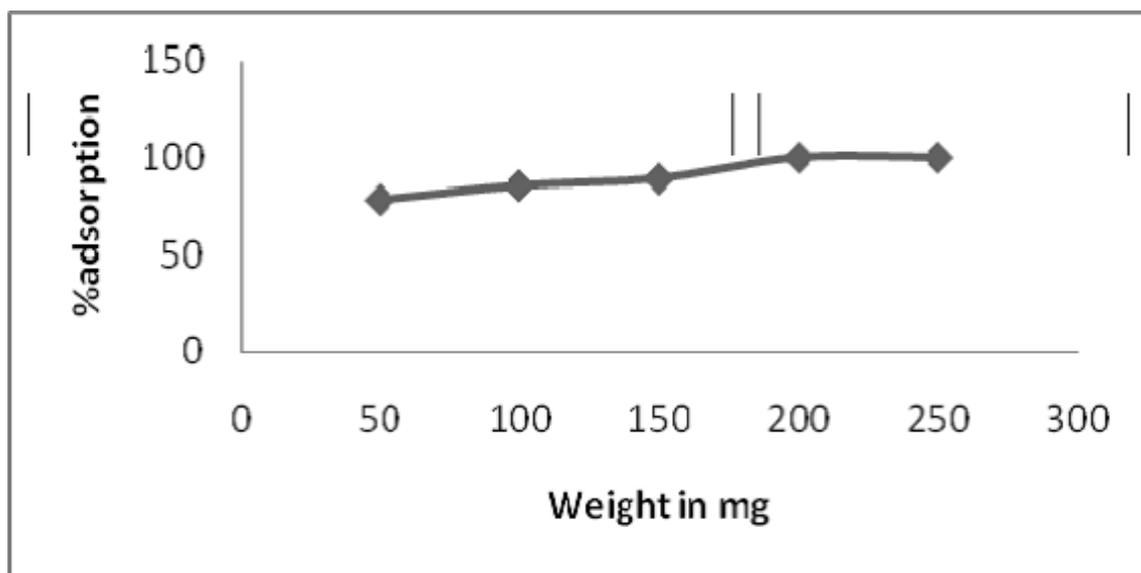


Fig .2. Effect of adsorbent dosage on the adsorption of lead on kaoline

Effect of contact time on metal adsorption:

The removal of metal ions as a function of contact time. Maximum adsorption was found to occur with a contact time of 180 min. All the batch experiments were carried out for this period.

Effect of temperature:

Batch adsorption experiments were carried out at four different temperatures namely 30,40,50 and 60^o C with varying initial concentrations of metal ions: 50,100 and 200 mg dm⁻³. Increase in temperature was found to be associated with increase in the adsorption of metal ions onto the adsorbent which explains the endothermic nature of the adsorption process. Increase in temperature probably increases the number of metal binding sites on the adsorbent. A maximum of 93.3% metal removal was found to occur at 60^o C when the initial concentration of metal ion was 100 mg dm⁻³.

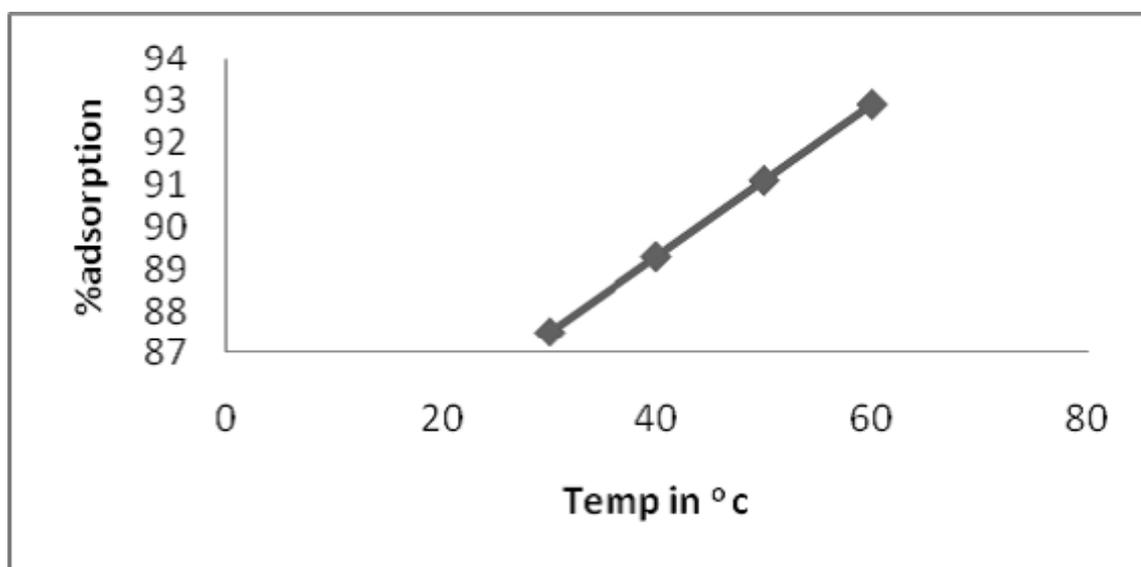


Fig.3. Effect of temperature on removal of lead (II) ions

FTIR analysis:

The FTIR spectra of kaoline before and after adsorption. The scanning electron microscope (SEM) pictures of dolomite before and after adsorption are SEM analysis: The surface morphology of the dolomite was examined using scanning electron microscopy (SEM), the corresponding SEM micrographs being obtained using at an accelerating voltage of 15 kV (Hitachi SE 900) at 5000 \times magnification. At such magnification, the kaoline particles showed rough areas of surface with in which micropores were clearly identifiable

XRD analysis:

Further, the X-ray Diffraction Studies of the kaoline were carried out using Rigaku corporation, Japan X-ray Diffractometer 40KV / 30mA, Model D/Max ULTIMA III .

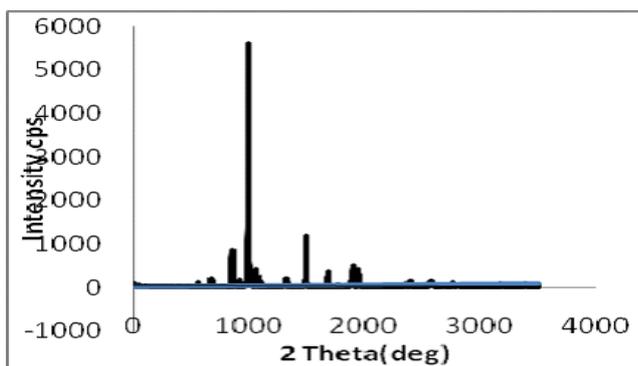


figure :4a

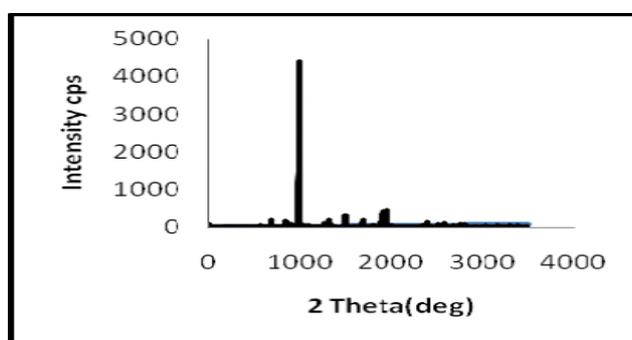


figure :4b

Fig.4a and 4b. The x-ray diffraction picture of the adsorbent before and after adsorption is given

SEM analysis:

The surface morphology of the kaoline was examined using scanning electron microscopy (SEM), the corresponding SEM micrographs being obtained using at an accelerating voltage of 15 kV (Hitachi SE 900) at 5000 \times magnification (Figure 5). At such magnification, the kaoline particles showed rough areas of surface within which micropores were clearly identifiable.

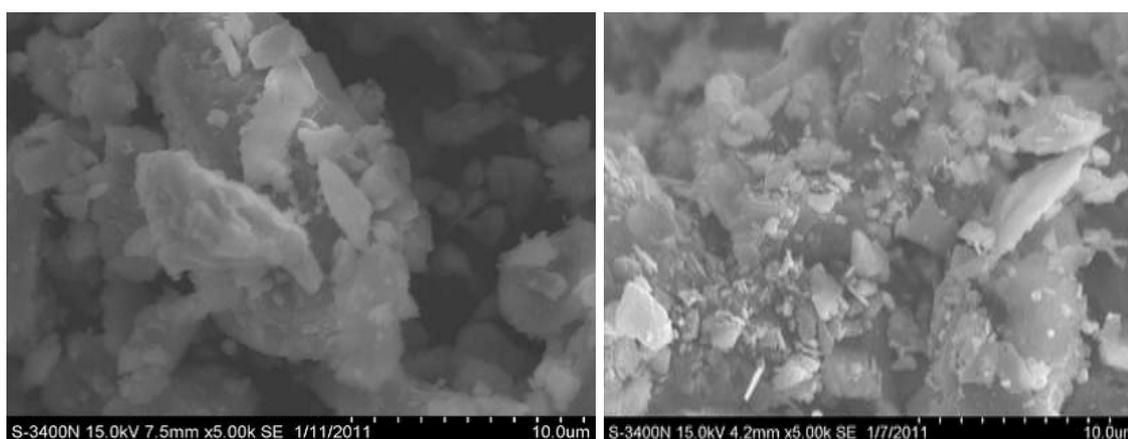


Fig. 5a and 5b. The vacant sites in the first picture are found to be filled with metal ions in the second

Kinetics of adsorption:

Kinetics of adsorption is a characteristic responsible for the efficiency of adsorption. Since the initial sorption rate plays a crucial role, adsorption was measured at time intervals 10,20,30,40, 50 and 60 min and kinetics of the

process was studied making use of four models namely Lagergren's first order, Pseudo second order, Elovich and Inter particle diffusion. The Lagergren's first order rate equation can be written as

$$\text{Log}(q_e - q_t) = \text{log} q_e - k_1 t / 2.303 \quad (1)$$

Where q_e and q_t are the amounts of lead(II) ions adsorbed (mg g^{-1}) at equilibrium and at time t and k_1 is the Lagergren's first order rate constant (in min^{-1}). Values of k_1 and q_e , calculated from the slope and y- intercept, respectively, of the plot of $\text{log}(q_e - q_t)$ against t are given. The pseudo-second order kinetics can be expressed by the rate equation,

$$t/q_t = 1/k_2 \cdot q_e^2 + t/q_e \quad (2)$$

where q_e and q_t are the amounts of lead(II) ions adsorbed (mg g^{-1}) at equilibrium and at time t ; k_2 is the second order rate constant ($\text{gmg}^{-1}\text{min}^{-1}$). Values of k_2 and q_e , calculated from plots of t/q_t against t , are given. The Elovich model can be expressed as

$$q_t = 1/\beta \ln \alpha\beta + 1/\beta \ln t \quad (3)$$

Where α refers to initial adsorption rate and β is the desorption constant. Both α and β can be calculated from the slope and y-intercept of the plot of q_t vs $\ln t$. The inter particle diffusion model of kinetics can be stated as the rate equation,

$$q_t = k_p \cdot t^{1/2} \quad (4)$$

where k_p is the rate constant for the diffusion process and c is a constant. The kinetics parameters are given. Considering the R^2 values the data best fits the Lagergren's first order model and the inter particle diffusion.

Adsorption isotherms:

The adsorption isotherms are one of the promising data to get an idea of the mechanism of adsorption. Four adsorption isotherms are selected in this study namely the Langmuir, Freundlich, Redlich-Peterson (R-P) and Dubinin-Radushkevich (D-R) isotherms. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites on the adsorbent and that a single layer is adsorbed. The linearized Langmuir isotherm can be represented by the equation [5]:

$$C_e/q_e = 1/q_0 \cdot K_L + C_e/q_0 \quad (5)$$

Where q_e is the adsorption capacity (mg g^{-1}) for lead(II) ions on the adsorbent at equilibrium, C_e is the equilibrium lead(II) ion concentration (mg dm^{-3}) in the solution, q_0 is the monolayer adsorption capacity (mg g^{-1}) of the adsorbent and K_L is the Langmuir adsorption constant ($\text{dm}^3 \text{g}^{-1}$) which is related to the free energy of adsorption. The plot of C_e/q_e vs C_e gives a straight line with a slope of $1/q_0$ and the intercept of $1/q_0 \cdot K_L$. The Freundlich isotherm is an empirical equation used to describe heterogeneous systems and can be represented by equation [6]

$$\text{Log } q_e = \text{log } K_F + 1/n \text{ log } C_e \quad (6)$$

Where K_F ($\text{dm}^3 \text{g}^{-1}$) and n (without dimension) are Freundlich isotherm constants, indicating the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. The Redlich-Peterson adsorption isotherm can be stated by the equation [7]:

$$\text{Log } C_e/q_e = \text{log } B_R + \beta \text{ log } C_e \quad (7)$$

Where C_e denotes the concentration of lead(II) ions in solution at equilibrium, q_e represents the adsorption capacity of the adsorbent, β is the desorption constant and B_R is called Redlich-Peterson isotherm constant. The Dubinin-Radushkevich (D-R) isotherm is more general than the Langmuir isotherm in that it does not assume a homogeneous surface or constant adsorption capacity. The linearised form of the D-R isotherm equation is

$$\text{Log } q_e = \text{log } q_0 - \beta \varepsilon^2 / 2.303 \quad (8)$$

Where q_0 is the theoretical saturation capacity, β is a constant ($\text{mol}^2 \text{kJ}^{-2}$) related to the mean free energy of adsorption per mole of the adsorbate and ε is called the Polanyi potential and is equal to $RT \ln(1+1/C_e)$ where R is

the gas constant (in J K⁻¹ mol⁻¹) and T is the temperature in Kelvin. The Langmuir, Freundlich, R-P and D-R isotherm parameters for the adsorption of lead(II) ions on dolomite at a constant temperature of 30°C

The essential feature of the Langmuir isotherm can be expressed by means of RL, a dimensionless constant referred to as the separation factor or equilibrium parameter which can be expressed as

$$RL = 1/(1+KLC_0) \quad (9)$$

Where C₀ is the initial concentration of lead(II) ions. The RL values calculated for this study are given. The adsorption process will be favourable if the RL values lie in between 0 and 1. RL values given very well lie in this range and hence the adsorption process was favourable. The parameter KL obtained from Langmuir isotherm is actually the equilibrium constant for the adsorption process and hence can be used to determine the Gibbs free energy change of the process as per the equation

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

The Freundlich constant n is a measure of the deviation from linearity of the adsorption. If the value of n lies above unity it indicates physisorption.

Thermodynamic parameters

The equilibrium constant (dm³ g⁻¹) for the adsorption process is a valuable parameter since it measures the extent of adsorption at the given temperature and pressure. It is calculated using the formula

$$K_a = (C_0 - C_e)V/m \quad (11)$$

Where C₀ and C_e are the initial and equilibrium concentrations (mg dm⁻³) of lead(II) ions, V is the volume of lead(II) ion solution (dm³) used and m is the mass (g) of the adsorbent employed. From the value of equilibrium constant (K_a), changes in enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) can be calculated using the following equations

$$\Delta G = -RT \ln K_a \quad (12)$$

$$\ln K_a = -\Delta G/RT = \Delta S/R - \Delta H/RT \quad (13)$$

A plot of ln K_a vs 1/T gives a straight line with the slope -ΔH/R and intercept ΔS/R. Free energy changes have a negative sign indicating that the adsorption is spontaneous. Enthalpy changes on the other hand are positive underlying the endothermic nature of the adsorption process. Entropy changes are positive since randomness increases due to adsorption. A free energy change between 0 and -20 kJ/mol and an enthalpy change below 80 kJ/mol indicates physisorption. A view of adsorption of lead(II) ions on kaoline is a physical process governed by weak hydrophobic and van der Waals forces. This is desirable since the adsorbent can be reused after desorption.

Table-1 Kinetics parameters for the adsorption of lead(II) on kaoline at 30°C Lagergren's first order model

q _e (mg, g ⁻¹)	K ₁ (min ⁻¹) x 10 ²	R ²
3.4075	1.8920	0.9791
6.2140	2.4287	0.9421

Pseudo-second order model

q _e (expt) b(mg, g ⁻¹)	K ² (g, min ⁻¹) x 10 ³	R ²
10.9863	1.420	0.8921
9.5691	1.529	0.9791

Inter Particle Diffusion Model

KP(mg.g ⁻¹ .min ^{-1/2})	C(mg, g ⁻¹)	R ²
0.4702	0.6868	0.9812
0.8921	1.1232	0.9513

Isotherm parameters for the adsorption of lead(II) ions on kaoline at 30⁰c**Langmuir Isotherm**

$K_L(\text{dm}^3, \text{g}^{-1})$	$q_0(\text{mg}, \text{g}^{-1})$	$B_L(\text{dm}^3, \text{mg}^{-1})$	R^2
9.9431	18.9141	0.5974	0.9533
5.1472	29.1421	0.1814	0.9412

Freundlich Isotherm

$1/n$	n	K_F	R^2
0.4669	2.2685	6.2234	0.9856
0.3656	2.8142	7.3772	0.9554

Redlich Peterson Isotherm

B	B_R	R^2
0.6345	0.1955	0.9421
0.4229	0.1428	0.9581

Dubinin – Radushkervich Isotherm

B	q_c	R^2
0.1814	12.199	0.9297
0.5499	14.546	0.9654

Table-3 Thermodynamic Parameters For The Adsorption of Lead (II) Ions on Kaoline

C_0 (mgdm^{-3})	$\Delta G(\text{mean})$ (KJ/mol)	ΔH (KJ/mol)	ΔS (J/kl mol)	R^2
50	-3.0467	16.947	63.744	0.9486
100	-2.4968	21.986	79.435	0.9456
150	-2.4845	11.298	42.154	0.9424

CONCLUSION

The research carried out in this study indicates that kaoline can be used as a good adsorbent for the removal of lead(II) ions from aqueous solutions. The following results have been obtained:

- (1) The functional groups on kaoline were determined using FTIR spectrophotometer.
- (2) Scanning electron microscope (SEM) pictures before and after adsorption clearly show the filling of voids in the adsorbent.
- (3) The structure of the adsorbent is not very much changed due to adsorption as shown by X-ray diffraction studies which confirms physisorption.
- (4) Batch studies suggest that maximum (92.86%) metal removal occurs at PH=5.0.
- (5) Adsorption follows Freundlich isotherm model as shown by R2 values
- (6) Lagergren's first order kinetics and inter particle diffusion can be applied to calculate rate constants and adsorption capacities.
- (7) Thermodynamic parameters indicate a feasible, physical, spontaneous and endothermic adsorption process.

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