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Kinetic Studies of Adsorption Process of Zambian Kapiri Mposhi Zeolites

MARINA G. XAVIER

Department of Chemistry, University of Zambia, Zambia.
*Corresponding author E-mail: marinajowetsy@gmail.com

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ABSTRACT

Batch adsorption studies were done on aqueous solutions of $Pb(NO_3)_2$ at varying solute concentration, adsorbent dose, contact time, temperature, calcination temperatures and pH. Residual concentrations of the solute were found out using AAS and optimum conditions were studied. Adsorbent used in this study is locally available silicate rich mineral which closely resembles zeolites. The net negative charge on the framework of hydrated aluminosilicates is responsible for ion exchange property. Freundlich model was used to validate the results obtained from batch experiments plotting lnCe vs lnqe. Objective of this work is to study the kinetics of adsorption considering the interplay of particle diffusion in addition to proving the effectiveness as an adsorbent. A diffusion model also was also applied apart from kinetic model to analyze the experimental results more specifically. For maximizing the efficiency of the adsorption process and minimizing the time involved, variables like temperature, reactants and pH were manipulated using kinetic studies. It establishes the optimum reaction conditions for various experimental parameters in the process of adsorption.

Keywords: Adsorption, Heavy metals, Batch experiments, Freundlich model, Kinetic modelling.

INTRODUCTION

The physical transfer of solute particles or ions from the solution site to the interior of an adsorbent through its pores is called adsorption. The adsorbent used in this study is clay based zeolitic aluminosilicates which are highly porous and very effective in adsorption[1]. The factors that affect rate of adsorption are initial concentration of a reactant, temperature, contact time, affinity of the solute to the adsorbent, pH of the medium, calcination temperature of adsorbent etc. The rate of adsorption which depends on number of active sites available on the adsorbent restricts the solute concentration. The optimum load has to be investigated with different initial concentrations. The work focusses on investigating the fit of experimental data in Freundlich model and determine the kinetic and thermodynamic parameters. Kinetic modelling can be adopted as an experimental tool for testing theories and clarifying assumptions. Freundlich model was used to interpret the characteristics of adsorption of Pb^{2+} ions and NO_3^- ions onto aluminosilicate adsorbent based on the experimental results. In a liquid solid adsorbent system kinetics of the process can be controlled by adsorption as well as diffusion. Contact time where the adsorption is at its best has to be investigated and proved. Adsorption in general is considered to be an exothermic reaction and a decrease in free energy and entropy is predicted. Presence of adsorbed solvent molecules in a charged adsorbent in the contact solution can lead to an increase in free energy and entropy[2]. Thus, spontaneity of the adsorption reaction has to be studied by changing parameters at different experimental temperatures[2]. A set of model parameters[3] were set up for the adsorption system by using an equation based on equilibrium data which represented the adsorption data qualitatively and quantitatively. The kinetic and equilibrium adsorption data were modelled using pseudo1st order kinetics. The thermodynamic parameters were found out using the linearized equation for Freundlich isotherm and Gibbs Helmholtz equation.

MATERIALS AND METHODS

Aqueous solutions of $Pb(NO_3)_2$ of different solute concentrations were prepared by dissolving required quantities in distilled water. Adsorbent was sieved to get particles of 0.2 mm size and heated in an air oven for 4 h at 150°C to get rid of all adsorbed impurities. 100 mL solutions of adsorbate with varying concentrations of 0.0125 M, 0.025 M, 0.05 M, 0.1 M and 0.2M were used to disperse one gram of zeolite. This mixture was agitated using a magnetic stirrer at 200 rpm for 4 hours. The supernatant liquid was filtered using Whatman No: 40 filter paper and filtrate analysed using atomic absorption spectroscopy. From the initial and final concentrations of $Pb(NO_3)_2$ solutions mass adsorbed was found out.

Batch experiments were conducted on 0.1 M solution of $Pb(NO_3)_2$ using varying masses of adsorbent, 1.0 g, 2.0 g, 3.0 g, 4.0 g and 5.0 g. From the difference in initial and final solute concentrations mass adsorbed was calculated. Similar batch experiments were done on a dispersion of one gram adsorbent in 0.1M $Pb(NO_3)_2$ solution at different temperatures of 30°C, 40°C, 50°C, 60°C, 70°C. Using AAS, mass of solute adsorbed in each case was found out. Adsorption studies were done at varying contact time of 1 h, 2 h, 3 h, 4 h and 5 h using a 100 mL mixture of 0.1 M $Pb(NO_3)_2$ solution and 1 g adsorbent. Mass of adsorbate removed was found out by analysing the initial and final mixtures in each case.

The adsorbent particles were calcined at 100°C, 200°C, 300°C, 400°C and 500°C and experiments were conducted in 0.1M of $Pb(NO_3)_2$ solution containing one gram of adsorbent. Initial and final concentrations of $Pb(NO_3)_2$ were found out before and after the adsorption experiments. Similar adsorption studies were done in 100 mL 0.1 M $Pb(NO_3)_2$ solution and adsorbent at three different pH of 2.5, 4.5 and 10. The initial pH of lead nitrate solution was 4.5 and pH was adjusted to 2.5 by adding one drop of concentrated HCl. Also, pH was raised to 10 by adding two drops of 4 M NaOH solution. Mass of solute adsorbed in each case was found out using atomic absorption spectroscopy.

RESULTS AND DISCUSSION

The adsorption nature of aluminosilicate adsorbent and $Pb(NO_3)_2$ adsorbate system was analysed using the values from batch experiments applied to Freundlich model and plotting $\ln C_e$ vs $\ln q_e$ where q_e is the dependent variable and C_e the independent variable implying amount of solute adsorbed per unit mass of adsorbent(mg/g) and equilibrium concentration (mg/L) of metal in the mixture. As is already known that the equilibrium data is essential to develop an equation which precisely expresses the adsorption data qualitatively and quantitatively for designing an appropriate adsorption system. This naturally occurring adsorbent having surface inhomogeneities works well with the suggested Freundlich isotherm model with multilayers and exponential nature with solute concentration. Freundlich model is the versatile kinetic model for a single solute system in solid liquid equilibrium phase. Freundlich isotherm equation can be empirically represented as, $q_e=K_f\, C_e{}^{1}/_{n}$

The equilibrium concentrations of liquid and solid phase of the adsorption unit are empirically represented in this equation. Also, it highlights multilayer adsorption mechanism especially on a heterogenous surface and was accepted that Freundlich isotherm is more suitable than Langmuir isotherm[4] in fitting the experimental data.

The above equation can also be represented in a linear way,

$\ln q_e = \ln K_F + 1/n \ln C_e$

Here 'K_F' is an empirical constant which depends on several experimental factors represents the magnitude of adsorption capacity. Another empirical parameter is '1/n' suggests the adsorption intensity or probability of adsorption which in turn is a measure of energetic heterogeneity of the reaction sites on the surface. A straight line was obtained when (log q_e) was plotted against (log C_e), which confirms the compatibility of Freundlich isotherm for adsorption. Using regression analysis, slope, 1/n, and y intercept, $\ln K_F$ were found out. 1/n, whose value falls between zero and one indicates favourable physical adsorption and closeness of 'n' value to zero refers to surface heterogeneity leading to multilayer adsorption. Correlation coefficient, R^2 represents the extent to which experimental data and model predicted values tally with each other (Table 1). The heterogenous nature of surface is again highlighted by deviation of R^2 value from linearity.

Using equations, $\Delta G^\circ = -RT\ln K$ and $\ln qe = \Delta S/R - \Delta H/RT$, corresponding values of ΔG, ΔH and ΔS were calculated and tabulated. Using the above constants and equation for straight line, linear plots were constructed for the experimental data. The impacts of several experimental conditions like varying initial concentration, adsorbent dosage, calcination temperature, contact time, reaction temperature and pH were look analysed. The deductions from these studies were relied on to attain the best possible conditions for maximising the rate of adsorption.

Effect of Concentration on adsorption of $Pb(NO_3)_2$ onto the adsorbent

The initial mass of solute was plotted against mass adsorbed. It was found that removal efficiency was decreasing with increasing metal ion concentration. This was due to lacking active sites on adsorbent. There was a strong uptake of ions from aqueous solution at a low adsorbate concentration for both ions. The isotherms were steeper at low concentrations indicating a higher efficiency at low solute concentrations. The available sites get saturated in a concentration as low as 0.025 M. The adsorption capacity, K_F for cation and anion was found to be very low. The relative low value of R^2 for lead ion indicates poor relationship between the parameters. This also says that this adsorbent is good at removing metal ions from a solution of very low concentrations. There will be increased columbic repulsion between adsorbed ion and approaching ion at high metal ion concentrations. Using the above kinetic parameters and equation for straight line, linear plots were also constructed for the experimental data (Fig. 1a, b). There is a negative correlation between mass adsorbed and initial concentration.

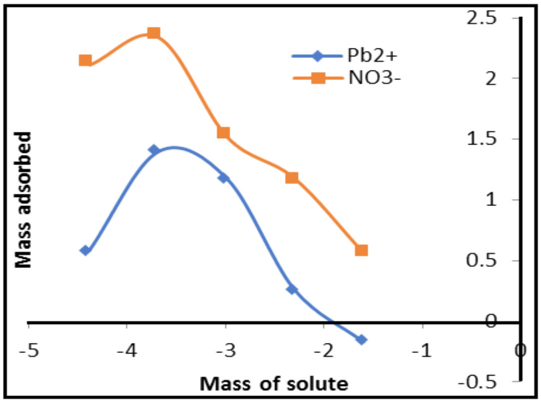

Fig. 1a. Uptake vs initial concentration

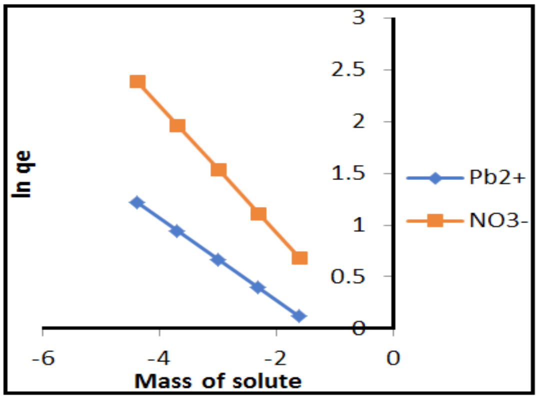

Fig. 1b. Linear plot

Effect of Adsorbent dose on adsorption of $Pb(NO_3)_2$ onto the adsorbent

To maximise the efficiency of adsorption system the adsorbent dose was optimised. For the same five batch experiments were done with varying adsorbent doses of 1.0, 2.0, 3.0, 4.0 and 5.0 g/mL of $Pb(NO_3)_2$ solution. A quick and remarkable increase in rate of adsorption was achieved at highest adsorbent dose i.e. 5.0 g/100 mL. Adsorption was more efficient with increasing adsorbent dose for both ions (Fig. 2a, b). This was because there were more available sites for adsorption to take place. Percentage removal of solute particles should level off after a certain dose of adsorbent. It can be explained by assuming that there is merging of potential adsorption sites at elevated levels which adversely affects the surface area[5]. A large increase in adsorbent dose also causes aggregation of particles decreasing the available active site. The aggregates diminish the attraction between adsorbent and adsorbate and enhance desorption from surface.

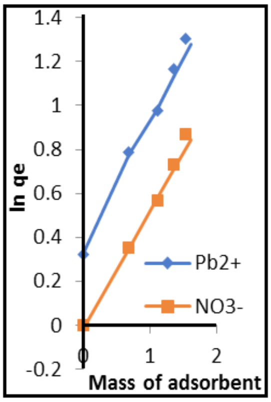

Fig. 2a. Uptake vs adsorbent dose

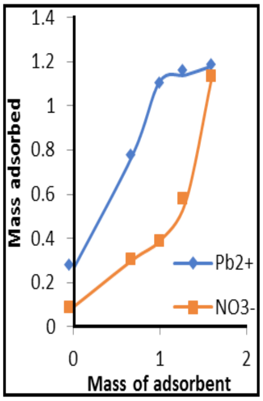

Fig. 2b. Linear plot

Effect of Contact Time on adsorption of $Pb(NO_3)_2$ onto the adsorbent

The adsorption process was monitored for different contact time and results are illustrated in Fig. 3a, b. The rate of removal of Pb^{2+} increases at first and then decreases but it remains almost constant for NO_3^- ions. The rate decreases as equilibrium was reached. The initial uptake of NO_3^- ions was found to be much higher than Pb^{2+} although there was no subsequent increase with contact time. The plot for nitrate ion was found to be linear over the entire contact period. The experimental data from this multicomponent adsorption unit implied that the competitive effects ions have led to a decreased level of adsorption of negatively charged nitrate ions. The model and experimental data of binary (multicomponent) system demonstrated that the presence of secondary ions of opposite charge suffered a decreased sorption capacity because of the competitive effects of ions for adsorption sites. This zeolitic adsorbent is having net negative charge on surfaces which results in preferential adsorption of cations over anions as reaction progresses. The zeolitic aluminosilicates are good at attracting heavy metal ions through cation exchange because of the surface net charge. But anions are also adsorbed due to the polarity of electric field generated, ion-dipole interaction or Van der Wall's forces. A concentration gradient would be set up because of repulsion caused as ions starts approaching the ions which are already adsorbed.

The rate of removal of lead ion was found to be very rapid during the initial 2.0 h, but it declines gradually and reaches equilibrium at around 3 hours. The fast initial stage of adsorption can be attributed to the presence of maximum number of vacant adsorption sites at the onset of adsorption process. The high concentration gradient between adsorbate in that liquid solid system enhances the rate of process. This will result not only in strong electrostatic attraction between solute particles and adsorbent but also rapid penetration of ions into the matrix[6]. Saturation process thus can be assumed to be quick and asymptotic[6]. In order for better validation of experimental observations apart from kinetic model diffusion model also was applied. Physical adsorption of charged particles onto an adsorbent is comprised of three steps.

(i) Transport of solute particles to the external surfaces of the adsorbent which is called film diffusion.
(ii) Intra particle diffusion (IPD) of ions within the pores.
(iii) Adsorbent surface gets adsorbed by adsorbate particles.

In an adsorption process, if the initial rate is high it suggests boundary layer effect or adsorption on surfaces. In the second half rate may be gradual or negative since equilibrium has already reached and is dominated by IPD or pore diffusion. As we proceed intraparticle diffusion comes into play, adversely affecting rate of removal of solute particles. Higher intraparticle diffusion rates corresponds to an efficient mechanism involving strong bonding[7]. The pH of the system indirectly influences IPD due to the formation of hydrated metal complexes. Corelation coefficient represents the fitting of model predicted values and actual data. The adsorption efficiency versus time profile was interpreted using linear form of Freundlich equation and the resulting plots are shown in Figure 3a, b.

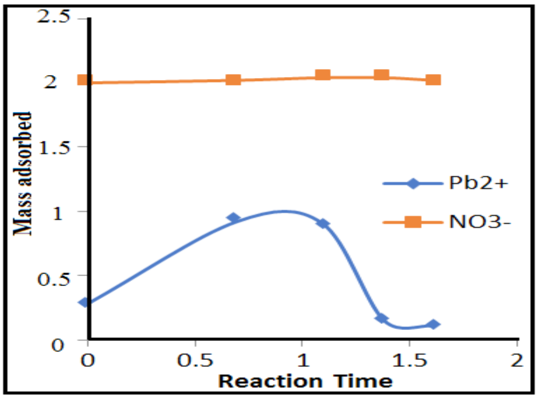

Fig. 3a. Uptake vs contact time

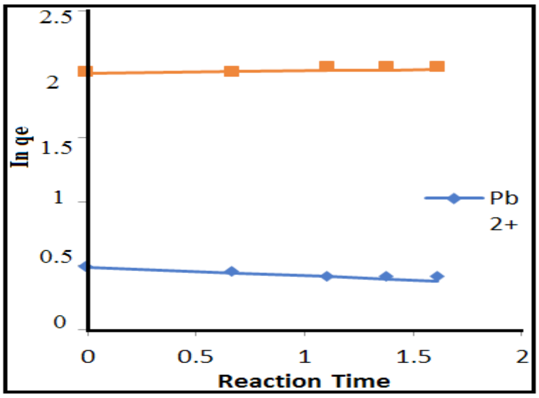

Fig. 3b. Linear plot

Effect of Calcination Temperature on adsorption of $Pb(NO_3)_2$ onto the adsorbent

Adsorption efficiency of the sample was investigated by conducting the experiment after calcining the adsorbent at temperatures 100°C, 200°C, 300°C, 400°C and 500°C. Calcination upto 300°C was found to be favorable since it makes it highly porous with a very high surface-area-to-weight ratio, due to the many "tunnel like" pores (Fig. 4a, b). The pulverised and oven dried sample retains its efficiency even after regeneration since honeycomb structure is not ruptured or deformed after the process. It retains its uniform pore size distribution, high pore volume and efficient absorptivity. Rate of adsorption process was found to reduce with exposure to the high temperature due to reduction in surface area and pore coarsening arising from structural changes. Temperatures as high as 300°C promotes solid diffusion and possibility of solid rearrangement[8]. But in a heterogeneous sample containing silica, the glass phase may soften and stop binding the grains together leading to reduced grain growth[9]. According to thermodynamics sintering process is irreversible and there will be decrease in free energy and decrease surface area. High temperature sintering of aluminosilicates can lead to low surface area and porosity due to the rupture of honeycomb structure thus compromising adsorption capacity[10].

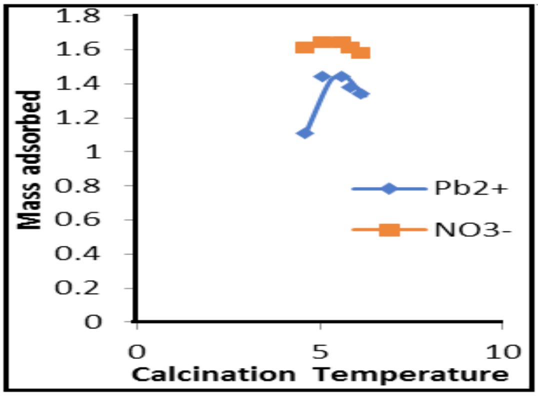

Fig. 4a. Uptake vs calcination temperature of adsorbent

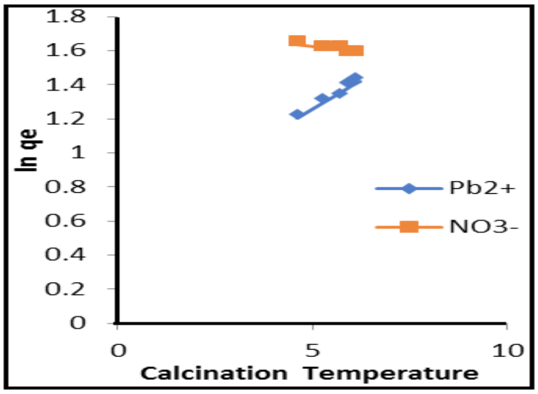

Fig. 4b. Linear plot

Effect of solution pH on adsorption of $Pb(NO_3)_2$ onto the adsorbent

Surface charge is an important deciding factor for adsorption of charged particles. Study of pH was undertaken to investigate the influence of acidic and basic solution conditions which governs the net charge of the aluminosilicate and the uptake of cations and anions. The change in pH in the reaction mixture was effected by adding a few drops of highly concentrated HCl/NaOH. The aluminosilicate layer structure has a net charge of negative over a wide range of pH from 3 to 9. The effect of pH in this adsorption system is studied at points 2.5, 4.5 and 10 keeping the initial concentration (0.1 M), adsorbent dose (1.0 g/100 mL) and temperature (303 K) constant. The adsorption capacity increases when the pH increases and the maximum adsorption of cations occur at pH 10 due to negative charge on surface in alkaline medium and that for anions at 2.5[11]. The variation of adsorption with different values of pH are shown in Fig. 5a, b. The H^+ ions in the acidic solution will be competing with the metal ions present, therefore removal of solute particles will be favoured at high pH[11]. The surface of the aluminosilicate would be protonated at low pH and resulted in a stronger attraction for negatively charged nitrate ions. Higher pH favours adsorption of cation. Higher pH adversely affects the removal of negative ions due to the presence of competing OH^- ions. The factors which can adversely affect adsorbate adsorbent interactions are repulsion between like charges and also the possible precipitation of metal ion at high pH[12]. When contact solution is at high pH adsorption occurs through ion exchange process and at low pH, the process is simply physical adsorption. Spontaneity of the process can be predicted from the free energy change involved and it is found that low acidity favours the process. The affinity between lead ions and zeolite decreases with a decrease in pH. At low pH hydrated metal complexes $Pb(H_2O)n^{2+}$ are formed which again makes physical adsorption difficult[12]. But at low pH, hydrolysis takes place and charged metal complexes formed are easily exchanged.

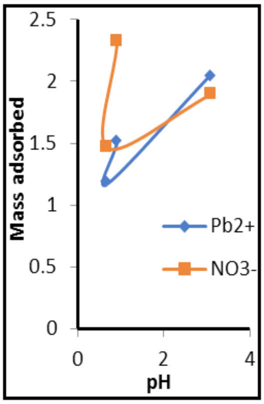

Fig. 5a. Uptake vs pH

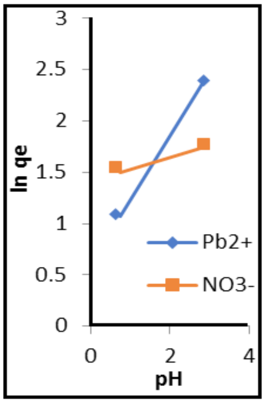

Fig. 5b. Linear plot

Effect of Reaction Temperature on adsorption of $Pb(NO_3)_2$ onto the adsorbent

The effect of reaction temperature on the rate of removal of Pb^{2+} and NO_3^{-1} ions using zeolitic aluminosilicate was examined at different temperatures of 30, 40, 50, 60 and 70°C. An increase in rate removal of both cation and anion were observed at higher temperatures (Fig. 6a, b). This observation implied that there have been more vacant sites created for the process of removal and conforms to the endothermic nature of adsorption. Getting rid of hydration sheath is easier at higher temperature as cations move faster and hydrated radii will be lesser which in turn helps with physical adsorption. Pre-existing adsorbent-adsorbate interaction leads to lower heats of sorption since removal of adsorbed solvent molecules consumes energy[13]. Adsorbent is found to be more efficient at higher temperature as diffusion process assists the transfer of solute particles to the active sites. The process slows down with high temperatures as the adsorbate particles fail to get itself attached to adsorption sites[14].

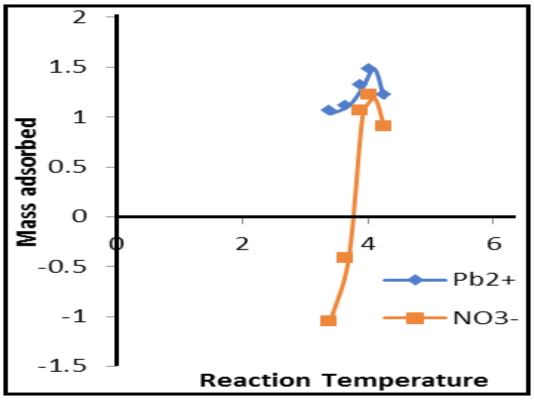

Fig. 6a. Uptake vs temperature

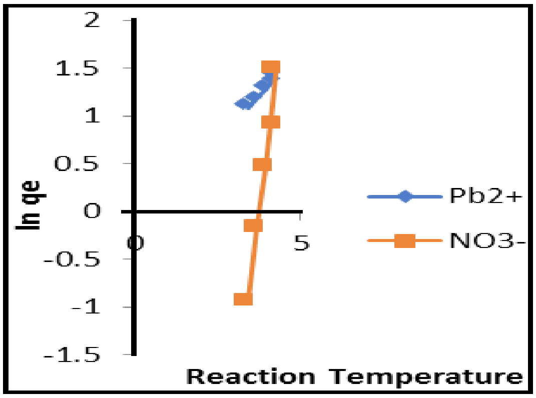

Fig. 6b. Linear plot

Thermodynamic equilibrium constants

The thermodynamic parameters like enthalpy change (ΔH^o), entropy change(ΔS^o), and free energy change (ΔG^o) are crucial in determining the progress of adsorption process in various batch experiments. The above thermodynamic parameters were found out using the linearised equation for Freundlich isotherm and Gibbs Helmholtz equation.

$$\ln q_e = \ln K_F + 1/n \ln C_e$$

$\ln q_e = \Delta S/R - \Delta H/RT$

Using equations, $\Delta G^o = -RT\ln K$ and $\Delta G = \Delta H - T\Delta S$, corresponding values of ΔG, ΔH and ΔS were calculated (Table 1).

If adsorption is exothermic, surroundings will be heated up and we expect higher entropy and a negative free energy change since a negative ΔH is larger than a positive -TΔS term. Increasing adsorptive removal of lead nitrate with increasing temperature shows that adsorption is endothermic[15]. So ΔH can be positive which also signifies low surface coverage and weak adsorbate-adsorbent interaction as evident from low K_F and n values. The ΔH in range of 2-20 kJ/mol signifies physical adsorption. For the process of adsorption although we expect a decrease in randomness, a positive entropy is observed at low or moderate loading of adsorbate. A positive value refers to considerable mobility of adsorbed metals at solid–liquid interface and vibrational freedom. The free solvent molecules got released will have more freedom of movement than what is lost by metal ions in solution. A positive ΔS also suggests structural changes including affinity of adsorbent and adsorbate. A negative ΔS indicates that adsorption is enthalpy driven and an intact honeycomb structure even after adsorption. If ΔS higher than -10 j/mol/k, adsorption conforms to a dissociative mechanism. Assuming that ΔH and ΔS is constant in the experimental range of temperatures, ΔG can be found out. The sign of ΔG depends on relative absolute values of ΔH and ΔS. Higher temperatures have favoured a decrease in free energy change confirming the endothermic nature of adsorption A positive ΔG suggests adsorption and desorption are not in mutual equilibrium. At equilibrium, ΔG = 0, if ΔG > 0 adsorption and desorption are not in mutual thermodynamic equilibrium. The reverse reaction, which is desorption would be the natural process taking place along a decreasing path of ΔG.

Table 1: Kinetic and thermodynamic parameters as deduced from Freundlich Isotherm model

Isotherm		Kinetic Parameters			Thermodynamic Parameters		
Freudlich	Ion	K_F	n	R^2	AH	AS	AG
Effect of mass of solute	Pb^{2+}	0.594	-2.5125	0.647	3.3089	-4.3299	1290.318
	NO_3^-	0.744	-1.6305	0.9402	5.0989	-0.2957	732.617
Effect of mass of adsorbent	Pb^{2+}	1.3852	1.6863	0.9706	-4.9302	2.7095	-807.44
	NO_3^-	0.9831	1.869	0.8679	-4.4463	-0.1413	42.1186
Effect of reaction temperature	Pb^{2+}	0.832	2.6723	0.5796	-3.1	-1.5339	457.1
	NO_3^-	3.85×10^{-5}	0.36842	0.9112	-22.563	-84.495	25179.5
Effect of reaction time	Pb^{2+}	1.628	-14.859	0.078	0.5595	0.4873	-1207.319
	NO_3^-	7.4409	55.5555	0.7229	-0.1496	16.6861	-4972.48
Effect of calcination temperature	Pb^{2+}	1.8072	7.5154	0.649	-1.1062	4.920	-1466.226
	NO_3^-	5.7511	-39.37	0.571	0.2111	14.544	-4334.26
Effect of pH	Pb^{2+}	1.314	1.876	0.973	-4.4313	2.2705	-676.624
	NO_3^-	36.3066	-1.245	0.882	6.676	107.27	-8899.43

Pseudo 1st order Lagergrens equation

Chemical kinetics takes into account the factors that influence rates of reactions and processes and validates the rate and attainment of equilibrium. Lagergren pseudo first order kinetics, which describes rate of adsorption from liquid phase system was applied here and the experiment was proceeded at an initial lead concentration of 0.1 M at pH 4.5. For many adsorption processes, the pseudo-first order (PFO) kinetics was found to be suitable for only the initial period of interaction and not for the complete span of contact. The k_1 and q_e can be evaluated from the graph of ln $(q_e$-$q_t)$ versus t, the straight line suggests a pseudo first order kinetics model for adsorption. The kinetic and equilibrium adsorption data were modelled using pseudo 1st order kinetics which is repesented as,

Here k_1 (min^{-1}) represents the kinetic coefficient and q_e and q_t, the adsorbed quantities at equilibrium and at time t, respectively[16]. The linearized form of Lagergren equation can be indicated as:

$\ln(q_e - q_t) = \ln qe - k_1{}^t$

The plot of ln $(q_e$-$q_t)$ against t should give a linear relationship if first order kinetics holds good.

The k_1 and q_e, equilibrium adsorption capacity can be determined by slope and intercept of the plot (Fig. 7). In Lagergrens equation, Inq_e is an adjustable parameter and its value is not equal to intercept by linear regression with $ln(q_e-q_t)$ and t. We cannot isolate q_e, equilibrium capacity from q_t, amount adsorbed at time, t. The PFO can be used for estimating rate constant k_1 and not q_e although the regression coefficient is as high as 0.9378. So, we need to assume values for q_e and get the best regression coefficient when we fit the experimental data. This was found to be true in the first 3 experiments. The k_1 ($time^{-1}$), the rate constant of pseudo first order adsorption reaction is found to be 0.5415 $minute^{-1}$.

Lagergren equation is not found to be valid for the entire phase of contact but in the initial phase of contact[17]. From the above results it was clear that equilibrium was reached in first 3 h and PFO kinetics was found to be followed for only initial 3 h of interaction and not for the entire contact period. The equation is of the form y = bx+c, b and c are obtained from regression analysis. The 'y' values are calculated using the independent variable, 'x', time. Since equilibrium reaches in the initial 3 h last two experimental values are ignored and a straight line is obtained using x and y values. The fast adsorption rates suggest that adsorption sites are readily available and easily attainable[18]. PFO assumes uptake of adsorbate follows 1st order rate equation, where concentration of adsorbent is assumed to be constant. Following the concentration of adsorbent and adsorbate simultaneously is difficult, so one reactant is assumed to be in excess and rate depends on concentration of the other reactant. So, 2nd order kinetics is approximated as 1st order kinetics. Gradient is not constant; they appear to be 2nd order but approximated. Also, it assumes that adsorbate do not interact with each other and adsorbed at localised sites. On saturation they form monolayer, it considers only forward reaction and disregards reversible desorption compound. According to PFO or Lagergren model the rate of adsorption is dependent on the number of vacant sites which again confirms the high initial uptake.

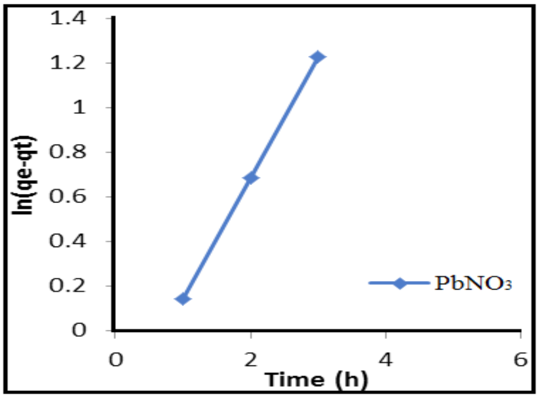

Fig. 7. PFO kinetic plot for $Pb(NO_3)_2$ at 298 K and initial concentration 0.1 M

CONCLUSION

The adsorption capacities of zeolitic aluminosilicate tuff for Pb^{2+} and NO_3^- was studied using batch technique. The effects of reaction conditions such as solute concentration, adsorbent dose, calcination temperature, contact time, reaction temperature and pH were studied. This study revealed that the efficiency of the adsorbent was improved at high pH, high temperature and high adsorbent dose. Adsorption capacity decreased with calcination temperature, solute concentration and contact time. The optimum conditions for efficient adsorption process were derived from the observations of the batch reactions. The kinetic and equilibrium adsorption data generated were satisfactorily modelled using pseudo 1st order kinetics and Freundlich isotherm model. The process of adsorption was concluded to be endothermic and pseudo first order by nature. By carefully manipulating the above conditions efficiency of solid-liquid adsorbent systems can be enhanced.

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Conflict of interest

Author declares that there is no conflict of interest.

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