Investigating the Reaction and Transport Controlled Mechanism for the Sorption of Cr(III) and Mn(II) Ions onto Acid Activated Shale using Non-Linear Error Functions

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ABSTRACT

Time dependent adsorption study on the sorption of Cr(III) and Mn(II) ions onto acid activated shale was conducted using batch adsorption techniques to investigate the effect of initial metal ion concentration on the process of adsorption. Experimental data obtained were fitted into different kinetic models to analyze the mechanism of adsorption in terms of reaction controlled and transport controlled mechanism. Some of the selected kinetic models 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 Cr^{3+} and Mn^{2+} ions on acid activated shale was chemical attachment (chemisorption) and the reaction mechanism follows the Pseudo-second order kinetic model.

Keywords: Chemisorption, film diffusion, intra-particle diffusion, pseudo-first order and parabolic diffusion model

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 (Lin and Juang, 2002). 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 (Hong *et al.*, 2009). 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 (Yuh-Shan, 2006).

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 (Hossain and Hossain, 2013). Recently, attempts have been made by several researchers to draw distinction between reaction controlled and transport controlled mechanism. In a research by Hossain and Hossain (2013) 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. Shanthi *et al.* (2014) employed film and pore diffusion model in addition to the popular pseudo-first order and pseudo-second order kinetic model for the adsorption of reactive red-4 onto shell waste as activated carbon.

Other researchers, namely; Ho and McKay (1999) and McKay *et al.* (1983) have also shown that adsorbent particle size can influence the rate and efficiency of metal ion adsorption.

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 as reported in (Ho and McKay, 2000).

In this study, an attempt has been made to analyze the sorption mechanism of Cr(III) and Mn(II) 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.

2.0. Materials and Methods

2.1. Collection and preparation of adsorbent

Shale was collected from its deposit site 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 being dried in hot air oven at 50-70°C for 8 hours. The dried shale was then reduced to fine particles and sieved using sieve size of 212µm before use (Mariadas *et al.*, 2012).

For acid activation, 500 g of the dried sieved shale mineral was placed in a furnace at a temperature of 550 °C for 10 hours. About 200 g of the calcinated shale mineral was then mixed with 1 liter of 0.25 M 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 (Krishna *et al.*, 2006).

2.2. Preparation of aqueous solution

All the chemicals used in this research were analytical grade. Stock solution of chromium and manganese were prepared by dissolving accurate quantities of manganese (II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) and chromium (III) hydroxide [$\text{Cr}_2(\text{OH})_3$] 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 1.0 g), contact time (20, 40, 60, 80, 100, and 120 minutes), adsorption temperature (288, 293, 298, 303 and 308 °K) and different initial metal ion concentration. A 250 ml conical flask containing the adsorbent and 50 ml aqueous solution of the metal was agitated at 150 rpm 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 150 mm 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 (Badmus *et al.*, 2007):

$$q = \frac{V}{m} [C_0 - C_e] \quad (1)$$

where:

q defines the metal uptake (mg/g);
 C_0 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 reported in Gunay *et al.* (2007), Gimbert *et al.* (2008) and Hong *et al.* (2009).

$$Efficiency (\%) = \left(\frac{C_0 - C_e}{C_0} \times 100 \right) \quad (2)$$

where:

C_0 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 (Tse and Shang, 2002). 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 Cr(III) and Mn(II) ions onto acid activated shale.

To determine the mechanism of reaction that characterized the uptake of Cr^{3+} and Mn^{2+} ions 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 1.

Table 1: Definition of selected kinetic models

Kinetic Model	Kinetic Equation	Plot Parameters	References
Pseudo-First Order	$\ln(q_e - q_t) = \ln(q_e) - kt$ (3)	$\ln(q_e - q_t)$ against (t)	(Lagergren and Svenska, 1998)
Pseudo-Second Order	$q_t = \frac{k_2 q_e^2 t}{1 + q_e k_2 t}$ (4)	$\left(\frac{t}{q_t}\right)$ against (t)	(Shamik and Papita, 2010)
Elovich	$q_t = \frac{1}{\beta} \ln(t + t_0) - \frac{1}{\beta} \ln(t)$ (5)	q_t against $\ln(t)$	(Chien and Clayton, 1980)
Parabolic Diffusion	$X = Dt^{\frac{1}{2}} + \text{constant}$ (6)	(X) against $(t^{\frac{1}{2}})$	(Mohammad and Hossain, 2013)
Film Diffusion	$\ln\left(\frac{C_t}{C_0}\right) = -\left[\frac{K_f \cdot W \cdot S_w}{V_f}(t)\right]$ (7)	$\left(\frac{C_t}{C_0}\right)$ against (t)	(Van-Lier, 1989)
Intra-Particle Diffusion	$q_t = K_{ad} t^{\frac{1}{2}} + I$ (8)	(q_t) against $(t^{\frac{1}{2}})$	Ashtoukhy <i>et al.</i> (2008)

3.0. Results and Discussion

To study the reaction mechanism for the adsorption of Cr^{3+} and Mn^{2+} ions onto acid activated shale, time dependent adsorption data were fitted into pseudo-first order, pseudo-second order and the Elovich kinetic model and the results are presented in Figures 1a, 1b, 2a, 2b, 3a and 3b respectively.

Figure 1a: Pseudo-first order kinetics for the sorption of Cr(III) ion onto acid activated shale at different initial metal ion concentration.

Figure 1b: Pseudo-first order kinetics for the sorption of Mn(II) ion onto acid activated shale at different initial metal ion concentration.

Figure 2a: Pseudo-second order kinetics for the sorption of Cr(III) ion onto acid activated shale at different initial metal ion concentration

Figure 2b: Pseudo-second order kinetics for the sorption of Mn(II) ion onto acid activated shale at different initial metal ion concentration

Figure 3a: Elovich kinetics for the sorption of Cr(III) ion onto acid activated shale at different initial metal ion concentration

Figure 3b: Elovich kinetics for the sorption of Mn(II) ion onto acid activated shale at different initial metal ion concentration

From the result of Figures 1a, 1b, 2a, 2b, 3a and 3b, 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 simple elovich kinetic model except for the sorption of Mn (II) ion at 28 mg/l. Determination of R^2 value and its subsequent application in the selection of best fit 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 (Obob, 2011). 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 2.

Table 2: Computed kinetic parameters for Cr(III) and Mn(II) ions adsorption onto acid activated shale at different initial metal ion concentration

	Cr(III)				Mn(II)			
	30	40	50	60mg/l	4	12	20	28mg/l
Pseudo-First Order Kinetic Model								
$q_e(\text{mg/g})$	162.54	168.62	293.18	277.82	142.39	119.74	210.47	278.59
$K_1(\text{min}^{-1})$	0.0010	0.0007	1.4E-07	9.3E-08	0.0013	0.0007	0.0004	0.0001
R^2	0.9989	0.9990	0.9974	0.9985	0.9998	0.9966	0.9999	0.9932
SSE	0.0120	0.0163	0.0236	0.0346	0.0163	0.0160	0.0191	0.0174
RMSE	0.0515	0.1017	0.0958	0.1187	0.0656	0.0817	0.0815	0.0534
Average Residual	-0.433	-0.599	-0.642	-0.513	-0.479	-0.591	-0.451	-0.369
Pseudo-Second Order Kinetic Model								
$q_e(\text{mg/g})$	2.8456	2.4456	2.6478	2.8376	21.233	11.167	10.546	13.247
$K_2(\text{g/mg/min})$	0.3333	0.3333	0.3333	0.3333	0.3339	0.3334	0.3334	0.3335
R^2	1.0000	1.0000	0.9999	0.9999	0.9990	0.9991	0.9896	0.9788
SSE	3.8E-06	0.0001	0.0002	0.0006	0.0014	0.0008	0.0018	0.0018
RMSE	0.0002	0.0011	0.0018	0.0025	0.0129	0.0092	0.0156	0.0166
Average Residual	-0.002	-0.004	-0.008	-0.008	-0.061	-0.045	-0.062	-0.080
Elovich Model Kinetic Model								
$A(\text{mg/g/min})$	74.320	86.605	79.328	74.401	10.058	18.947	19.918	16.072
$B(\text{g/mg})$	271.47	316.79	289.94	271.77	34.415	67.203	70.786	56.598
R^2	0.9963	0.9995	0.9998	0.9998	0.9849	0.9948	0.9711	0.9831
SSE	6.6514	6.8827	3.7916	10.677	0.3796	0.6867	1.2395	0.6881
RMSE	28.413	19.271	2.9190	17.033	0.2430	2.5233	14.802	8.4383
Average Residual	-90.31	-58.84	23.744	6.7846	0.7388	16.081	48.716	43.750

From the result of Table 2, it was observed that pseudo-second order kinetic model had a better fit to the experimental data for the two metallic ions studied compared to pseudo-first order and the elovich kinetic model. for Cr(III) and Mn(II) ion adsorption, it was also observed that pseudo second order kinetic model had the highest R^2 value and the lowest SSE, RMSE and residual average compared to pseudo-first order and the elovich kinetic model. The simple explanation is that pseudo-second order had predicted data which were closer to the experimental data compared to the other kinetic models. 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 pseudo-first order and Elovich kinetic model 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 fitting of the experimental data to pseudo-second order kinetic model explained the fact that Cr(III) and Mn(II) ions 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 Jacques *et al.* (2007). In addition, the result recommends the adoption of pseudo second

order kinetic equation in the derivation of empirical model for computing the sorption capacity of acid activated shale for the removal of Cr(III) and Mn(II) ions.

To study the transport mechanism of Cr(III) and Mn(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 Cr(III) and Mn(II) ions onto acid activated shale. Experimental data obtained were thereafter fitted into film, parabolic and intra-particle diffusion model as presented in Figures 4a, 4b, 5a, 5b, 6a and 6b respectively.

Figure 4a: Film diffusion modelling for the sorption of Cr(III) ion onto acid activated shale at different initial metal ion Concentration

Figure 4b: Film diffusion modelling for the sorption of Mn(II) ion onto acid activated shale at different initial metal ion concentration

Figure 5a: Intra-particle diffusion modelling for the sorption of Cr(III) ion onto acid activated shale at different initial metal ion concentration

Figure 5b: Intra-particle diffusion modelling for the sorption of Mn(II) ion onto acid activated shale at different initial metal ion concentration

Figure 6a: Parabolic diffusion modelling for the sorption of Cr(III) ion onto acid activated shale at different initial metal ion concentration

Figure 6b: Parabolic diffusion modelling for the sorption of Mn(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 (Taparcevska *et al.*, 2010). If parabolic diffusion was found to be rate limiting, it means therefore that the transport mechanism of Cr(III) and Mn(II) ions 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 (Yesim and Yucel, 2000; Karthikeyan *et al.*, 2010). 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 Figures 4a, 4b, 5a, 5b, 6a and 6b show that the experimental data fitted well into the selected transport model. The non-linear nature of the film diffusion plot as observed in Figure 4a and 4b suggested that the transport mechanism of Cr(III) and Mn(II) ions onto acid activated shale may not be controlled by film diffusion. For intra-particle diffusion model observed in Figures 5a and 5b, it was observed that the two plots possess identical linear nature. More also, the computed values of coefficient of determination (R^2) was observed to vary with increasing initial metal ion concentration for the two metal ions studied. The linear nature of the plots and the high R^2 values revealed that the transport mechanism of Cr(III) and Mn(II) onto acid activated shale may be controlled by intra-particle diffusion model. For parabolic diffusion model as observed in Figures 6a and 6b, it was observed that the computed coefficient of determination R^2 are equally very high. In addition, the graphical plots possess the same linear nature as those of intra-particle diffusion model an indication that the transport mechanism of Cr(III) and Mn(II) on 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 be insufficient 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 Cr(III) and Mn(II) onto acid activated shale. Therefore, to select the model that best explain the transport mechanism of Cr(III) and Mn(II) onto acid activated shale, non-linear error functions were employed. Use of error functions such as error sum of square (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.

Table 3: Computed transport parameters for Cr(III) and Mn(II) ion adsorption onto acid activated shale at different initial metal ion concentration

	Cr(III)				Mn(II)			
	30	40	50	60mg/l	4	12	20	28mg/l
Parabolic Diffusion Model								
D_p (cm ² /sec)	13.024	14.070	13.461	13.031	4.6276	6.4729	6.6445	5.9390
q_e (mg/g)	13.024	14.070	13.461	13.031	4.6276	6.4729	6.6445	5.9390
C	2.9013	3.0666	2.9702	2.9024	1.5720	1.8647	1.8143	1.7804
R^2	0.9714	0.9707	0.9709	0.8704	0.9783	0.9672	0.9263	0.8615
SSE	14.858	16.436	12.461	2.9646	1.3976	2.6830	0.8059	0.9533
RMSE	73.028	71.348	44.738	27.632	5.8570	8.4771	3.2065	0.8191
Average Residual	-5297	-5272	-3255	-3360	-424.8	-539.5	66.656	150.25
Intra-Particle Diffusion Model								
K_{ad} (mg/g min)	169.01	197.36	180.57	169.20	20.709	41.222	43.463	34.587
I	6.8232	6.9740	6.8847	6.8242	6.0343	6.1434	6.1553	6.1081
R^2	0.9704	0.9702	0.9717	0.8700	0.9780	0.9672	0.9270	0.8621
SSE	14.379	15.914	12.051	2.9409	1.2903	2.5423	0.7171	0.8605
RMSE	72.737	71.059	44.448	27.341	5.5264	8.1602	3.5281	0.4986
Average Residual	-5277	-5251	-3234	-3339	-400.9	-516.7	89.867	173.39

From the computed parameters presented in Table 3, it was observed that; for Cr(III) ion adsorption onto acid activated shale, the computed error sum of square (SSE) based on parabolic and intra-particle diffusion were: 14.858, 16.436, 12.461, 2.9646 and 14.379, 15.914, 12.051, 2.9409 at 30, 40 50 and 60mg/l respectively. For the adsorption of Mn(II) ion onto acid activated shale, the computed error sum of square (SSE) based on parabolic and intra-particle diffusion are: 1.3976, 2.6830, 0.8059, 0.9533 and 1.2903, 2.5423, 0.7171, 0.8605 at 4, 12, 20 and 28mg/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 for the two metal ions studied.

It was also observed from results of Table 3 that; for parabolic diffusion and intra-particle diffusion model, the root mean square error (RMSE) based on the adsorption of Cr(III) ion onto acid activated shale were computed to be 73.028, 71.348, 44.738, 27.632 and 72.737, 71.059, 44.448, 27.341 at 30, 40 50 and 60mg/l respectively. For Mn(II) ion adsorption on acid activated shale, the computed root mean square error (RMSE) based on parabolic and intra-particle diffusion are: 5.8570, 8.4771, 3.2065, 0.8191 and 5.5264, 8.1602, 3.5281, 0.4986 at 4, 12, 20 and 28mg/l respectively. Again we concluded based on the 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. Evaluation of the computed kinetic parameters for both the reaction controlled and transport controlled mechanism for the adsorption of Cr(III) and Mn(II) ions onto acid activated shale revealed that pseudo-second order kinetic model possesses the lowest sum of square error (SSE) and root mean square error (RMSE) with residual average very close to zero. It means therefore, that the adsorption of Cr(III) and Mn(II) ions onto acid activated shale (AAS) was a reaction controlled mechanism. On the bases of these, it was concluded that the rate limiting step for the adsorption of Cr(III) and Mn(II) ions onto acid activated shale was chemical attachment (chemisorption) and the reaction mechanism follows the pseudo-second order kinetic model.

4.0 Conclusion

On the possible reaction mechanism that controls the adsorption of Cr³⁺ and Mn²⁺ ions onto acid activated shale, it was found that the rate limiting step for the adsorption of Cr³⁺ and Mn²⁺ ions onto acid activated shale was chemical attachment (chemisorption) and the reaction mechanism follows the pseudo-second order kinetic model. Hence, it was concluded that the sorption of Cr³⁺ and Mn²⁺ ions onto acid activated shale is a reaction controlled process. In addition, the study has further established that non-linear error function models such as error sum of square (SSE), root mean square error (RMSE) and residual average (RA) are better tools to select kinetic models compared to coefficient of determination (R^2) since the transformation of a non-linear model into its linear form explicitly alter the error variance and violates the normality assumption of a standard least square regression.

References

- Ashtoukhy, E. S. Z., Amin, N. K. and Abdelwahab, O. (2008). Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent. *Desalination Journal*, 223, pp. 162-173.
- Badmus, M. A. O., Audu, T. O. K. and Anyata, B. U. (2007). Removal of lead ion from industrial wastewaters by activated carbon prepared from periwinkle shells. *Turkish Journal of Engineering and Environmental Science*, pp. 251 – 263.
- Chien, S. H. and Clayton, W. R. (1980). Application of Elovich equation to the kinetics of phosphate release and sorption in soils. *Journal of Soil Science Society, America*, 44, pp. 265-268.
- Gimbert, F., Morin-Crini, N., Renault, F., Badof, P. M. and Crini, G. (2008). Adsorption isotherm models for dye removal by cationized starch-based materials in a single component system; Error analysis. *Journal of Hazardous Materials*, 157, pp. 34-46.
- Gunay, A., Arslankaya, E. and Tosun, I. (2007). Lead removal from aqueous solution by natural and pretreated clinoptilolite; adsorption equilibrium and kinetics. *Journal of Hazardous Materials*, 146, pp. 362-371.
- Ho, Y. S. and McKay, G. (1999). Pseudo-second order model for sorption process. *Process Biochemistry*, 34, pp. 451-465.
- Ho, Y. S. and McKay, G. (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Resource Journal*, 34(3), pp. 735-742.
- Hong, Z., Donghong, L., Yan, Z., Shuping, L. and Zhe, L. (2009). Sorption isotherm and kinetic modeling of aniline on Cr-bentonite. *Journal of Hazardous Materials*, 167, pp. 141 – 147.
- Hossain, J. and Hossain, W. E. (2013). Dynamic modelling of the transport mechanism of malachite green to adsorb on used black tea leaves. *International Journal of Recent Scientific Research*, 4(10), pp. 1575-1579.
- Jacques, R. A., Bernardi, R., Caovila, M., Lima, E. C., Pavan, F. A., Vaghetti, J. C. P. *et al.* (2007). Removal of Cu (II), Fe(III) and Cr(III) from aqueous solution by aniline grafted silica gel. *Separation Science and Technology*, 42, pp. 591–609.
- Karthikeyan, S., Sivakumar, B. and Sivakumar, N. (2010). Film and pore diffusion modeling for adsorption of reactive red-2 from aqueous solution onto activated carbon prepared from Bio-Diesel industrial waste. *E-Journal of Chemistry*, 7(S1), pp. 175-184.
- Krishna, G. B. and Susmita, S. G. (2006). Adsorption of chromium (VI) from water by clays. *Industrial Engineering and Chemical Resource Journal*, 45, pp. 7232-7240.
- Lagergren, S. and Svenska, B. K. (1998). Zur theorie der sogenannten adsorption gelöster stoffe. *Vetenskapsakad Handlingar*, 24(4), pp. 1–39.
- Lin, S. H. and Juang, R. S. (2002). Heavy metal removal from water by sorption using surfactant-modified montmorillonite. *Journal of Hazardous Materials*, B92, pp. 315 – 322.
- Mariadas, K., Kalyani, G., Joga, H. R., Kumar, P. Y. and King, P. (2012). The removal and equilibrium studies of cadmium by natural clay as adsorbent. *International Journal of Scientific Engineering Research*, 3(8), pp. 1-6.
- McKay, G., Blair, H. S. and Garden, J. R. (1983). Adsorption of dyes on Chitin, equilibrium studies. *Journal of Applied Polymer Science*, pp. 3045 – 3057.

- Mohammad, A. H. and Hossain, M. L. (2013). Dynamic modeling of the transport mechanism of malachite green to adsorb on used black tea leaves. *International Journal of Recent Scientific Research*, 4(10), pp. 1575-1579.
- Oboh, I. O. (2011). Evaluation of luffa cylindrical as a biosorbent in heavy metal sorption from aqueous solution. PhD Thesis, Department of Chemical Engineering, University of Benin, Benin City, Nigeria.
- Shamik, C. and Papita, S. (2010). Pseudo-second-order kinetic model for sorption of malachite green onto sea shells; comparison of linear and non-linear methods. *The IIOAB Journals (Research Bio-Physics)*, 1(3), pp. 3-7.
- Shanthi, P., Tamilarasan, G., Anitha, K. and Karthikeyan, S. (2014). Film and pore diffusion modeling for adsorption of reactive red-4 onto shell waste as activated carbon. *Rasayan Journal of Chemistry*, 7(3), pp. 229-240.
- Taparcevska, J., Markovska, L., Koumanova, B. and Meshko, V. (2010). Diffusion models for adsorption kinetics of Zn^{2+} , Cd^{2+} and Pb^{2+} onto natural zeolite. *Water Science and Technology Journal*, 62(5), pp. 1136-1142.
- Tse, K. K. C. and Shang-Lien, L. (2002). Desorption kinetics of PCP-contaminated soil: effect of temperature. *Water Resources Journal*, 36, pp. 284-290.
- Van-Lier, W. C. (1989). Mass Transfer to Activated Carbon in Aqueous Solutions. Ph. D. Thesis, Technical University of Delft, the Netherlands.
- Yesim, S. and Yucel, A. (2000). Mass transfer and equilibrium studies for the sorption of chromium ions onto chitin. *Process Biochemistry*, 36, pp. 157-173.
- Yuh-Shan, H. O. (2006). Review of second-order models for adsorption systems. *Journal of Hazardous materials*, B136, pp. 681-689.