Development of optimum conditions for modification of Kpautagi clay for application in petroleum refinery wastewater treatment

Matthew A. ONU[1*], Joseph O. OKAFOR[1], Abdusalami S. KOVO[1], and Yahaya S. MOHAMMAD[2]

[1]*Department of Chemical Engineering, F.U.T., Minna, Nigeria*
[2]*Department of Water Resources and Environmental Engineering, A.B.U., Zaria, Nigeria*
E-mails: [*]onu.matthew@yahoo.com; jookai2003@yahoo.com; kovoabdusalami@yahoo.com; yahsaymoh@yahoo.co.uk
[*]Corresponding author, phone: +2348069081188

Abstract

Kautagi clay is a kaolin type deposit that is abundantly available in Niger State, Nigeria with potential for application in pollution control such as wastewater treatment. This study investigates the optimum conditions for modification of Kpautagi clay for application in refinery wastewater treatment. Sulphuric acid was used in the modification of the clay and the modification variables considered were acid concentration, activation time and temperature. To develop the optimum conditions for the modification variables, the sulphuric acid modified Kpautagi clay was applied in the treatment of refinery wastewater in column mode at a fixed flow rate and mass of adsorbent. The results obtained indicate that the optimum conditions for modification of Kpautagi clay for application in the treatment of petroleum refinery wastewater are: acid concentration of *4M*; activation time of *120min* and activation temperature of *100°C*. Therefore, the optimum conditions developed in this study for modification of Kpautagi clay could be applied for improved performance in the treatment of petroleum refinery wastewater.

Keywords

Kaolin material; Adsorbent production; Adsorption experiment; Column effluent; Concentration; Time; Temperature; Kaolin; Activation

Introduction

Kaolin is one type of clay materials which is widely used for a quite number of applications such as catalyst, cement additive, water and wastewater treatment [1] Kaolin consists of a group of hydrous aluminosilicate minerals with chemical formula $Al_2Si_2O_5(OH)_4$. The industrial application of kaolin is strongly connected to its adsorptive properties which depend on surface modification that enhances its surface properties thereby making it a potential alternative to activated carbon [2]. These modification methods include heat treatment and acid activation [3]. Thermal activation is a physical treatment which involves calcination of clays at high temperatures [4] to remove impurities and possible moisture [5]. The acid modification of clay is normally carried out using HCl, HNO_3 or H_2SO_4 [6] and this results in alteration of the physical properties such as surface area, average pore volume, cationic exchange capacity and acidity of the surface of the clays [7, 8]. The most important variables for acid activation of clay minerals include the nature and type of clay, acid concentration, activation temperature and time.

Nigeria is blessed with abundant clay deposits such as Kpautagi clay (kaolin) in Niger State that have not been fully utilized industrially and to the best of our knowledge there is little or no information about the application of Kpautagi clay in refinery wastewater treatment. Therefore the objective of this study is to develop optimum conditions for modification of Kpautagi clay using sulphuric acid for application in refinery wastewater treatment.

Material and method

Sample collection/processing

A whitish-colored clay sample was obtained from Kpautagi town in Niger State, Nigeria and was used in the preparation of adsorbent for subsequent application in the treatment of refinery wastewater. The clay sample was crushed using porcelain mortar and pestle and thereafter sieved to obtain particle size of less than 75µm.

Production of adsorbent

250ml of 2M sulphuric acid solution was added to 25g of the clay sample in a 300ml

flask and the resulting suspension was heated under refluxing on a magnetically stirred hot plate at 100°C for 150min. At the end of experimental period, the reaction was quenched with distilled water and the resulting slurry was filtered using Watman filter paper. The residual clay cake obtained was washed several times with distilled water until a pH of 6 to 7 was attained. The product obtained was then oven-dried for 12 hours at 80°C. The dried samples were then crushed again and sieved to less than 75µm particle size. The process was repeated with 4, 6, and 8M sulphuric acid. Therefore, the optimum concentration was selected to further study the effect of activation time varied at 60, 90, 120 and 150min and activation temperature varied at 60, 80 and 100°C. In each case, the product obtained was stored in an air-tight sample bottle and labeled according to activation concentration of acid.

Column adsorption experiment

The adsorption experiments were carried out in a simple continuous column process with a glass column of 10cm length and 0.35cm internal diameter. The column was packed with 2g of adsorbent and a glass wool was placed at the bottom as a support and also at the top to prevent flotation of adsorbent in excess wastewater [9] The wastewater employed in this study is process wastewater which was collected from Kaduna Refinery and the following wastewater parameters pH, conductivity, hardness, alkalinity, Nitrate, Phosphate, Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) were analyzed before treatment. The wastewater was fed to the column at a fixed flow rate of 1.6cm^3/min in a downward flow mode through a pipe having a valve as the flow regulator [10]. The effluent wastewater was continuously generated at the column outlet and collected after 150min for analysis of the wastewater parameters after treatment.

Results and discussions

Effect of acid concentration

The effect of acid concentration was studied as presented in Table 1. Application of different acid concentration in the clay modification was observed to reduce the BOD and COD of the wastewater sample from 38mg/l and 188mg/l respectively. Among the acid concentrations considered, 4M concentration was noted for highest reduction to 14mg/l and 38mg/l for BOD and COD respectively. This was followed by 6M concentration with

reduction in BOD and COD concentration to 14mg/l and 36mg/l respectively. Reduction in other parameters was also observed by all the different acid concentration and except for alkalinity and pH, 4M acid concentration showed highest reduction for electrical conductivity, hardness, nitrate and phosphate from 875µs, 146mg/l, 4mg/l and 1mg/l to 717µs, 70mg/l, 1.5mg/l and 0.25mg/l respectively. According to [11], high removal resulting from increased hydrogen ion concentration as the acid concentration is increased is due to the neutralization of the negatively charged clay surface which enhances the adsorption of the negatively charged species via reduction in the adsorbent/adsorbate repulsion. Therefore, 4M acid concentration was selected as the optimum for Kpautagi clay modification.

Table 1. Effect of acid concentration at 100°C and 150min activation

Parameters	Before Treatment	After Treatment			
		KP2M	KP4M	KP6M	KP8M
BOD (mg/l)	38	35	14	14	32
COD (mg/l)	188	58	34	36	40
Conductivity (µs/ml)	875	720	717	720	720
Alkalinity (mg/l)	54	48	48	48	46
Hardness (mg/l)	146	84	70	84	136
Nitrate (mg/l)	4	2.1	1.5	1.5	2.9
Phosphate (mg/l)	1	0.55	0.25	0.25	0.25
pH	5.2	6.7	6.94	6.22	6.61

BOD=Biochemical Oxygen Demand, *COD*=Chemical Oxygen Demand,
KP2M=Kpautagi clay modified 2M acid concentration,
KP4M=Kpautagi clay modified 4M acid concentration,
KP6M=Kpautagi clay modified 6M acid concentration,
KP8M=Kpautagi clay modified 8M acid concentration

Effect of activation time

Effect of activation time on the performance of Kpautagi clay in the treatment of refinery wastewater was studied as presented in Table 2. The table revealed reduction in concentration of sample parameters as the activation time was increased from 60 to 90 min. As the activation time was additionally increased to 120 min, further reduction was achieved in BOD, COD, electrical conductivity, alkalinity, hardness, nitrate, phosphate and pH to 12mg/l, 30mg/l, 695µs, 42mg/l, 54mg/l, 2.8mg/l, 0mg/l, 6.61 respectively while increasing the activation time further to 150min was noted for little or no effect except for alkalinity and hardness. The Kpautagi activated clay demonstrated complete removal of phosphate from the refinery wastewater and similar observation was also reported by [12] this could be as a result of the existence of aluminum ion on the surface of the clay which spontaneously forms

aluminum sulphate with the sulphate ion. Activation time of 120min was observed to be enough for considerable removal and was therefore taken as the optimum activation time for Kpautagi clay.

Table 2. Effect of activation time at 100°C and 4M acid concentration

Parameters	Before Treatment	After Treatment (activation time)			
		60min	90min	120min	150min
BOD (mg/l)	38	17	15	12	12
COD (mg/l)	188	36	33	30	30
Conductivity (µs/ml)	875	703	696	695	694
Alkalinity (mg/l)	54	45	44	42	44
Hardness (mg/l)	146	64	66	54	64
Nitrate (mg/l)	4	3.1	3.1	2.8	2.8
Phosphate (mg/l)	1	0.2	0.2	0	0
pH	5.2	6.8	6.63	6.61	6.61

BOD=Biochemical Oxygen Demand, *COD*=Chemical Oxygen Demand

Effect of activation temperature

Table 3 presents results on the effect of activation temperature on performance of Kpautagi clay in the treatment of refinery wastewater.

Table 3. Effect of activation temperature at 120min and 4M acid concentration

Parameters	Before Treatment	After Treatment (activation temperature)		
		60°C	80°C	100°C
BOD (mg/l)	38	16	15	12
COD (mg/l)	188	37	36	30
Conductivity (µs/ml)	875	721	702	695
Alkalinity (mg/l)	54	46	45	42
Hardness (mg/l)	146	58	52	54
Nitrate (mg/l)	4	3.1	2.5	2.8
Phosphate (mg/l)	1	0.45	0	0
pH	5.2	6.85	6.88	6.61

BOD=Biochemical Oxygen Demand, *COD*=Chemical Oxygen Demand

The table shows reduction in concentration of parameters at activation temperature of 60°C. When activation temperature was increased to 100°C, significant reduction in BOD, COD, conductivity, alkalinity, phosphate and pH to 12mg/l, 30mg/l, 695µs, 42mg/l, 0mg/l and 6.61 was observed respectively with the exception of hardness and nitrate which were noted for highest reduction to 52mg/l and 2.5mg/l at activation temperature of 80°C. Therefore, optimum activation temperature was taken as 100°C.

Conclusion

The optimum condition for modification of Kpautagi clay for application in the treatment of petroleum refinery wastewater has been successfully established. These optimum conditions are: acid concentration of *4M*; activation time of *120min*; activation temperature of *100°C*. Therefore the optimum conditions developed in this study for modification of Kpautagi clay could be applied for improved performance in the treatment of refinery wastewater.

References

1. Eze K. A., Nwadiogbu, J. O., Nwankwere E. T., *Effect of acid on the physicochemical properties of kaolin clay*, Archives of Applied Science Research, 2012, 4(2), p. 792-794.
2. Ajemba O. R., *Modification of the physico-chemical properties of Udi clay minerals to enhance its adsorptive capacity*, Pelagia Research Library: Advances in Applied Science Research, 2012, 3(4), p. 2042-2049.
3. Vimonses V., *Development of multifunctional nanomaterials and adsorption-photocatalysis hybrid system for wastewater reclamation*, PhD Dissertation, The University of Adelaide, Australia, 2011.
4. Al-Asheh S., Banat F., Abu-Aitah I., *Adsorption of phenol using different types of activated bentonite,* Separation and Purification Technology, 2003, 33, p. 1-10.
5. Steudel A., Batenburg L. F., Fischer H. R., Weidler P. G., Emmerich K., *Alteration of swelling clay minerals by acid activation,* Applied Clay Science, 2009, 44, p. 105-115.
6. Diaz F., De Souza S. R., *Studies on the acid activation of Brazillian smectic clays.* Journal of Hazardous Materials, 2001, 24, p. 343-353.
7. Doulia D., Leodopoloud C. H., Gimouhopoulos K., Rigas F., *Adsorption of humic acid on acid activated Greek bentonite*, Journal of Colloid and Interface Science, 2009, 340, p. 131-141.
8. Lian L., Guo L., Guo, C., *Adsorption of congo red from aqueous solution on Calcium bentonite*, Journal of Hazardous Materials, 2009, 16, p. 126-131.
9. Mohammad Y. S., Shaibu-Imodagbe E. M., Igboro S. B., Giwa, A., Okuofu C. A., *Adsorption of phenol from refinery wastewater using rice husk activated carbon*, Iranica

Journal of Energy and Environment, 2014, 5(4), p. 393-399.

10. Mohammad Y. S., Shaibu-Imodagbe E. M., Igboro S. B., Giwa A., Okuofu C. A., *Application of low-cost adsorbent in the treatment of Samaru stream water*, Journal of Engineering Studies and Research, 2014, 20(4), p. 61-65.
11. Madukasi E. I., Ajuebor F. N., Ojo B. I., Meadows A. B., *Pollutant removal from paint effluents using modified clay minerals*, Journal of Industrial Research and Technology, 2009, 2(1), p. 49-55.
12. Jatto E. O., Asia I. O., Egbon E. E., Otutu J. O., Chukwuedo M. E., Ewansiha C. J., *Treatment of wastewater from food industry using snail shell*, Academia Arena, 2010, 2(1), p. 32-36.