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DEVELOPMENT OF CALCIUM RICH ZEOLITE A FROM AHOKO KAOLIN FOR THE ADSORPTION STUDY OF METHYLENE BLUE

KOVO, A. S., ABDULKAREEM, A. S., TOBA OGUNMOLA, LONGTONG DAFYAK, ISAH, A. G. & EYIBIO UDUAK PROMISE

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Abstract

This work report the development of calcium rich zeolite A obtained through the process of ion exchange of sodium type Zeolite A synthesized from Ahoko kaolin at different ageing period and crystallization time using hydrothermal technique. The synthesised Zeolite was thereafter used for the adsorption of Methylene Blue (MB). The synthesised zeolite A (SZA) and calcium rich zeolite (CRZ) were characterized using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and the concentration of calcium present after ion exchange was analysed using Atomic Absorption Spectroscopy (AAS). The effects of pH, contact time, MB initial concentration and adsorbent dosage were studied for CRZ to investigate its adsorption capacity. The adsorption of MB increased with an increase in pH, contact time, MB initial concentration and adsorbent dosage. The equilibrium process was well described by Langmuir and Freundlich isotherm models. The Langmuir parameters maximum adsorption capacity q_m (mg/g) and energy of adsorption K_a (L/mg) were obtained as 19.268 and 0.032 respectively. The regression parameters and correlation coefficient (R) indicate that the adsorption data for MB removal fit better with Langmuir isotherm model. The present work suggests that calcium rich zeolite material used as a sorbent material with relatively low cost, obtained from Ahoko Kaolin; is a good material for removal of dyes such as MB from wastewater.

Introduction

Zeolites are crystalline solids structures comprising of silicon, aluminum and oxygen that form a framework with cavities and channels inside where cations, water and/or small molecules may reside [1-2]. They are hydrated aluminosilicate minerals made from interlinked tetrahedra of AlO_4 and SiO_4 framework. In simpler terms, they are solids with a relatively open, three-dimensional crystal structure built from the elements aluminium, oxygen, and silicon, with alkaline or alkaline-earth metals (such as sodium, potassium, and magnesium) plus water molecules trapped in the gaps between them [2].

Preparation of tailor made zeolitic material have continued to draw special research attention over the years because of their unique properties and potential applications in operation such as adsorption, catalysis and other separation processes. Obtaining a consistent route for development of zeolite will always be welcomed as the continuously increasing demands for materials with highly specific chemical and physical properties as zeolites have inspired scientists to make new porous materials with unique structures. The synthesis of zeolites with a wide variety of engineered structures and properties therefore requires intense laboratory experiments. There is an increasing interest in the field of designing and preparation of synthetic zeolites in three main ways. These include treatment of natural zeolites (which preserves their initial crystalline structure), the use of natural clay minerals and by conventional use of commercial chemical sources. Zeolites found in nature are usually either calcium or sodium varieties. The most abundant calcium zeolites in such environments are wairakite, scolecite, mesolite, thomsonite, heulandite,stilbite, gismondine, epistilbite, chabazite, levynite, and laumontite[3] .

Since the principal raw materials used to manufacture zeolites are silica and alumina, which are among the most abundant mineral components on earth, the potential therefore to supply zeolites is virtually unlimited. Synthetic zeolites hold some key advantages over their natural analogs; the synthetic materials are manufactured in a uniform, phase-pure state.

The shape-selective properties of zeolites are the basis for their use in molecular adsorption. Adsorption has been recognized as a potential technology for dye removal because it is economical, effective and has simple design compared to other techniques, however, the nature of adsorbate and its substituents greatly affects the adsorption process [2]. Likewise, the adsorbent properties such as porous structure, chemical structure and concentration of surface functional groups, play important role in the adsorption capacity and the removal mechanism of the adsorbate [1].

The preferential ability of zeolite to adsorb certain molecules while excluding others has opened up a wide range of molecular sieving applications. Sometimes it depends merely on the size and shape of pores controlling access into the zeolites; in other cases different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind [4]. In this work, our aim is to develop calcium rich zeolite A from Ahoko Kaolin for the adsorption study of methylene blue.

Experimental

Materials

All chemicals used in zeolite synthesis and adsorption study of Methylene Blue were of analytical grade. The aluminosilicate source used in zeolite synthesis was kaolin procured from Ahoko, Kogi state- Nigeria. The sodium hydroxide (97.5%) and calcium chloridewere sourced from BDH Chemical.

Refinement and Metakaolinization of Ahoko Kaolin

One kilogram sample of kaolin clay was procured from Ahoko, Kogi state, Nigeria. The kaolin sample was pounded using mortar and pestle to crush into smaller particle and then sieved using 350 mesh.

500g of the sieved sample was sedimented by stirring with 1 L distilled water for 10 min. 2.5wt (%) of sodium hexametaphosphate (>65% w/w P_2O_5,) and a litre of sodium bicarbonate solution at ratio 4:1 was used as deflocculant to remove impurities from sample during the sedimentation process. The mixture of sample and sodium hexametaphosphate was stirred with a magnetic stirrer and left to stand for 8 hours to settle down before the supernatant was decanted and dried at 45°C in an oven for 2 days and labeled as treated sample. Treated sample was pounded using mortar and pestle to crush into smaller particles and then sieved using 350 μm mesh again. The treated sample was analysed with the aid of X-ray fluorescence (XRF). 250 g of the treated sample was weighed and put in a furnace (model S336RD) using a crucible at a temperature of 600°C for 2 hour to undergo metakaolinization process. At the end of the process, the samples were removed and allowed to cool in air.

Synthesis of as-synthesized Zeolite A and Calcium rich Zeolite A from Ahoko Kaolin

The aluminosilicate gel used for the synthesis of the sodium type zeolite was prepared from reaction mixture with molar composition of $3.165Na_2O$: Al_2O_3: $1.926SiO_2$: $128H_2O$ batch composition. Sodium hydroxide pellets of 97.5% (BDH Chemical) were used as a source of Na_2O and Ahoko metakaolin serve as a combined source of alumina and silica.

The synthesis gel was formed by dissolving 6.60 g of NaOH in 58.13g of distilled water and

stirred gently until NaOH was completely dissolved. 5.61g of Ahoko metakaolin were then added to the mixture to get the synthesis gel. The resulting gel was then aged at different ageing periods of 6hr at room temperature on a magnetic stirrer. Hydrothermal treatment of aged samples were performed using a Teflon lined- autoclave and crystallized in an oven maintained at 100 ° C at different periods of 2, 8 and 10 hrs. The crystallized products were allowed to cool and washed severally with distilled water until the filtrate became very clear and pH was below 8. The sample were then dried in an oven at temperature of 60°C for 6 hours.

The calcium rich form of zeolite material was made by ion exchange with the sodium zeolite type (the exchangeable cation of this zeolite type is Na^+). In this case, ion exchanges were made with calcium chloride. The reaction products were analysed using XRD and SEM.

Adsorption Studies

Batch technique was employed in studying and evaluating the kinetic and equilibrium of adsorption of Methylene blue unto the synthesised Zeolite A and calcium rich zeolite A as a result of its straightforwardness. Equilibrium isotherms were obtained by carrying out experiment at different initial concentration, pH, temperature and adsorbent dosage. The effect of pH was observed by varying the pH from 2 to 8 and that of temperature at 30, 40 and 50°C, in order to evaluate the adsorption thermodynamics parameters. Effects of adsorbent dosage were also studied at 0.25g, 0.5g, 1g, and 1.5g respectively. All these were done on Methylene Blue at a constant temperature of 30°C except those studies in which temperatures were studied and pH of 7 except those studies in which pH were studied. The final concentrations of the dyes were estimated at maximum wavelength (662 nm) corresponding to maximum absorbance for MB using a UV-Spectrophotometer. The graph of q_t was plotted against time, using equation 1 to obtain q_t

$$Q_t = (C_o - C_t)\frac{V}{X} \qquad (1)$$

Where C_o (mg/L) is initial MB solution
C_t (mg/L) is its concentration at time t,
V (L) is the volume of the solution and
X (g) is the mass of the adsorbent.

At the end of equilibrium time of 24 hours, the reaction mixture was filtered and the residual MB concentration analysed. The amount of MB adsorbent at equilibrium qe(mg/g) was calculated from equation 2.

$$Q_e = (C_o - C_e)\frac{V}{X} \qquad (2)$$

Q_e = amount of dye adsorbed per unit mass of adsorbent (mg/L)
C_o = initial dye concentration in (mg/L)
C_e = final dye concentration (mg/L)
X = dose of adsorbent (g/L)
The kinetics of methylene blue adsorption was analysed using Langmuir and Fredlinch models.

Results and discussion

Table 1 shows the various chemical compositions of both raw and refined Ahoko Kaolin. The result shows that raw kaolin contains SiO_2, Al_2O_3 and some oxides of P, Mg, Fe, Ca, Ti and Na. The main constituents are Silica (52.978 %) and alumina (11.327%) as shown. The high percentage of SiO_2 in the AK is an indication of presence of high percentage of quartz.

Table 1:- X-ray Fluorescence of raw and refined Ahoko Kaolin

Element	Concentration (wt %)	
	Raw Ahoko Kaolin	Refined Ahoko Kaolin
Na_2O	1.16	2.58
MgO	1.49	1.67
Al_2O_3	11.33	12.19
SiO_2	52.98	51.03
P_2O_5	1.12	3.51
K_2O	1.17	1.10
CaO	0.14	0.13
TiO_2	1.24	1.21
Fe_2O_3	5.90	5.95

The SiO_2/Al_2O_3 proportion obtained from XRF analysis is 3.2 but whose expected approximate value should have been 1 for the zeolite synthesis. However, it does not affect the synthesis as zeolite A can be prepared from reaction mixtures with low Si/Al ratio ($Si/Al \leq 5$) and strong alkalinity [2].

Like most other naturally occurring minerals, kaolin requires refining and purification before it can be used in the synthesis of zeolites. The presence of quartz and other non-clay minerals can impede the application of zeolites because of their abrasivity. Quartz is not desirable because it is difficult to dissolve hence it is essential to remove or reduce the quantity of quartz before the kaolin is used in the synthesis of the zeolites [3].

A comparison of the oxide composition of the raw Ahoko kaolin with the refined Ahoko kaolin as represented in table1 shows a slight reduction in the percentage composition of SiO_2 (52.978% to 51.031%) and corresponding slight increase in the percentage composition of Al_2O_3 (11.327% to 12.193%) for the refined kaolin. The insignificant change in SiO_2/ Al_2O_3 ratio may be as a result of the low level of non-silica mineral i.e. quartz which ordinarily impede the formation of zeolite , therefore it low level is an indication of likelihood of that the Ahoko Kaolin when formulated will lead to quick formation of zeolites

Xrd pattern of synthesized zeolite a and the exchanged calcium rich zeolite

Figure 1 to 6 shows the X-ray diffraction pattern of synthesised zeolite A and exchanged calcium rich zeolite respectively at different synthesis conditions. In this work ageing time was fixed while varying the crystallization time for both the as-synthesised zeolite A samples and Calcium rich Zeolite A samples. Crystallization temperature was also kept constant at 100°C during the hydrothermal reaction.

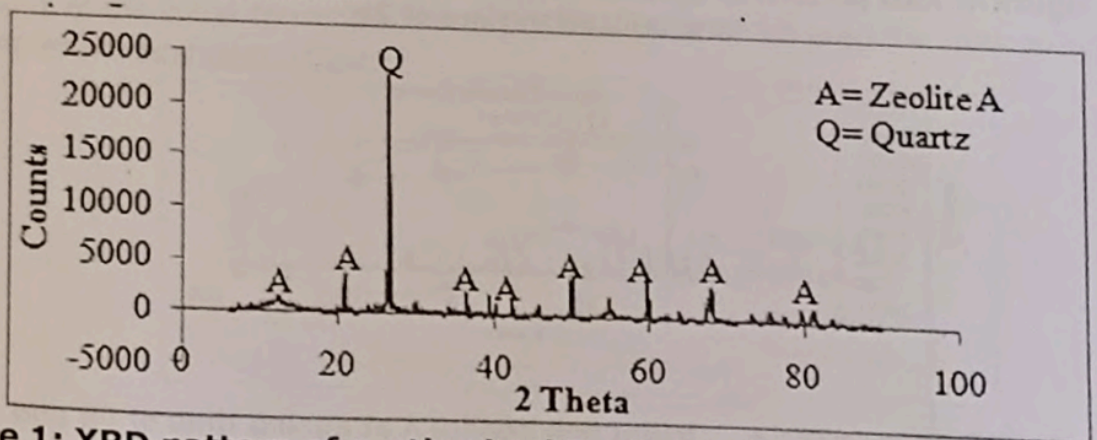

Figure 1: XRD pattern of synthesized Zeolite Aat ageing time of 6h and crystallization time of 2h

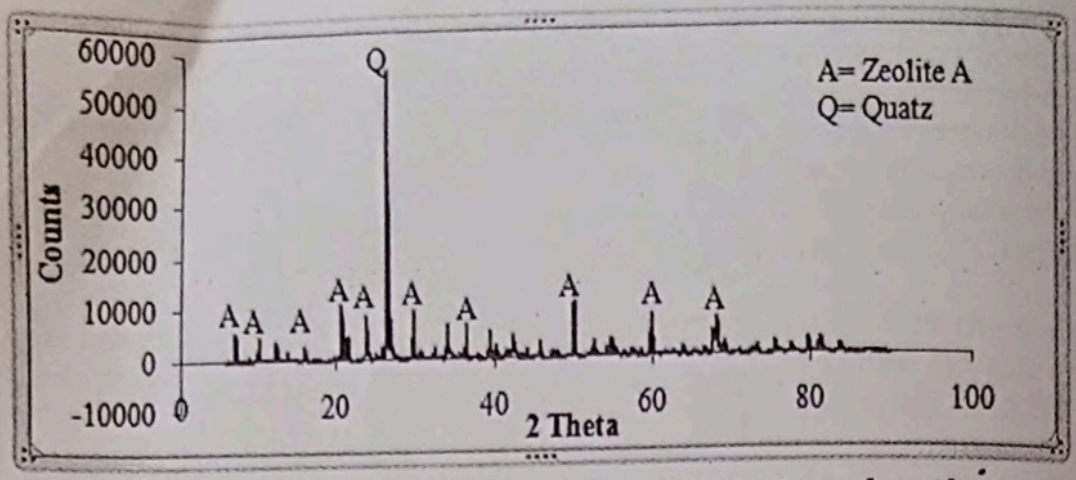

Figure 2: XRD pattern of synthesised Zeolite A at ageing time of 6h and crystallization time of 8h

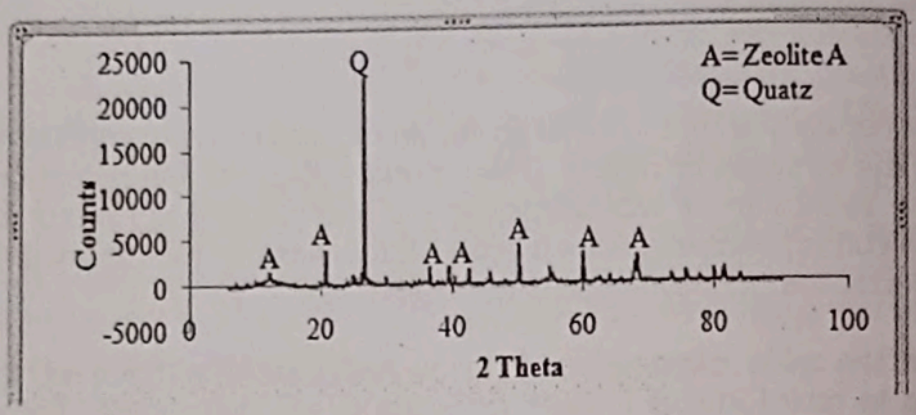

Figure 3: XRD pattern of synthesized Zeolite A at ageing time of 6h and crystallization time of 10 h

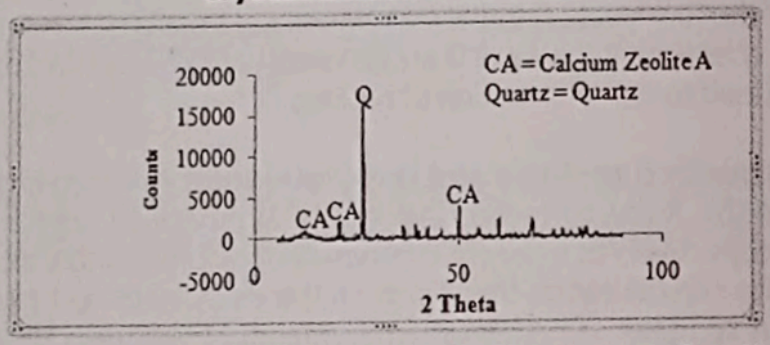

Figure 4: XRD pattern of Calcium rich Zeolite A at ageing time of 6h and crystallization time of 2h

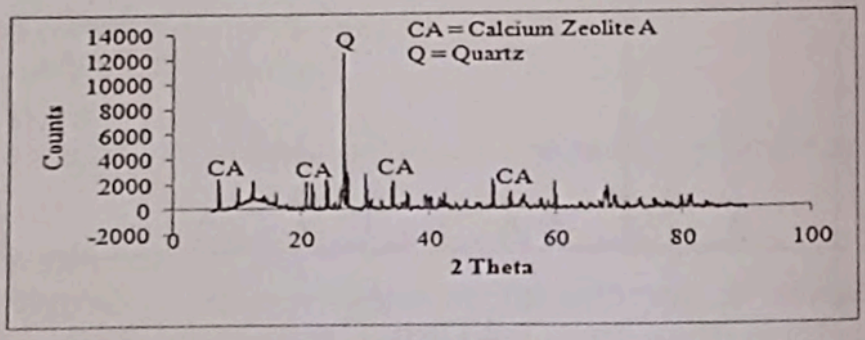

Figure 5: XRD pattern of Ca lcium rich Zeolite A at ageing time of 6h and crystallization time of 8h

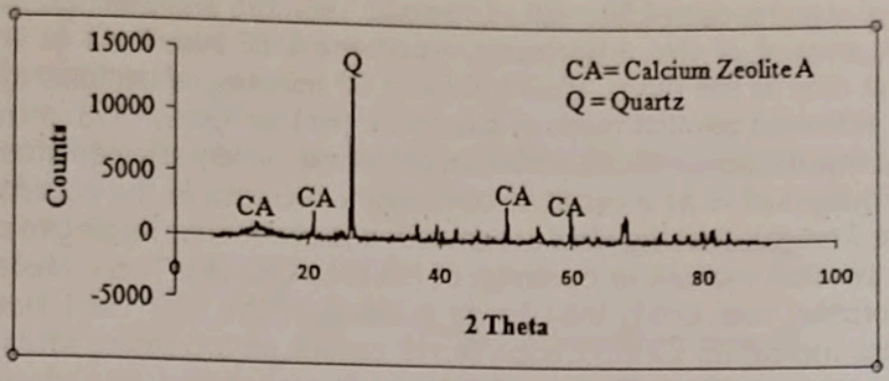

Figure 6; XRD pattern of Calcium rich Zeolite A at ageing time of 6h and crystallization time of 10h

The patterns obtained in Figure 1 compared well with literature [3] with all the diffraction peaks matching with those of standard zeolite A. The result also shows that zeolite A was formed after the ageing periods of 6, 8 and 10hrs studied as depicted in figure 2 and 3. Ageing increases the numbers of nuclei present in the synthesis mixture and growth of more crystals. The result show that zeolite crystallinity increases with increased in ageing period of the synthesis mixture represented from the increase in the intensity of the reflection of the main peak corresponding to the formation of zeolite A. Traces of quartz are found in all patterns at 2 theta= 26.500° indicating the unreactive behaviour of quartz however, quartz does not impair or impede the formation of zeolite A [3]. Also, no reflection was noticed by the first two hour of crystallisation. The reason is likely due to the fact that some time was needed for complete dissolution of the metakaolin from the initial period of heating after mixing of the synthesis gel.

As the crystallization time increased to 8hrs and 10hrs, the XRD pattern shows Zeolite A with moderate crystallinity and peaks at 2 theta= 7.20°, 10°, 12°, 23°, 27° completely matching those from literature. From all these, Zeolite A synthesised at ageing period of 6 hrs and crystallisation time of 10 hrs best matches the standard zeolite A. It is important to note that the moderate intensity of reflection of the main peaks of the results presented in Figures 1-3 may be as result of refined kaolin used in the synthesis. Result for exchanged calcium rich zeolite figures 3.2 is similar to figure 1 except with difference in main peak position similar to calcium rich zeolite. Ageing period of 6hrs and crystallization time of 8hrs best matches the standard calcium rich zeolite.

Adsorption Studies

Effect of Initial Concentration on adsorption of MB

The results of the initial concentration on the adsorption of MB unto the calcium rich zeolite (CRZ) material is as shown in figure 7

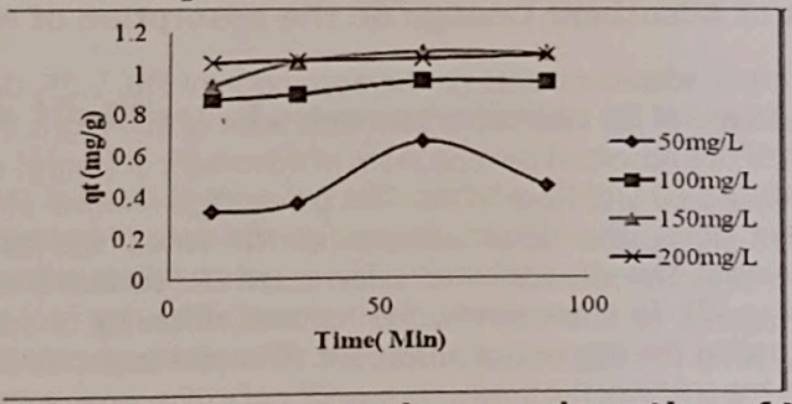

Figure 7: Effect of Initial Concentration on adsorption of MB onto CRZ

In order to achieve accurate effect of MB concentration, 0.5 g of CRZ was added to 50 mL of MB with initial concentrations of 50 mg/L, 100mg/L, 150mg/L and 200mg/L. The results are expressed with amount of dye adsorbed per unit mass of adsorbent **qt (mg/g)** versus different contact time in the range 10, 30, 60 and 90 minutes as depicted in Figure 7. The amount of dye adsorbed per unit mass of adsorbent (**qt**) increases when increasing contact time and occurs that the adsorption equilibrium of MB was rapidly attained after 60 minutes of contact time. Equilibrium is as a result of continuous decrease in the concentration driving force [5]. Figure 7 reveals that the plots are smooth and continuous leading to saturation, that suggesting the possible monolayer coverage of MB onto CRZ [6]. There was an insignificant change in adsorption rate which may be as a result of the CRZ used was being locally synthesised. Also increasing concentration of MB causes an increasing of its concentration equilibrium and amount of equilibrium adsorption. It means that the adsorption is highly dependent on initial concentration of dye. The best effect of initial concentration of MB after adsorption was observed at 50mg/L concentration dye. It is because of the fact that at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the rate of removal of the dye dependents upon concentration [6]. The initial faster rate of removal of MB could be due to the availability of the vacant surface areas of the adsorbents and increase in the electrostatic interaction between the metal ions and the absorbent active sites.

Effect of adsorbent dosage on adsorption of MB

The effects of adsorbent dosage of the CRZ material on adsorption of MB was also carried out as shown in figure 8

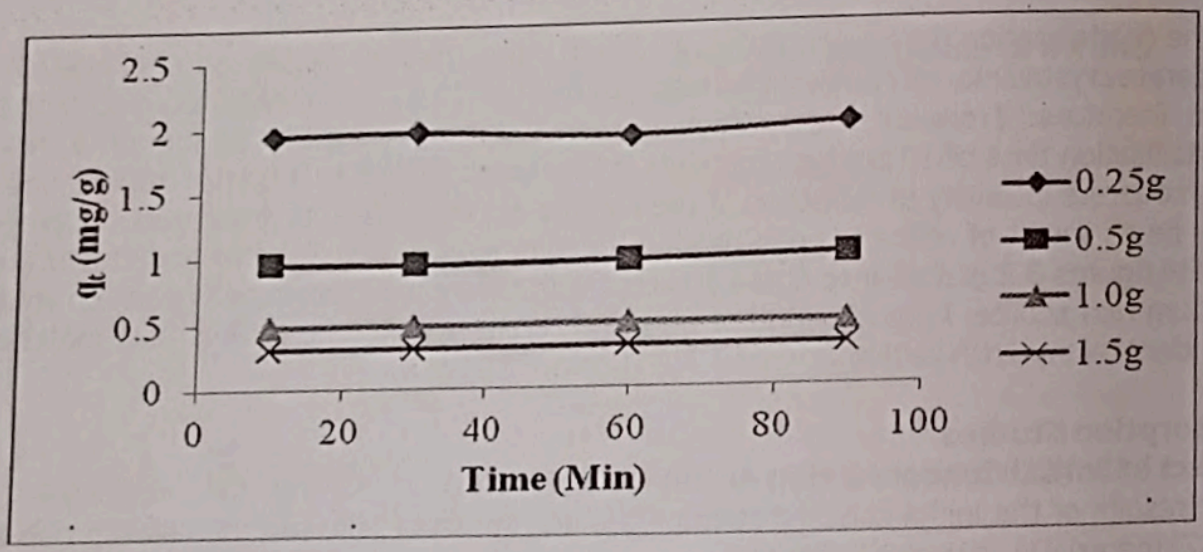

Figure 8: Effect of Adsorbent Dosage on the adsorption of MB onto CRZ

To evaluate the effect of adsorbent dose on the adsorption of MB, 0.25, 0.5, 1.0 and 1.5g of CRZ was added to 50 mL of MB with initial concentrations of 100 mg/L. Figure 8 shows the variation of amount of dye adsorbed per unit mass of adsorbent qt (mg/g) at different contact time in the range 10, 30, 60 and 90 minutes. The percentage removal of MB increases with increasing adsorbent dose. The decolourization of MB varied spontaneously when the adsorbent dose increased, this was attributed to increased CRZ surface area and availability of more adsorption sites [7]. In other words, the removal efficiency of adsorbents generally improved with increasing the amount of adsorbent. This was expected because the higher dose of adsorbent in the solution, the greater availability of exchangeable sites for the ions.

Effect of Temperature on adsorption of MB

The effect of temperature was also studied on the adsorption of MB onto CRZ material at temperatures of 30, 40 and 50°C while other parameters were kept constant. The results are represented in Figures 9

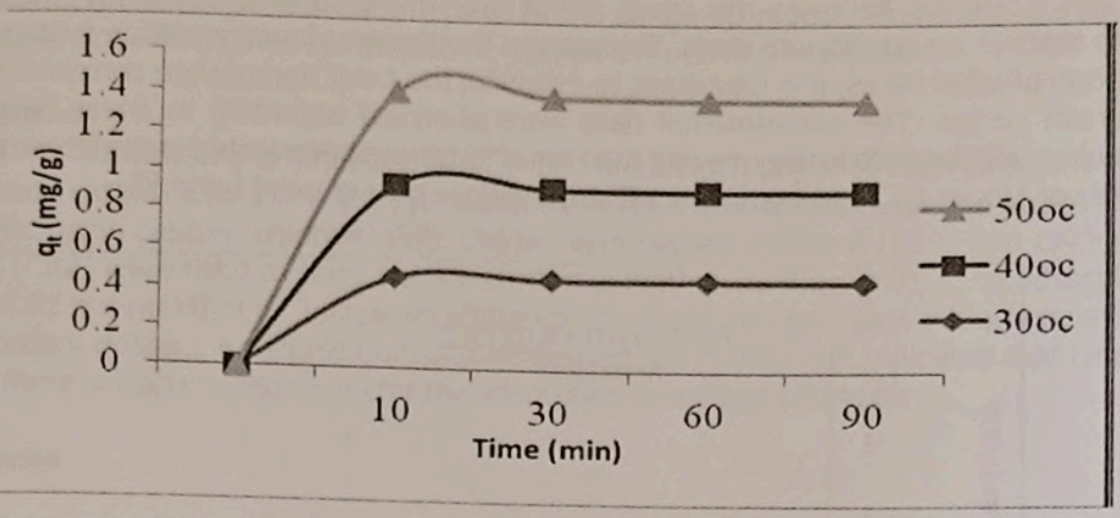

Figure 9: Effects of temperature on adsorption of MB unto CRZ

From Figures 9, the uptake of MB increased with increase in temperature (30, 40 and 50°C) but decreased with increase in contact time. This behaviour has also been reported in previous reports [6]. The increase of dye uptake with temperature rise can be attributed to the increase in the mobility of the dye molecules as the temperature increased, thus, producing a swelling effect within the internal structure of CRZ which enables large dye molecules to penetrate further [8].

Effect of PH on Adsorption of MB

Figure 10 below shows the plot of effect of pH on the adsorption of MB onto CRZ material at pH of 2 to 8.

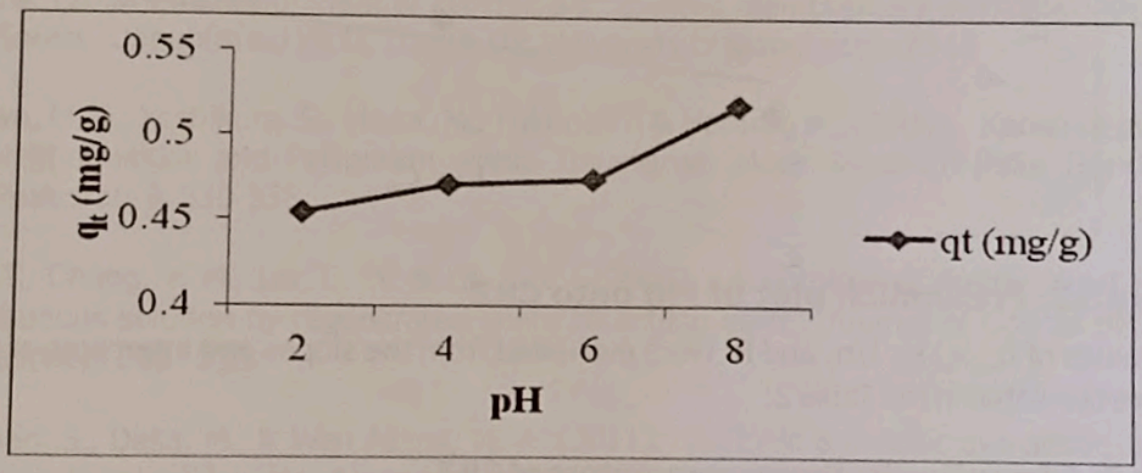

Figure 10: Effect of pH on adsorption of MB onto CRZ

It is observed from above that the adsorption of MB with CRZ increased with increase in pH from 2 to 8 as reported in previous work [6, 9]. This is because the basic pH increases the negative charge on the zeolite surface which in turn causes an increase in adsorption capacity of MB [10]. At a low pH, adsorption is relatively low due to increase in competition for adsorption sites by ion in solution. As the pH increased (pH>7) adsorption increased. The enhanced rate of adsorption with increasing pH implies that the surfaces of adsorbents became

more negatively charged. This is also in accordance with the findings of Abdel-Halim and Al-Deyab [11].

Adsorption Isotherms

Adsorption isotherm is the most important information which indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. The experimental data were analyzed according to linear form of the Langmuir and Freundlich isotherms and their equations have been stated in the literature. The plots of $1/q_e$ vs $1/C_e$ and log q_e vs log C_e are shown in the Figures 11 and 12:

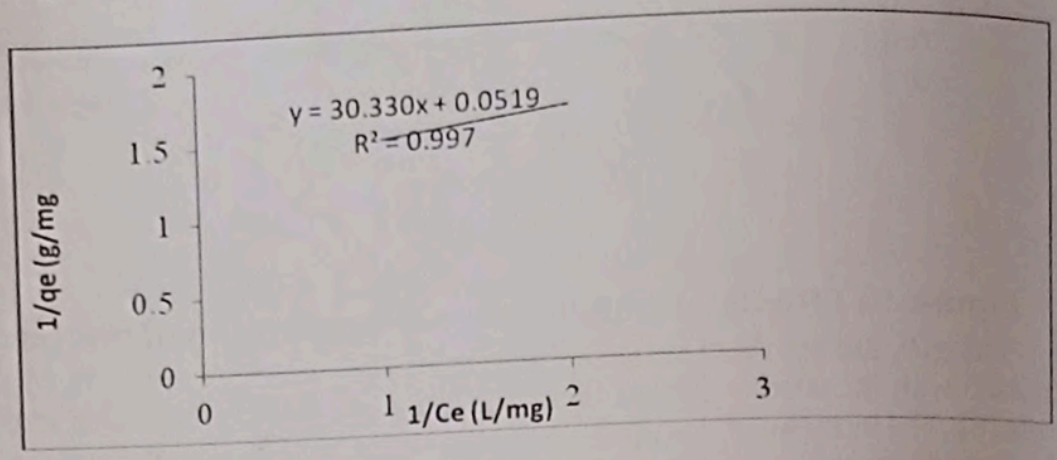

Figure 11: Langmuir plots of MB onto CRZ

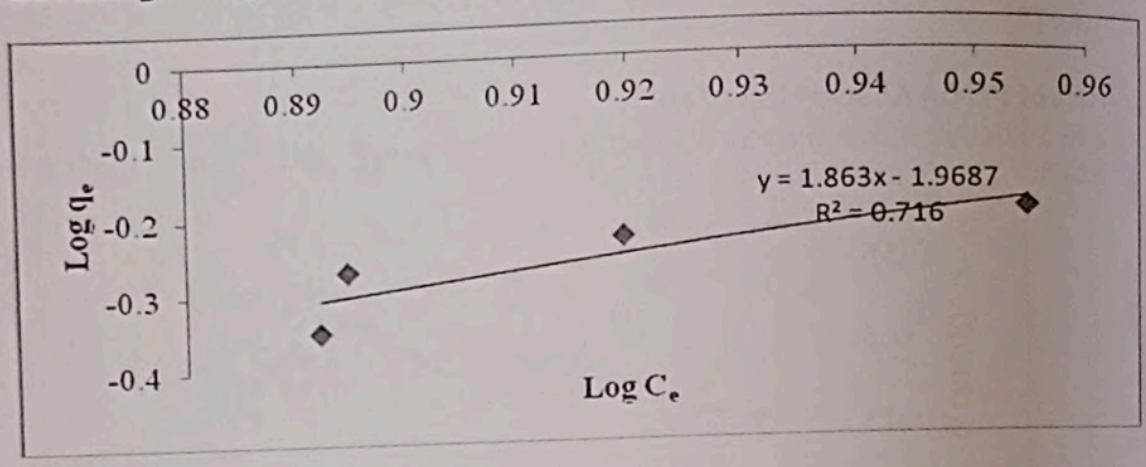

Figure 12: Freundlich plot of MB onto CRZ

The values of q_m, k_a, k_f, 1/n, and R^2 were evaluated from the slopes and intercepts of the plots and are tabulated in the Table 2;

Table 2: Adsorption isotherm parameters of CRZ

Langmuir	
q_m (mg/g)	19.268
K_a (L/mg)	0.032
R^2	0.997
Freundlich	
K_f (L/g)	0.011
1/n	1.863
R^2	0.716

Table 2 shows that the data fitted the Langmuir isothermal model correctly for the studies with R^2 =0.997. Thus, confirming the monolayer coverage of MB onto CRZ particles and also the homogeneous distribution of active sites on the material as assumed by Langmuir equation. The value of K_r is smaller than 1 and it represents the favorable removal conditions and the high affinity for MB. So, the correlation coefficients obtained from Langmuir and Freundlich indicates that the experimental data fits well to the Langmuir model. Therefore, the coverage of MB examined on the surface of the zeolite may be defined as a monolayer.

Conclusions

Zeolite A was successfully synthesized from Ahoko metakaolin obtained from calcination of the refined kaolin at 600°C for 2hrs. The synthesised Zeolite A was ion exchanged to obtain calcium rich zeolite using calcium chloride. Both the as- synthesised zeolite A (SZA) and calcium rich zeolite A (CRZ) were used to carry out adsorption of Methylene Blue (MB). The adsorption of MB onto CRZ showed that it increased with increase in pH, temperature, initial concentration and adsorbent dosage. An equilibrium studies carried out in this work indicated that Langmuir model is more suitable to represent for the adsorption processes taking place.

References

Gupta, S. S. & Bhattacharya, K.G, (2005). Interaction of metal ions with clays: I. A Case study with Pb (II). *Application of clay science*, 30, 199-208.

Cejka, J., Bekkum, H. V., Corma, A. & Scuth, F., (2007). *Introduction to zeolite science & practice.* Study of Surface Science Catalysis 3rd revised Edition. Elsevier, Amsterdam. 69-70 & 377-389.

Ulrke, W. (1981), Experiment on the hydtothermal formation of calcium zeolites. *Clays and Clay Minerals*, 29(3), 171-180.

Kovo, A. S. (2011). *Development of zeolites and zeolites membranes from Ahoko Nigerian Kaolin.* Unpublished Ph.D. Thesis, UK, University of Manchester. P318

Nakagawa, M. S., Yoshikura, S., Miura, M., Fukuda, T. & Harada, A., (2006). Kaolin deposit at Melthonnakkal and Pallipuram within Trivandrum block *Southern India Gondwana Research*, 9, 530-538.

Tsai, W. T., Chang, Y. M., Lai, C. W. & Lo, C. C., (2005). Adsorption of methy violet dye in aqueous solution by regenerated spent bleaching earth. *Journal of Colloid Interface Science*, 289 - 333.

Mohammed, S., Dalia, M., & Wan Azlina, W. A. (2011). Cationic & anionic dye adsorption by agricultural solid waste: A comprehensive review. *Elsevier Desalination*, 280, 1-13.

Ogugbue, C. J. & Sawidis, T., (2011). Bioremediation and detoxification of synthetic wastewater containing triarylmethane dyes by Aeromonas hydrophilia isolated from industrial effluent. Biotechnology Research International; DOI 10.4061/2011/967925.

Ofomaje, A. E. (2008). Sorption removal of methylene blue from aqueous solutions using palm kernel fibre: effect of fibre dose. *Biochemical Engineering Journal*, 40, 8-18.

Acemioglu, B. (2004). Adsorption of Congo red from aqueous solution onto calcium-rich ash. *Journal of Colloid Interface Science*, 273, 371.

Boukadir, D., Bettahar, N., & Derriche, Z. (2002). Synthesis of zeolites 4A and HS from natural material, *Annales de Chimie-Science des Materiaux*, 27, 1-13.

Dogan, K., Eda, A., Sema, T., Ferruh, E., Mehnet, A., & Mustafa, T. (2007). Basic & reactive dye removal using natural and modified zeolites. *Journal of Chemical Engineering Data*, 52, 2436-2441.

materials from proximate analysis, *Thermochim. Acta* 164, 135.

Orfao, J.J.M., Antunes, F.J.A., Figueiredo, J.L. (1999). Pyrolysis kinetics of lignocellulosic materials – Three independent reactions model, *Fuel 78, 349*–358,

Font, R. A. Marcilla, E. Verdú and J. Devesa: (1991). Thermogravimetric kinetic study of the pyrolyisis of almond shells and almond shells impregnated with CoCl2. *J. Anal. Appl. Pyrolysis,* 21 , 249-264.

Koufopanos, C.A., Lucchesi, A., Maschio, G. (1989). Kinetic modelling of the pyrolysis of biomass and biomass components, Can. J. Chem. Eng. 67, 75-84.

Rao, T.R. A. (1998). Sharma, Pyrolysis rates of biomass materials, *Energy* 23, 973-978.

Liangfeng S., J. Y. Chen, I. I. Negulescu, M. A. Moore, B. J. Collier (2011). Kinetics modeling of dynamic pyrolysis of bagasse fibers, *Bioresource Technology,* Vol. 102, No. 2, 1951–1958.

Rajeev S., Sheth, P. N., Ashish M. (2016) Kinetic modeling and simulation: Pyrolysis of Jatropha residue de-oiled cake Renewable Energy 86, 554-562

Vamvuka, D., Sfakiotakis, S. (2011). Effects of heating rate and water leaching of perennial energy crops on pyrolysis characteristics and kinetics. *Renewable Energy* 36, 2433-2439

Wang X., Xin-jun, W., Ming-qiang, C. Jun, W. (2012). Kinetic model of biomass pyrolysis based on three-component independent parallel first order reactions, *the Chinese Journal of Process Engineering*, vol. 2, No. 6

Pasangulapati, V., (2012). Effects of cellulose, hemicellulose and lignin on thermochemical conversion characteristics of the selected biomass, *Bioresource Technology*, 114, 663-669.

Sanchez-Silva' , L., López-González, D., Villaseñor, J., Sánchez, P., Valverde, J.L. (2012) Thermogravimetric–mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis, *Bioresource Technology,* Vol. 109,163-172.

Jeguirim M. and Trouvé, G. (2009). Pyrolysis characteristics and kinetics of Arundo donax using thermogravimetric analysis, *Bioresource Technology*, Vol. 100 No. 17, 4026-4031.

Vamvuka, D., Kastanaki, E., Grammelis P. and Kakaras, E. (2003). Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite, Fuel Vol. 82, 1949-1960.

Xiong, S., Zhuo, J., Zhou, H., Pang, R., and Yao, Q., (2015). Study on the co-pyrolysis of high density polyethylene and potato blends using thermogravimetric analyser and tubular furnance. *J. Anal. Appl. Pyrolysis,* Vol. 112, 66 -73