

Research Article

Polyvinyl chloride Waste as an Adsorbent for the Sorption of Pb^{2+} from Aqueous Solution

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The sorption of Pb^{2+} from solution by polyvinyl chloride waste was investigated. The morphological features of the polymer sample were studied using the energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), X-ray diffraction spectroscopy (XRD), and the Fourier transform infrared spectroscopy (FTIR). Equilibrium, kinetic, and thermodynamic batch adsorption experiments were carried out by the concentration, time, and temperature effects, respectively. The morphological image of the polymer showed irregular small size particles which indicated a high surface area and porosity that facilitated sorption. The adsorption studies recorded relatively rapid uptake of Pb^{2+} by the polymer which was mainly diffusion controlled and followed a second order kinetic process. The thermodynamic studies suggested relatively low temperature (low energy) favoured sorption which was exothermic with a physisorption mechanism.

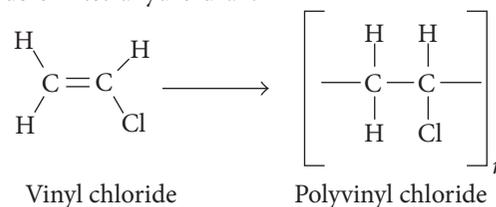
1. Introduction

The most respective and widely used adsorbent material in the adsorption processes is activated carbon. Even though it has a high adsorption capacity, surface area, and a microporous structure, the use is restricted due to its relatively high price, high operation costs, and problems with regeneration for industrial scale operation [1]. This has led to the search for low-cost and locally available adsorbent materials with maximum adsorption capacity.

Information on the use of polyvinyl chloride waste for the removal of metal ions from solutions is very scanty which has led to this study. In fact literature on the removal of Pb^{2+} from aqueous solution using PVC is almost unavailable which makes this research project novel.

Polyvinyl chloride, commonly abbreviated as PVC, is a thermoplastic made up of 57% chlorine and 43% carbon and is the third most widely produced plastic, after polyethylene and polypropylene [2]. The chlorine gives PVC excellent fire resistance. It can be made softer and more flexible by the addition of plasticizers, the most widely used being

phthalates. Pure polyvinyl chloride without any stabilizer is a white, brittle solid. It is insoluble in alcohol but slightly soluble in tetrahydrofuran:



PVC is used as pipes in construction because it is cheaper than more durable long lasting alternatives such as ductile iron. As one of the most widely used plastics, PVC is found in a wide use of consumer products such as tubing (hoses), gloves, photographic dishes, tanks, trays, troughs, footwear, cable jacketing, bottles, credit cards, audio records frames, cables, flooring materials, wallpaper, window blinds, car interiors, and medical hospital disposables.

PVC is difficult to recycle and no known microorganism has yet been shown to biodegrade it, resulting in much being dumped in landfills and often abundant as a form of pollution

in the outdoor environment, particularly along shores and waterways and waste dumps, due to its variety of uses [2].

In recent years the surge of industrial activities has intensified more environmental problems as, for example, in the deterioration of several ecosystems due to the accumulation of dangerous pollutants such as lead (Pb) [3].

There is, therefore, the need for the removal of these toxic metal ions from municipal, commercial, and industrial effluents before discharge into our environment.

The conventional methods of removal of these metals from waste water, which include precipitation, flocculation, filtration, ion exchange, and reverse osmosis, are very much capital intensive. However cheaper and renewable materials have been used for the removal of metals from effluents which include biomasses like nipa palm, *Manihot esculenta* Crantz, sea weed, and *Medicago sativa* [4–7]. Specifically, the biomasses of nipa palm and *Medicago sativa* have been used to remove Pb^{2+} from aqueous solution [4, 7].

2. Materials and Methods

2.1. Sample Preparation. Polyvinylchloride was obtained from the waste bins and thoroughly washed with the deionized water and oven-dried at 30°C. The dry samples were ground and passed through the 100-mesh screens using a Wiley mill. These particle sizes were then washed twice with 0.01 M HCl to remove any metals and debris that might be in the polymer prior to experimental metal ion exposure. The acid washed polymer samples were washed twice with deionized water to remove acid and then oven-dried at 30°C to constant weight.

2.2. Characterization of Polymer Sample. The morphological features of the polymer sample were analysed by FE-SEM, EDS, and XRD. The surface morphology and EDS measurements were recorded with a JEOL 7500F Field Emission scanning electron microscope. The HR-TEM images of the sample were obtained by a CM 200 electron microscope operated at 100 KV. Powder X-ray diffraction (PXRD) patterns were collected with a Bruker AXS D8 Advanced diffractometer operated at 45 kV and 40 mA with monochromated copper $K\alpha_1$ radiation wavelength ($\lambda = 1.540598$) and $K\alpha_2$ radiation wavelength ($\lambda = 1.544426$) and scan speed of s/step and step size of 0.03°.

2.3. Batch Adsorption Experiment. Batch adsorption experiments were carried out to determine concentration and temperature effects and time dependent studies. 0.2 g of the polymer sample and initial Pb ion concentrations of 21.8, 48.0, 72.0, 97.7, 120.9, and 141.5 mg/L were used for the concentration effect. For the temperature effect, the same weight of polymer sample was used with time intervals of 5, 10, 20, 40, and 60 minutes. The values of 28°, 40°, 60°, and 80°C were used with the same weight of polymer to study the temperature effect. Standard methods of the batch equilibrium studies were applied for the concentration, temperature, and time dependent experiments.

Metal analysis was performed by AAS using a Bulk Scientific Atomic Absorption/Emission Spectrophotometer 200A (AAES).

2.4. Data Analysis. Various equilibrium, kinetic, and thermodynamic models (equations) were employed to interpret the data and establish the extent of adsorption. The amount of metal uptake was computed using the material balance equation for batch dynamic studies [6]:

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

with q_e as metal uptake capacity (mg/L polymer at equilibrium), C_e , metal ion concentration in solution (mg/L) at equilibrium, C_o , the initial metal ion solution (mg/L), V , the volume of solution in litres, and M , the dry weight of polymer used in (g).

Langmuir plots were carried out using the linearized equation

$$\frac{M}{X} = \frac{1}{abC_e} + \frac{1}{b}, \quad (2)$$

where X is the amount of Pb^{2+} adsorbed per mass M of polymer in mg/L a and b are the Langmuir constants obtained from the slope and intercepts of the plots.

The essential characteristics of the Langmuir isotherm were expressed in terms of a dimensionless separation factor or equilibrium parameter S_f [8]:

$$S_f = \frac{1}{(1 + aC_o)}, \quad (3)$$

where C_o is initial concentration of Pb^{2+} in solution. Poots et al. [8] have shown by mathematical calculations that the magnitude of the parameter S_f provides a measure of the type of adsorption isotherm. If $S_f > 1.0$, the isotherm is unfavourable; $S_f = 1.0$ (linear), $0 < S_f < 1.0$ (favourable), and $S_f = 0$ (irreversible).

The adsorption intensity of the Pb^{2+} was assessed from the Freundlich plots using the linearized equation

$$\ln \frac{X}{M} = \frac{1}{n} (\ln C_e) + \ln K, \quad (4)$$

where K and n are the Freundlich constants and $1/n$ is approximately equal to the adsorption capacity.

The fraction of polymer surface covered by the Pb^{2+} was computed using

$$\theta = 1 - \frac{C_e}{C_o} \quad (5)$$

with θ as degree of surface coverage.

The effectiveness of the adsorbent (polymer) was assessed by the number of cycles of equilibrium sorption process required to reduce the levels of Pb^{2+} in solution according to the value of the distribution (partition coefficient (K_d)) [9] in

$$K_d = \frac{C_{aq}}{C_{ads}}, \quad (6)$$

where C_{aq} is concentration of Pb^{2+} in solution, mg/L; C_{ads} is concentration of Pb^{2+} in polymer in mg/L.

The heat of adsorption (Q_{ads}) was obtained using the following Suzuki equation [10]:

$$\ln \theta = \frac{\ln K_o C_o}{T^{0.5}} + \frac{Q_{ads}}{RT}, \quad (7)$$

where T is solution temperature (K), K_o a constant, and R gas constant (8.314 J/Kmol).

The linear form of the modified Arrhenius expression was applied to the experimental data to evaluate the activation energy (E_a) and sticking probability S^* as follows [8]:

$$\ln(1 - \theta) = S^* + \frac{E_a}{RT}. \quad (8)$$

The apparent Gibbs free energy of sorption ΔG^o , which is a fundamental criterion for a spontaneous process, was evaluated using the following equation:

$$\Delta G^o = -RT \ln K_o, \quad (9)$$

where K_o is obtained from the Suzuki equation (7).

The experimental data was further subjected to thermodynamic treatment in order to evaluate the apparent enthalpy (ΔH^o) and entropy (ΔS^o) of sorption using

$$\ln K_o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}. \quad (10)$$

To evaluate the packing of Pb^{2+} on the polymer surface, thermodynamic analysis of adsorption density (ρ) was carried out with the following equation:

$$\rho = ZrC_e e^{-(\Delta G^o/RT)}, \quad (11)$$

where Z is the valency of the Pb^{2+} , r the effective radius of the Pb^{2+} in cm, and C_e the equilibrium concentration in mol/cm³.

The expression relating the number of hopping (n) and that of the surface coverage (θ) as shown in the following equation was applied to the experimental data:

$$n = \frac{1}{(1 - \theta)\theta}. \quad (12)$$

Other thermodynamic parameters such as adsorption potential (A) were tested by applying

$$A = -RT \ln \frac{C_o}{C_e} \quad (13)$$

with C_o and C_e as initial and equilibrium concentrations in mol/cm³, R , the gas constant, and T , the solution temperature in K.

The kinetic behaviour of the sorption process was investigated by testing the data using the second order kinetic model expressed in

$$\frac{1}{q_t} = \frac{1}{q_o} + K_2 t, \quad (14)$$

where q_t is the amount of Pb^{2+} on the polymer (mg/g or Mmol/g) at time t , q_o is the amount of Pb^{2+} on the polymer at time t_o , and k_2 is the second order rate constant.

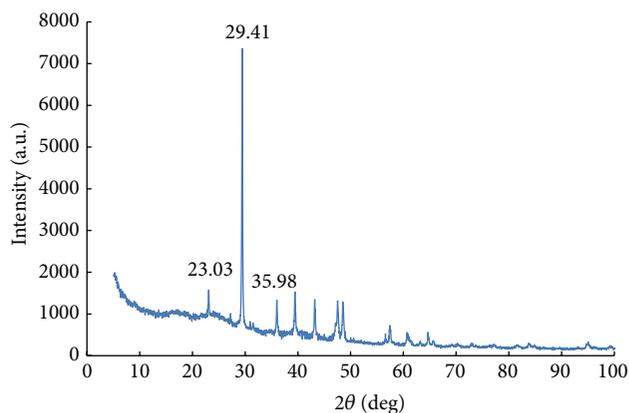


FIGURE 1: X-ray diffraction (XRD) pattern of polymer (polyvinyl chloride) sample.

3. Results and Discussion

X-ray diffraction pattern of polyvinyl chloride powder used in this study is presented in Figure 1. X-ray powder diffraction is a powerful tool for characterizing a solid state sample. Each crystalline species has a unique X-ray diffraction pattern. With a diffraction pattern an investigator can identify unknown species or characterize the atomic scale structure of an already identified substance. Figure 1 gives the diffractogram of the polymer sample. The XRD pattern shows notable high intensity Bragg diffraction peaks at $2\theta = 23.03^\circ$, 29.41° and 35.98° . These peaks are characteristic XRD peaks of polyvinyl chloride [11] and correspond to high amount of crystalline material in the polymer. Crystals have high surface area which enhances adsorption.

Energy dispersive X-ray (EDX) was applied for elemental analysis of the polymer sample. The EDX spectrum presented in Figure 2 confirmed sharp peaks due to the following elements: C (30%), Al (4%), Cl (17%), Ca (15%), and O (30%) in addition to hydrogen. The presence of these elements will produce charges on the surface of the polymer and create electrostatic forces of attraction between the sample and Pb^{2+} in solution. The presence of Ca and Al may be from the fillers added to the polymer during processing to enhance its mechanical properties.

In order to determine the morphology of the polymer, scanning electron microscope (SEM) image of the sample was taken at magnification $\times 270$. The SEM image shows that the surface of the polymer sample had irregular small size particles which indicated a high surface area and porous nature as shown in Figure 3. Large surface area of any adsorbent facilitates maximum adsorption [12].

The percentage of sorption of Pb^{2+} by the polymer sample at different concentrations of the Pb^{2+} is presented in Figure 4. The maximum adsorption of 98% took place at equilibrium concentration of 20 mg/L Pb^{2+} . This is because at lower concentration more polymer pore spaces were available for the Pb^{2+} , but as the concentration of Pb^{2+} increased, the adsorption capacity of the polymer decreased due to reduced availability of free pore spaces. The results indicated

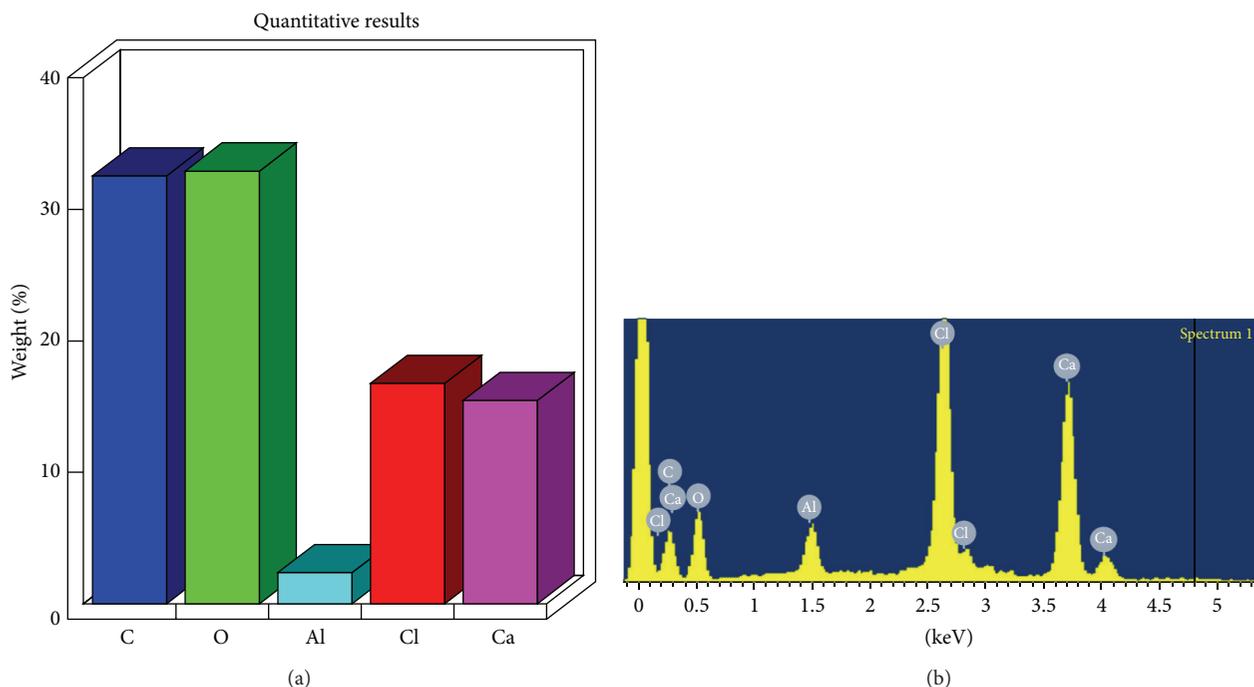


FIGURE 2: Energy dispersive X-ray (EDX) of polymer (polyvinyl chloride) sample: (a) quantitative result and (b) spectrum.

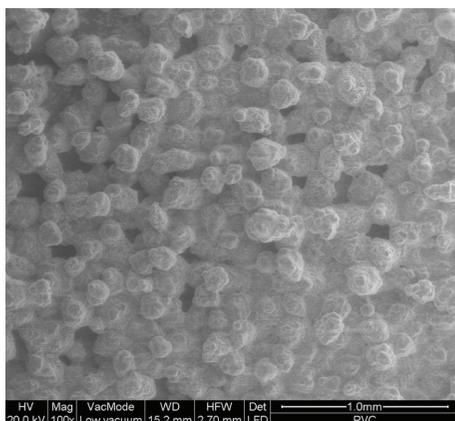


FIGURE 3: Scanning electron microscope (SEM) image of polymer (polyvinyl chloride) sample.

that the sorption of Pb^{2+} was very much dependent on the concentration of the Pb^{2+} .

Time dependency studies show the amount of time needed for maximum adsorption to occur. The variation in percentage removal of Pb^{2+} with time has been presented in Figure 5. It indicates that a maximum of 99% removal of Pb^{2+} was observed in 5 minutes and remained constant afterwards. The relatively short contact time required to attain equilibrium suggests that a rapid uptake of Pb^{2+} by the polymer occurred to fill some of the vacant pores in the polymer after which the remaining spaces were difficult to be occupied due to repulsive forces between the Pb ions.

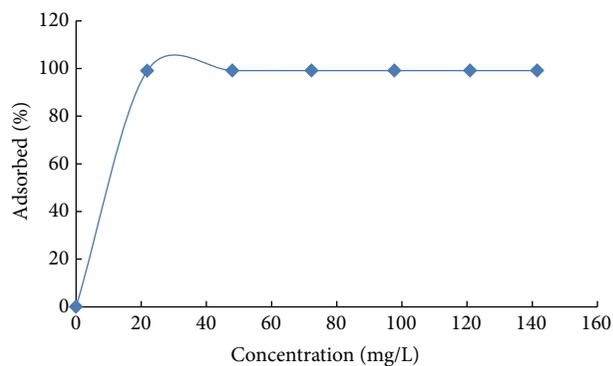


FIGURE 4: Effect of initial concentration of Pb^{2+} on the sorption by polymer (polyvinyl chloride) sample.

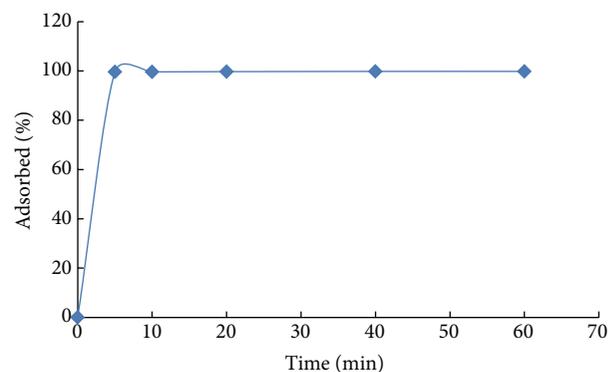


FIGURE 5: Effect of contact time on the sorption of Pb^{2+} by the polymer (polyvinyl chloride) sample.

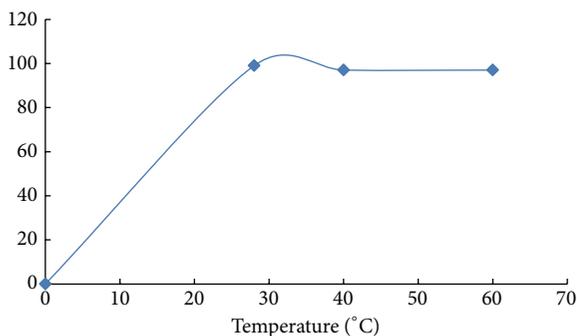


FIGURE 6: Effect of temperature on the sorption of Pb^{2+} by polymer (polyvinyl chloride) sample.

TABLE 1: Equilibrium and kinetic parameters.

Surface coverage θ	Separation factor S_f	Sorption coefficient K_d	Adsorption capacity mol/g
0.9960	0.0218	0.0041	1.000

Figure 6 presents the plot of percentage adsorption of Pb^{2+} by the polymer at varying temperatures with optimum sorption of 99% occurring at 30°C. The plot showed that further increase in temperature resulted in a slight decrease in adsorption. This is in agreement with the general principle that physical adsorption decreases with increase in temperature [12]. This behaviour could be attributed to the weakening of the attractive forces between the polymer and Pb^{2+} , the increased kinetic energy of the Pb^{2+} , and the decrease in the thickness of the boundary layers of the polymer due to the higher tendency of the Pb^{2+} to escape from the polymer.

The fraction of the polymer surface covered by the Pb^{2+} is given as 0.996 (Table 1). This value indicates that over 95% of the pore spaces of the polymer surface were covered by the Pb^{2+} , which means high degree of adsorption.

In order to determine the nature of the adsorption process, whether favourable or unfavourable, the dimensionless constant separation term S_f was investigated (3). The result ($S_f = 0.0218$) in Table 1 was less than one and greater than zero which showed that the sorption of Pb^{2+} onto the polymer was favourable.

The effectiveness of the polymer as an adsorbent for Pb^{2+} from solution was assessed through the sorption distribution or partition coefficient K_d presented in Table 1. The value of K_d (0.0041) suggests that the polymer is an effective adsorbent and that a very small number of cycles of equilibrium sorption process will be required to reduce the levels of Pb^{2+} in solution.

Applying the Freundlich model, the adsorption capacity of the polymer was calculated to be 1.00 mol/g.

In order to calculate the heat of adsorption (Q_{ads}) for the sorption of Pb^{2+} onto the polymer, (7) was used. The value of Q_{ads} (-48.45 KJ/Kmol) is negative as presented in Table 2, which indicates that the adsorption was exothermic, that is, low temperatures favour the adsorption of Pb^{2+} by

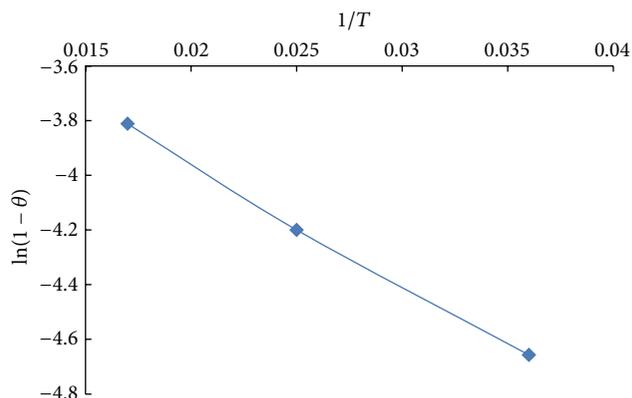


FIGURE 7: Plot of $\ln(1 - \theta)$ versus $1/T$ for the sorption of Pb^{2+} by the polymer (polyvinyl chloride) sample.

the polymer, and also suggested a diffusion controlled second order kinetic process. Temperature increase did not enhance the sorption process.

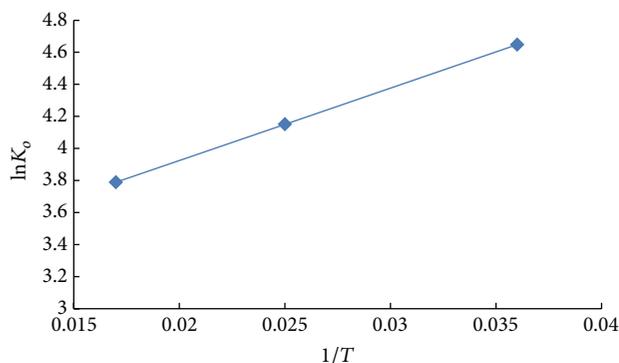
The plot of $\ln(1 - \theta)$ versus $1/T$ using (8) yielded a straight line as presented in Figure 7. The activation energy E_a and the sticking probability S^* were calculated from the slope and intercept, respectively. The values of E_a and S^* were shown in Table 2 as $-345.0 \text{ Jk}^{-1} \text{ mol}^{-1}$ and 0.0498, respectively. The relatively low and negative E_a value indicates that low temperature or energy favours the sorption and the adsorption process is exothermic. Relatively low value of E_a also suggests that the sorption process is diffusion controlled [12]. The sticking probability S^* indicates the measure of the potential of an adsorbate to remain on the adsorbent. It is often interpreted as $S^* > 1$ (no sorption), $S^* = 1$ (mixture of physisorption and chemisorption), $S^* = 0$ (indefinite sticking-chemisorption), and $0 < S^* < 1$ (favourable sticking-physisorption). The value of S^* obtained for the sorption of Pb^{2+} by the polymer was between zero and one which indicates that the adsorption was favourable and followed a physisorption mechanism.

Table 2 also presents the Gibbs free energy ΔG^o for the sorption of Pb^{2+} by the polymer which was calculated from (9). The Gibbs free energy is the fundamental criterion of spontaneity. The ΔG^o value of -10.70 KJ/mol was negative indicating that the sorption process was spontaneous. The value obtained for ΔG^o was also less than -20 KJ/mol suggesting electrostatic interaction between the Pb^{2+} and the polymer which supported physisorption mechanism.

The plot of $\ln K_o$ versus $1/T$ from (10) was linear as presented in Figure 8, with the slope and intercept equal to $-\Delta H^o/R$ and $\Delta S^o/R$, respectively. The value of the enthalpy change (ΔH^o) calculated from the slope was -376.4 J/mol . A negative ΔH^o suggests that sorption proceeded favourably at a lower temperature and the sorption mechanism was exothermic. The value of the entropy change computed from the intercept was 24.9 J/Kmol and was presented in Table 2. A positive ΔS suggests that the freedom of the adsorbed Pb^{2+} was not restricted in the polymer, indicating that physisorption mechanism predominates.

TABLE 2: Thermodynamic parameters.

Heat of adsorption Q_{ads} (KJ/Kmol)	Sticking probability S^*	Activation energy E_a (J/K mol)	Gibbs free energy of adsorption ΔG° (KJ/mol)	Apparent entropy ΔS° (J/Kmol)	Apparent enthalpy ΔH° (J/mol)	Adsorption density ρ (mol/cm ²)	Hopping number n	Adsorption potential A (KJ/mol)
-48.45	0.0498	-345.0	-10.70	24.94	-376.4	9.67×10^{-4}	11	10.74

FIGURE 8: Plot of $\ln K_0$ versus $1/T$ for the sorption of Pb^{2+} by the polymer sample.

The packing of Pb^{2+} in the polymer was assessed using (11) and results were presented in Table 2. The adsorption density, ρ , obtained was 9.67×10^{-4} mol/cm².

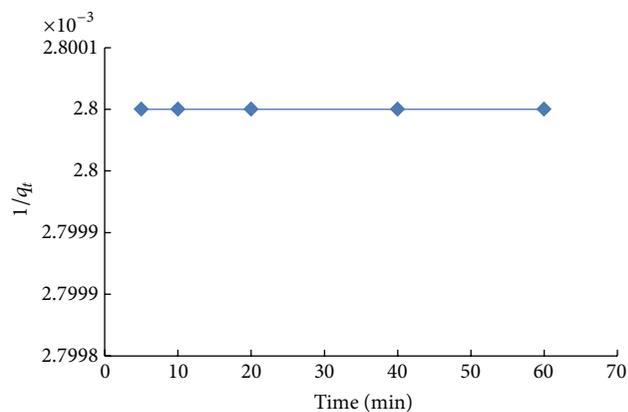
The change in the chemical potential that occurred as the Pb^{2+} moved from the solution to the surface of the polymer was calculated using (13). Table 2 gives the adsorption potential as 10.74 KJ/mol.

The probability of Pb^{2+} finding vacant site on the polymer surface during the sorption was correlated by the number of hopping (n) done by the Pb^{2+} . The hopping number presented in Table 2 was 11. The lower the hopping number, the faster the adsorption [8]. The relatively low value of n obtained suggests that the adsorption of Pb^{2+} on the polymer was fast.

The rate at which adsorption proceeds is very important in designing a batch sorption system. Consequently, it was important to establish the time dependence of such system under various process conditions. In an attempt to understand the sorption process, the second order kinetic rate expression model was applied to the experimental data. The second order kinetic model was applicable to the experimental data because a linear relationship was obtained by the plot of t/q_t versus t as presented in Figure 9. The R^2 value is 0.94.

4. Conclusion

The equilibrium, kinetic, and thermodynamic studies recorded a relatively rapid uptake of Pb^{2+} by the polymer (polyvinyl chloride) which was a diffusion controlled second order process. The adsorption was favoured by low temperature and energy which was exothermic with a physisorption mechanism. The polymer is an effective adsorbent for the removal of Pb^{2+} from aqueous solution. The results from this study will be useful for a novel filtration

FIGURE 9: Second order kinetic plot for the sorption of Pb^{2+} by the polymer (polyvinyl chloride) sample.

technology which is effective and environment friendly to remove and recover Pb^{2+} from aqueous solutions. This will replace the most conventional relatively expensive treatment techniques presently in existence, which are not economically viable for small scale industries due to huge capital investment.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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