

STUDIES ON THE MECHANISM OF REACTION INVOLVED IN THE SORPTION OF Pb(II) ION ONTO ACID ACTIVATED SHALE

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Abstract

Adsorption study on the sorption of Pb(II) ion onto acid activated shale was conducted using batch experimental technique to investigate the influence of initial metal ion concentration on the process of adsorption. Experimental data obtained were fitted into different kinetic model to analyze the mechanism of adsorption in terms of reaction controlled and transport controlled mechanism. Some of the selected kinetic model include; Pseudo-first order, Pseudo-second order, Elovich, Film diffusion, Parabolic diffusion and Intra-particle diffusion model. From the result, it was observed based on the linear coefficient of determination (r^2) that the experimental data fitted well into the various kinetic model tested. Application of non-linear error function such as error sum of square (SSE), root mean square error (RMSE) and residual average (RA) revealed that the rate limiting step for the adsorption of Pb^{2+} ion on acid activated shale was chemical attachment (chemisorption) and the reaction mechanism follows the Pseudo-second order kinetic model.

Keywords: Parabolic diffusion, film diffusion, intra-particle diffusion, pseudo-first order and pseudo-second order.

1.0 Introduction

The simplicity and cost effectiveness of adsorption process in the treatment of effluent wastewater has made it one of the most popular techniques employed by most researchers in the field of environmental pollution studies [1]. To understand the mechanism of adsorption process and provide a clear description of the rate of metal ion uptake onto porous solid adsorbent, there is need to undertake a comprehensive study of the kinetics of adsorption process [2]. Adsorption kinetic study will not only help describe the rate of metal ion uptake; it will also provide suitable information regarding the transport mechanism involved in the process [3].

Although, several researchers have employed different kinetic models to predict the mechanism involved in the sorption process such as pseudo-first order model, pseudo-second order model, Weber and Morris sorption kinetic model, first-order reversible reaction model, Bhattacharya and Venkobachar diffusion model, Elovich model, parabolic diffusion model, intra particle diffusion model, Ritchies's equation and film diffusion model. It is pertinent to also note that adsorption mechanism is both reaction controlled and transport controlled hence the need to distinguish between kinetic model that are reaction based and model that are transport based [4].

Recently, attempts have been made by several researchers to draw distinction between reaction controlled and transport controlled mechanism. In a research reported in [4] on the dynamic modelling of the transport mechanism of malachite green absorption onto used black tea leaves, a clear distinction was presented when the authors employed the film diffusion, parabolic diffusion and intra particle diffusion model to analyze the transport mechanism. Film and pore diffusion model in addition to the popular pseudo-first order and pseudo-second order kinetic model where employed in [5] for the adsorption of reactive red-4 onto shell waste as activated carbon. Other researchers [6, 7] have also shown that adsorbent particle size can influence the rate and efficiency of metal ion adsorption.

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Except for few literatures on adsorption kinetic studies, determination of the overall rate limiting step using both the reaction controlled and transport controlled model have been based on the application of linear coefficient of determination obtained by least square regression analysis involving the transformation of non-linear kinetic equation to its linear form. This method has been proved incorrect due to the violation of the error structure brought about by such transformation [8].

In this study, an attempt has been made to analyze the sorption mechanism of Pb(II) ion onto acid activated shale using selected reaction based and transport based kinetic model and determine the overall rate limiting step using selected non-linear error function such as root mean square error (RMSE) and residual average.

2. Research Methodology

2.1. Collection and preparation of adsorbent

Shale was collected from its deposit at Okada the administrative headquarter of Ovia North East Local Govt Area of Edo State, Nigeria. First, it was soaked in a plastic containing 5% hydrogen peroxide to remove any carbonaceous matter that can interfere with the metal adsorption capacity of the shale. Thereafter, it was washed with distilled water to remove any water soluble impurities before been dried in hot air oven at 50-70°C for 8 hours. The dried shale was then reduced to fine and sieved using sieve size of 212µm before use [9].

For acid activation, 500g of the dried sieved shale mineral was placed in a furnace at a temperature of 550 °C for 10 hours. 200 g of the calcinated shale mineral was then mixed with 1 liter 0.25M sulphuric acid, the mixture was heated at 105°C for 30 minutes. After slow cooling, the slurry was filtered and washed free of acid using distilled water as indicated by a pH meter. The shale was dried at a temperature of 100°C for 30 – 45 minutes, ground using mortar and pestle, sieved to 212 µm and stored in a desiccator to cool before use [10].

2.2. Preparation of aqueous solution

All the chemicals used in this research were analytical grade. Stock solution of lead was prepared by dissolving accurate quantity of lead (II) nitrate [Pb (NO₃)₂] in one liter of distilled water. All working solutions were obtained by diluting the stock solution with distilled water and the concentration of metal ion present in solution was analyzed by atomic absorption spectrophotometer (AAS). A duplicate was analyzed for each sample to track experimental error and show capability of reproducing results. The pH of the solution was adjusted to the desired values for each experiment.

2.3. Adsorption studies

Adsorption study was carried out to determine the effect of pH, adsorbent dose, adsorption temperature, contact time and initial metal ion concentration using batch adsorption technique. The adsorption experiment was performed at different variable range as follows; pH (2, 4, 6, 8, and 10), adsorbent dose (0.2, 0.4, 0.6, 0.8 and 1.0g), contact time (20, 40, 60, 80, 100, and 120 minutes), adsorption temperature (288, 293, 298, 303 and 308K) and different initial metal ion concentration. A 250ml conical flask containing the adsorbent and 50ml aqueous solution of the metal was agitated at 150rpm using a mantle fitted with magnetic stirrer. The pH values of the aqueous solutions were kept at the optimum for each heavy metal.

The separation of the adsorbent and aqueous solution of heavy metals was carried out by filtration with 150mm whatman filter paper and the filtrates were stored in sample cans in a refrigerator prior to analysis. The residual metal ion concentration was also determined using an Atomic Absorption Spectrophotometer (AAS)

The amount of heavy metal ions removed during the series of batch investigation was determined using the mass balance equation of the form [11].

$$q = \frac{V}{m} [C_0 - C_e] \quad (2.1)$$

Where: q, defines the metal uptake (mg/g); C₀ and C_e: are the initial and equilibrium metal ion concentrations in the aqueous solution [mg/l] respectively; V: is the aqueous sample volume (ml) and m: is the mass of adsorbent used (g). The efficiency of metal ion removal (%) was calculated using the mass balance equation of the form [1, 12, 13].

$$\text{Efficiency (\%)} = \left(\frac{C_0 - C_e}{C_0} \times 100 \right) \quad (2.2)$$

Where: C₀ and C_e are the metal ion concentrations (mg/l) in aqueous solution before and after adsorption respectively.

2.4. Adsorption kinetics study

Kinetically, adsorption mechanism can be described by reaction-controlled (chemisorption) or transport-controlled (diffusion) model as in the case of film and intra-particle diffusion [14]. Pseudo-first order, pseudo-second order and elovich kinetic model were applied in this study to describe the reaction-controlled mechanism for the sorption of Pb(II) ion onto acid activated shale.

To determine the mechanism of reaction that characterized the uptake of Pb²⁺ ion onto shale and identify the rate limiting step, data obtained from the batch adsorption experiment were analyzed using reaction controlled and diffusion controlled kinetic models presented in Table 2.1

Table 2.1: Definition of selected kinetic models

Kinetic Model	Kinetic Equation	Plot Parameters
Pseudo-First Order	$\ln(q_e - q_t) = \ln(q_e) - kt$ (2.3)	$\ln(q_e - q_t)$ against (t) [15]
Pseudo-Second Order	$q_t = \frac{k_2 q_e^2 t}{1 + q_e k_2 t}$ (2.4)	$(\frac{t}{q_t})$ against (t) [16]
Elovich	$q_t = \frac{1}{\beta} \ln(t + t_0) - \frac{1}{\beta} \ln(t)$ (2.5)	q_t against $\ln(t)$ [17]
Parabolic Diffusion	$X = Dt^{\frac{1}{2}} + \text{constant}$ (2.6)	(X) against $(t^{\frac{1}{2}})$ [18]
Film Diffusion	$\ln\left(\frac{C_t}{C_0}\right) = -\left[\frac{K_f \cdot W \cdot S_w}{V_f}\right](t)$ (2.7)	$(\frac{C_t}{C_0})$ against (t) [19]
Intra-Particle Diffusion	$q_t = K_{ad} t^{\frac{1}{2}} + I$ (2.8)	(q_t) against $(t^{\frac{1}{2}})$ [20]

3. Results and discussion

To study the reaction mechanism for the adsorption of Pb(II) ion onto acid activated shale, time dependent adsorption data were fitted into pseudo-first order, pseudo-second order and the elovich kinetic model and results is presented in Figures 3.1a, 3.1b and 3.1c respectively.

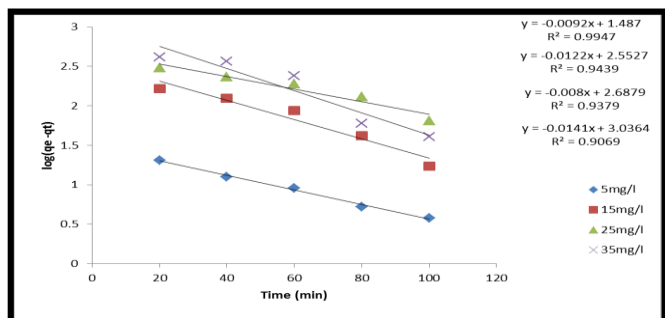


Figure 3.1a: Pseudo-first order kinetic modelling for the sorption of Pb(II) ion onto acid activated shale at different initial metal ion concentration

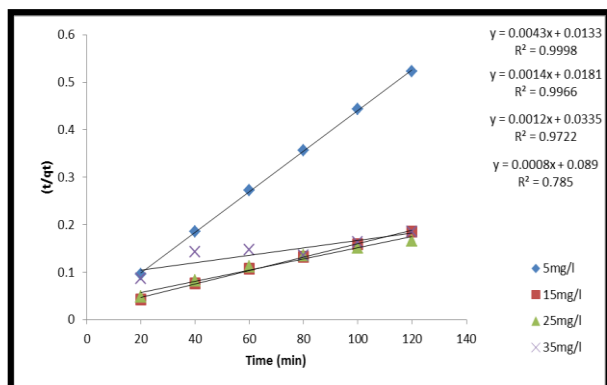


Figure 3.1b: Pseudo-second order kinetic modelling for the sorption of Pb(II) ion onto acid activated shale at different initial metal ion concentration

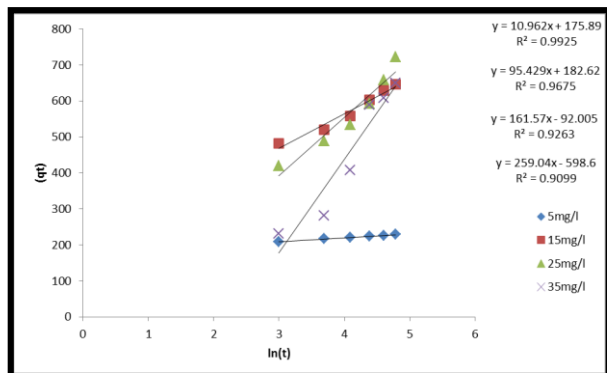


Figure 3.1c: Elovich kinetic modeling for the sorption of Pb(II) ion onto acid activated shale at different initial metal ion concentration

From the result of Figure 3.1a-c, it was observed based on the computed coefficient of determination (R^2) that pseudo second order kinetic model had a better fit to the adsorption data compared to pseudo first order and the elovich kinetic model. Determination of R^2 value and its subsequent application in the selection of best fitting kinetic model is not satisfactory owing to the alteration in the error structure associated with the transformation of non-linear kinetic equation to its linear form [21]. In addition, R^2 value only account for the difference associated with each individual point fitted by the model in relation to the overall average of the fitted curve. Therefore, to have an accurate judgement in the selection of best fitting kinetic model, non-linear error functions were employed. Error functions such as error sum of square (SSE), root mean square error (RMSE) and the residual average (RA) unlike R^2 accounts for the difference associated with each individual point fitted by the model in relation to each experimental point measured. Results of the computed kinetic parameters using the selected error functions are presented in Table 3.1

Table 3.1: Computed kinetic parameters for Pb(II) ion adsorption onto acid activated shale at different initial metal ion concentration

	Pb(II)			
	5	15	25	35mg/l
Pseudo-first order				
q_e (mg/g)	114.91	148.54	270.28	280.94
K_1 (min^{-1})	0.0012	0.0007	0.0002	4.4E-07
R^2	0.9952	0.9971	0.9972	0.9911
SSE	0.0210	0.0209	0.0205	0.0272
RMSE	0.0738	0.0883	0.0582	0.1481
Average Residual	-0.408	-0.611	-0.493	-0.794
Pseudo-second order				
q_e (mg/g)	13.712	5.2348	6.1365	10.734
K_2 (g/mg/min)	0.3335	0.3334	0.3334	0.3334
R^2	1.0000	1.0000	1.0000	0.9891
SSE	0.0003	0.0003	0.0005	0.0029
RMSE	0.0022	0.0034	0.0044	0.0261
Average Residual	-0.009	-0.016	-0.024	-0.100
Elovich kinetic model				
A(mg/g/min)	15.498	36.210	34.074	19.149
B(g/mg)	54.480	130.88	123.01	67.949
R^2	0.9970	0.9989	0.9999	0.9911
SSE	1.3517	1.7089	0.6888	4.7132
RMSE	5.6683	2.3210	1.0767	45.876
Average Residual	-18.26	-1.721	23.816	155.66

From the result of Table 3.1, it was observed that pseudo second order kinetic model had a better fit to the experimental data compared to pseudo-first order and the simple elovich kinetic model. For Pb(II) ion adsorption, pseudo second order had R^2 value of 0.9891 to 1.000, SSE value of 0.0005 to 0.0029, RMSE of 0.0022 to 0.0261 and residual average of -0.009 to -0.100. For pseudo-first order, R^2 was between 0.9911 to 0.997, SSE value of 0.0209 to 0.0272, RMSE of 0.0582 to 0.1481 and residual average of -0.408 to -0.794. For elovich kinetic model, R^2 was between 0.9911 to 0.9999, SSE value of 1.3517 to 4.7132, RMSE of 1.0721 to 45.876 and residual average of -1.721 to 155.66. The simple explanation is that pseudo second order had predicted data which were closer to the experimental data compared to the other kinetic model. The residual analysis also confirm the fact that pseudo second order was better since the average values of the residuals are closer to zero than those of the other kinetic models indicating that on the average, the difference in the amount adsorbed (q) fitted by pseudo second order kinetic model was closer to amount adsorbed (q) measured experimentally.

The accurate fit of the experimental data to pseudo-second order kinetic model explained the fact that Pb(II) ion uptake by acid activated shale was due to the chemical interaction between the metallic ions and the hydroxyl group present in the shale structure. This result supports the application of non-linear error function for the evaluation and selection of best kinetic models, as previously reported in [22].

To study the transport mechanism of Pb(II) ions from the bulk aqueous solution through the boundary film to the surface of the adsorbent (acid activated shale) and subsequently from the adsorbent surface to the intra-particle active sites, batch adsorption experiment was conducted to investigate the effects of initial metal ion concentration on the sorption of Pb(II) ion onto acid activated shale. Experimental data obtained were thereafter fitted into parabolic, film and intra-particle diffusion model as presented in Figures 3.2a, 3.2b and 3.2c respectively.

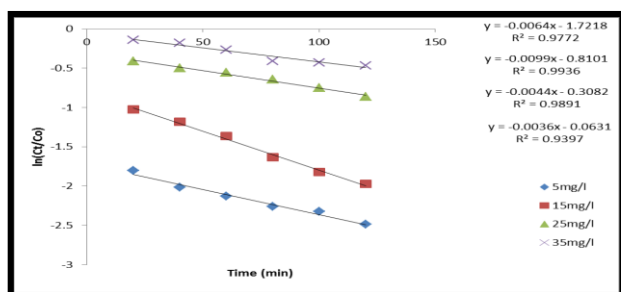


Figure 3.2a: Film diffusion modeling for the sorption of Pb(II) ion onto acid activated shale at different initial metal ion concentration

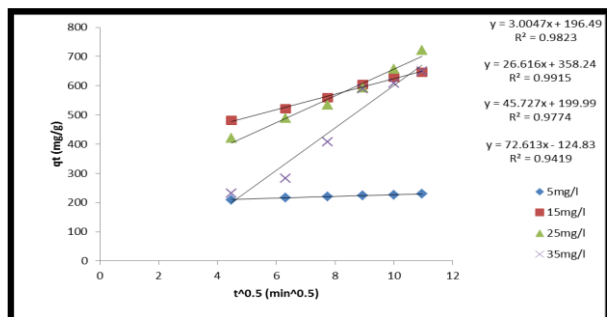


Figure 3.2b: Intra-particle diffusion modeling for the sorption of Pb(II) ion onto acid activated shale at different initial metal ion concentration

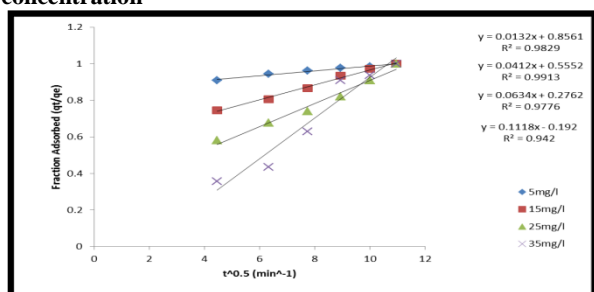


Figure 3.2c: Parabolic diffusion modeling for the sorption of Pb(II) ion onto acid activated shale at different initial metal ion concentration

Parabolic diffusion model was employed to verify the assumption that macropore and micropore diffusion occurs in series and to test the dominance of pore diffusion step (transport of the adsorbate to the external surface of the porous solids) in the overall transport process [23]. If parabolic diffusion was found to be rate limiting, it means therefore that the transport mechanism of Pb(II) ion onto acid activated shale may be controlled by pore diffusion. Intraparticle diffusion model was studied to understand the rate of internal diffusion occasioned by the transport of the adsorbate ions within the pores of the adsorbent to the active site where chemisorption takes place [24, 25, 26]. Diffusion through the boundary layer also known as film diffusion was tested to look at the diffusion of the adsorbate through the boundary layer.

Results of Figure 3.2a, 3.2b and 3.2c shows that the experimental data fitted well into the selected transport model. The non-linear nature of the film diffusion plot as observed in Figure 3.2a suggested that the transport mechanism of Pb(II) ion onto acid activated shale may not be controlled by film diffusion. For intra-particle diffusion model presented in Figure 3.2b, it was observed that the calculated value of the coefficient of determination R^2 varies with increasing initial metal ion concentration. In the adsorption of Pb(II) ion onto acid activated shale for example, computed R^2 was 0.9823, 0.9915, 0.9774 and 0.9419 at 5, 15, 25 and 35mg/l initial metal ion concentration. The linear nature of the plots and the high R^2 values revealed that the transport mechanism of Pb(II) onto acid activated shale may be controlled by intra-particle diffusion model. For the parabolic diffusion model as observed in Figures 3.2c, it was observed that the computed coefficient of determination R^2 are equally very high in addition to the fact that the graphical plots possess the same linear nature as those of intra-particle diffusion model an indication that the transport mechanism of Pb(II) onto acid activated shale may also be controlled by the parabolic diffusion model.

The argument that the value of the coefficient of determination R^2 may not be enough to select the kinetic model that best explained the adsorption data has also come to play in this regards as both the intra-particle and parabolic diffusion model seems to have control over the transport mechanism of Pb(II) ion onto acid activated shale. Therefore, to select the model that best explain the transport mechanism of Pb(II) ion onto acid activated shale, non-linear error functions were employed. Use of error functions such as sum of square error (SSE), root mean square error (RMSE) and the residual average (RA) are better and more accurate in handling non-linear model compare to R^2 since they accounts for the difference associated with each individual point fitted by the model in relation to each experimental point measured. The non-linear regression analysis based on selected error functions was done using the Solver Function in Microsoft Excel Spread Sheet and results obtained are presented in Table 3.2. From the computed parameters presented in Table 3.2, it was observed that; for parabolic diffusion and intra-particle diffusion model, the error sum of square (SSE) based on the adsorption of Pb(II) ion on acid activated shale was computed to be: 2.9897, 5.6173, 4.3346, 2.8534 and 2.8394, 5.3939, 4.1472, 2.8382 at 5, 15, 25 and 35mg/l respectively. Based on the computed error sum of square (SSE), it was observed that intra-particle diffusion model had a better fit to the experimental data than parabolic diffusion model since it possesses lower error sum of square values compared to parabolic diffusion model. Again the computed root mean square error values based on parabolic diffusion and intra-particle diffusion model for lead ion adsorption onto acid activated shale were observed to be; 14.577, 23.809, 19.115, 34.753 and 14.256, 23.492, 18.797, 35.070 at 5, 15, 25 and 35mg/l respectively. Again, it was concluded based on the computed root mean square error that intra-particle diffusion model had the best fit to the experimental data since it has the lowest root mean square error.

Table 3.2: Computed transport parameters for Pb(II) ion adsorption onto acid activated shale at different initial metal ion concentration

	Pb(II)			
	5	15	25	35mg/l
Parabolic Diffusion				
D_p (cm ² /sec)	5.8265	9.0409	8.7641	6.5088
q_e (mg/g)	5.8265	9.0409	8.7641	6.5088
C	1.7624	2.0760	2.0411	1.8697
R^2	0.9829	0.9913	0.9776	0.9420
SSE	2.9897	5.6173	4.3346	2.8534
RMSE	14.577	23.809	19.115	34.753
Average Residual	-1062	-1716	-1104	2242.4
Intra-particle Diffusion				
K_{ad} (mg/g min)	33.262	81.061	76.132	41.688
I	6.1010	6.3553	6.3291	6.1459
R^2	0.9823	0.9915	0.9774	0.9419
SSE	2.8394	5.3939	4.1472	2.8382
RMSE	14.256	23.492	18.797	35.070
Average Residual	-1040	-1693	-1081	2265.2

Evaluation of the computed kinetic parameters for both the reaction controlled and transport controlled mechanism for the adsorption of Pb(II) ion onto acid activated shale revealed that the pseudo second order kinetic model possesses the lowest sum of square error (SSE) and root mean square error (RMSE) having residual average very close to zero. It means therefore, that the adsorption of Pb(II) ion onto acid activated shale is a reaction controlled mechanism. On the bases of these, it was concluded that the rate limiting step for the adsorption of Pb(II) ion onto acid activated shale is a chemical attachment (chemisorption) and that the reaction mechanism follows the pseudo second order kinetic model.

4. Conclusion

On the possible reaction mechanism that controls the adsorption of Pb²⁺ ion onto acid activated shale, kinetic study was done to investigate the reaction controlled and transport controlled mechanism using suitable kinetic models, namely; pseudo first order, pseudo second order, elovich, film diffusion, parabolic diffusion and intraparticle diffusion. To estimate the kinetic parameters and select the kinetic model that best explained the adsorption data, selected non-linear error functions, namely; error sum of square (SSE), root mean square error (RMSE) and residual average (RA) were employed. From the results, it was found that the rate limiting step for the adsorption of Pb²⁺ ion onto acid activated shale was chemical attachment (chemisorption) and the reaction mechanism follows the pseudo second order kinetic model.

5. References

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