



Synthesis of Zeolite A from Nigerian Ahoko Kaolin and its Functionalization for Adsorption studies of Methylene Blue

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ABSTRACT

The Synthesis and functionalization of Zeolite A from Nigerian Ahoko Kaolin for adsorption studies of Methylene blue (MB) was studied in this paper. Zeolite A was successfully synthesised from metakaolin earlier developed from refined kaolin using conventional hydrothermal method. The synthesised zeolite A was thereafter functionalized using Hexamethyltetraamine (HMTA) and characterized. The effect of initial concentration, adsorbate dosage, pH, temperature and contact time were studied in a batch adsorption system for both unfunctionalized zeolite (UFZA) and functionalized zeolite A (FZA) under the following condition of initial concentration of 100 mg/l, temperature of 303 K, and pH of 7. The adsorption rate increases with increase pH, temperature, initial concentration but decrease with adsorbent dosage for both UFZA and FZA. Langmuir, Freundlich and temkim isothermal were also investigated and was found out that Langmuir isotherm is the most suitable. The pseudo-first order and pseudo-second order kinetic equation were evaluated and adsorption of MB onto UFZA and FZA followed the later. The thermodynamic studies indicate that adsorption of MB onto UFZA and FZA are spontaneous and endothermic reaction.

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Introduction

Dyes are important substances which find applications in many chemical industries such as dyeing, plastics, leathers, paper and pulp (Nigam P, 2000). There are over 100,000 commercially available dyes with over 7x 10⁵ ton of dye stuff produced annually (Nigam P, 2000). Dyes are classified as acidic, basic, direct, disperse, reactive, sulphur and vat. These different dye stuffs appear in effluent of some industrial wastewater (Ghoreishi, 2003) as shown by studies and are very difficult to remove, due to their recalcitrant organic molecules, resistant to aerobic digestion and their stability to light (Fu, 2001). Thus, posing great danger to the ecosystem because it is highly visible, even in small amount and this influences the water environment considerably. Also, their ability to reflect sunlight has drastic effect on the growth of bacteria and biological activities (Fu, 2001). Hence, there is need for extensive research to find the effective and efficient alternative for the removal of dyes.

The technologies used in removal of dyes is divided into three categories; biological, chemical and physical (Robinson, 2001). The physical (adsorption) has been recognized as a potential technology for dye removal because it is economical, effective and has simple design. However, the nature of adsorbate and its substituents greatly affects the adsorption process. Likewise, the properties of adsorbent 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 (Gupta, 2005).

Activated carbon has been the most popular adsorbent and has been used with great success. This is due to its high adsorption capacity, high surface area, micro porous structure and high degree of surface reactivity. But, its application is limited due to high cost and minimal decomposition, which may

cause more environmental problems (Robinson, 2002). This has led to studying the feasibility of using inexpensive alternative materials by many investigators and these include clay (Bingol, 2010), sepiolite (Bingol, 2010), egg shell (Arami 2008), zeolite (Turan, 2005), wheat and rice (Aydin, 2008) among others. However, zeolite A has rarely been reported. More so, adsorption of dyes onto functionalized zeolite A has not been investigated. Zeolite A is the first synthetic zeolite made from Na, Si, and Al at Linde's laboratory in Towanda, NY (Chester, 2009). It has a three dimensional pore system and molecules which can diffuse in all three directions in space by moving across the 8- ring windows that connect the cavities. The windows have a free diameter of approximately 40Å. It can be hydrothermally synthesised from silica and alumina chemical sources or kaolin as the starting material. Even though, studies reveals that zeolites synthesised using kaolin as the starting material are relatively cheaper than using commercial chemicals (Rios, 2009) because of the abundance of principal raw materials on earth. However, they are always contaminated with trace amount of iron, titanium, calcium, magnesium, feldspar and quartz, which are originally present in the natural kaolin. Such elements might influence the brightness, hardness, catalytic and electrical properties of the zeolites (Rios, C.A.,2009).

The main advantage of zeolite A like every other synthetic zeolite over naturally occurring ones is that they can be engineered with a wide variety of chemical properties and pore sizes to suit a particular purpose. They also have greater thermal stability and their manufacturing processes usually require less time than the 50- 50,000 years prescribed by nature . Above all, they are environmentally friendly.

Zeolite A can be functionalized using hexamethylene diamine (HMDA), hexadecyltrimethylammoniumbromide

(HTAB), or n-octadecyltrichlorosilane. After functionalizing with any of these cationic surfactants, the organic groups are attached to the surface of the zeolite A which largely changes the surface properties (Dai, J.C., 1991). This in turn enlarges the surface area, thus, increases its adsorption capacities and its range of applicability. The physical, chemical and biological properties of functionalized adsorbents are different from the original adsorbent (Jiuhui, Q.U., 2008). This paper presents our work on the synthesis of zeolite A from kaolin and its functionalization for adsorption studies of methylene blue.

Materials and Methods

The raw kaolin used in this work was collected from Ahoko, Kogi state of Nigeria. 100g of Ahoko kaolin collected was crushed using mortar and pestle, sieved using 250 mesh and thoroughly washed with distilled water. It was allowed to freely settle and the supernatant was collected. The supernatant was allowed to settle for 24hrs and the settled clay was obtained by decantation. The clay obtained was then dried overnight using GENLAB oven at 100°C

The metakaolinization process was carried out by firstly producing smaller particles of the refined kaolin with the aid of mortar and pestle and sieved using 250 mesh. 100g of the sieved sample was kept in crucibles and were then put into the furnace and calcined at a temperature of 600°C for a period of 1hr

The synthesis of Zeolite A was based on 3.165Na₂O:Al₂O₃:1.926SiO₂:128H₂O batch composition (Cejka, J.,2007). The synthesis gel was formed by dissolving 6.6 g of NaOH in 60ml of distilled water and 5.7 g of metakaolin was added to it. The resulting gel was then aged at an ageing period of 36hrs at a room temperature on a magnetic stirrer before crystallizing it in an oven at 100 °C at crystallization time of 10 hrs. The crystallized products were allowed to cool and washed severally with distilled water until the filtrate became very clear. After which, they were dried in an oven for a period of 4hrs. The reaction products were analysed using X-ray diffraction (XRD) and scanning electron microscope (SEM). For the functionalization, 10⁻² M HMDA was prepared and mix with 150 g of synthesised zeolite A. This mixture was stirred at room temperature for 4 hrs at 300 rpm before separating the zeolite A from the mixture by filtration; it was then washed using distilled water and dried in the oven at 100 °C for 12 hrs. Fourier Transform Infrared Spectroscopy (FTIR) was used to confirm the modification. BET Nitrogen adsorption was used to determined the pore size and surface area of zeolite A obtained at 10 h and its functionalized state.

Batch adsorption technique was employed in evaluating the rate and equilibrium data because of its simplicity. Equilibrium isotherms were obtained by studying the adsorption process at different initial dye concentration, pH, temperature and adsorbent dosage. The effect of pH was observed by varying the pH from 2- 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 0.5, 1, 1.5 & 2g/l. 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 concentration were estimated at maximum wavelength of 662nm corresponding to maximum absorbance for MB.

Results and Discussions

The characterization of adsorbents: the raw kaolin, the UFZA and FZA were characterized using XRF, XRD, SEM, FT-IR, and BET N₂ adsorption. The results of XRF of raw and refined

kaolin was shown in table 1 while the SEM image of the refined kaolin is presented in figure 1. The table shows that the raw kaolin contains 79.08% of SiO₂ but after refining, it reduces to 60.96%. The SEM reveal clearly kaolinite particles with varying sizes. These come with a low aspect (crystal-width to thickness) ratio. Apart from the usual pseudo-hexagonal platelet which is still visible, rough edge are also observed in most of the particles, however the observed platelets show thinness of kaolinite flakes indicating finesse of the kaolinite surface. The SEM also reveal highly ordered and crystalline particles, an indicative of the refinement that have taken place and removal of non-clay mineral with a lot of influence on the crystallinity of the starting material. The XRD results for both UFZA & FZA as shown in figure 2 & 3 revealed several peaks depicting zeolite A crystals. All the peaks of zeolite A such as 2 theta = 7.20°, 10°, 12° completely match those of standard zeolite A sample. The functionalization did not completely change the crystallinity but the insertion of the anion that open up the pore or channel take place. some Impurities seen such as quartz, mica, are not unusual (Eva, 2001) and it can also influence their adsorption capacities. The SEMs (Not shown) of UFZA and FZA indicate an uneven platelets with low porosity but after functionalization with HMTA, uneven platelets with voids were found. The BET revealed that the surface area of UFZA and FZA were 21.11m²/g and 21.46m²/g respectively.

Table 1 X-Ray Fluorescence Analysis of Raw and Refined Nigerian Ahoko kaolin

Sample	Elemental composition, %				
	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	Fe ₂ O ₃
Raw Ahoko kaolin	79.08	17.148	0.023	0.5	1.065
	1.588	0.113	0.005		
Refined Ahoko kaolin	60.958	33.832	0.12	0.602	1.871
	1.469	0.191	0.002		

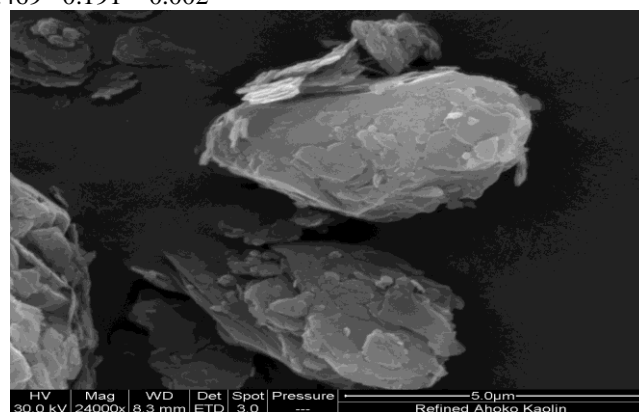


Figure 1 : SEM image of refined Ahoko kaolin

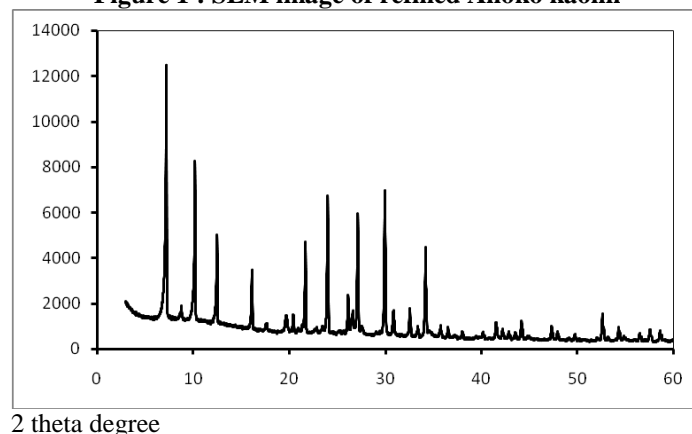


Figure 2. XRD pattern of synthesised UFZA

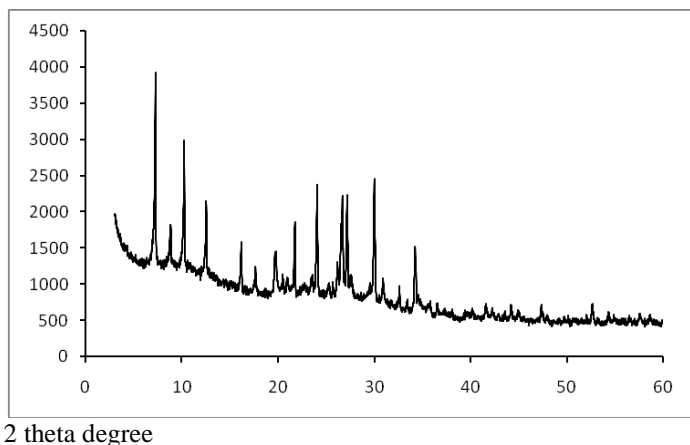


Figure 3. XRD pattern of FZA

The FT-IR spectra: The FT-IR spectra of both synthesised and functionalized zeolite A were done in the range of (500- 4000) cm^{-1} and (500- 4500) cm^{-1} respectively to study the effect of cationic surfactant on the zeolite A as shown in figure 4 & 5. It can be deduced that the peaks shown at (423.31 and 1438.94) cm^{-1} in figure 2a and (433.03 and 1440.87) cm^{-1} in figure 2b are as a result of symmetric stretching vibrations of SiO_4 and adsorbed water in the zeolite (Korkua and Prasetyoko, 2006). The drastic decrease in the peak of the bands is as a result severity of the cationic treatment on the zeolite A as observed at peak 2353.2 cm^{-1} . This is also an indication of vibration stretching of $-\text{CH}_3$ group of HMTA (Zhaohui, 2005).

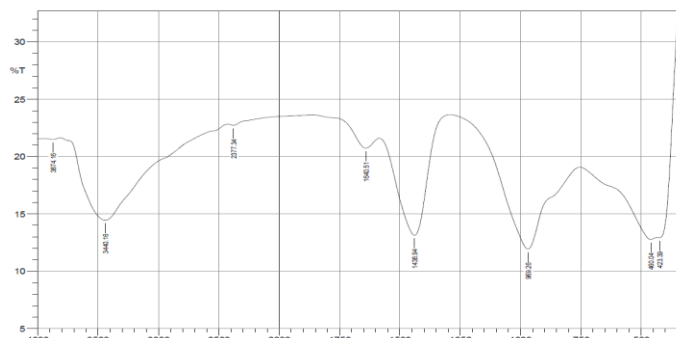


Figure 4. FT-IR of synthesised zeolite A

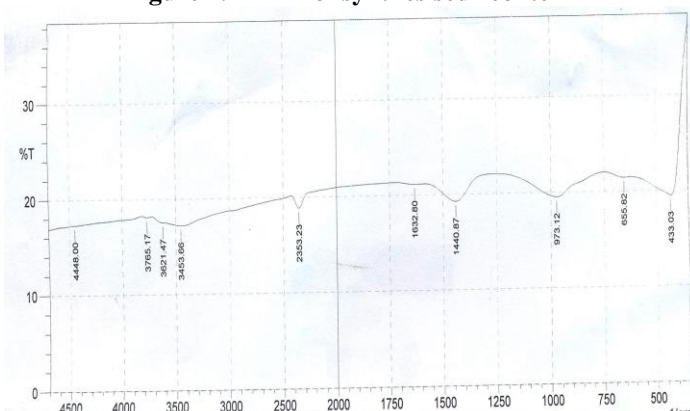


Figure 5. FT-IR of functionalized zeolite A

Adsorption Studies

Effect of pH on adsorption of MB

One of the most important variables that influence adsorption studies is pH. It does not only influences the surface charge of the adsorbent but also the degree of ionization of the present material in the solution, the dissociation of the functional groups on the active sites of the adsorbent and also the chemistry of the dye solution (Crini, 2008, and Nandi, 2009). The effect of pH was investigated on adsorption of MB on both

UFZA and FZA as shown in the figure 6 (range of 2- 8, initial concentration of 100mg/L, temperature of 30°C and adsorbent dosage of 2g/L).

From the figure, it was observed that the adsorption of MB increases with increasing pH as reported in previous work (Tsai, 2005 and Wang, 2005). This is because the optimum pH as frequently reported is 7 (Nandi, 2005) and at a lower pH, the zeolite A surface acquires positive charge resulting to electrostatic repulsion between the cationic dye molecules and zeolite A. In addition, the surface of zeolite A is more negative at higher pH leading to the increase in adsorption capacity of MB (Ho, 1999)].

Effect of initial concentration on adsorption of MB

From figure 7 and 8, it is evident that the adsorption of methylene blue onto unfunctionalized and functionalized zeolite A increases with increase in initial concentration and contact time. This is consistent with the earlier reports (Gunasekar, 2013, Hameed, 2008, Ponnusami, 2008 and Ponnusami, 2009). It was also noticed that the rate of uptake increases gradually until equilibrium were attained before decreases at 90mins of contact time due to continuous decrease in the concentration driving force (Tsai, 2005).

The equilibrium adsorption capacity was achieved at 60mins for both unfunctionalized and functionalized zeolite A. However, it is obvious that the adsorption rate was higher in functionalized zeolite A than unfunctionalized one. This is because; the functionalized one has a larger surface area than unfunctionalized one as shown in BET analyses.

Effect of Adsorbent dosage on adsorption of MB

The effects of adsorbent dosage of UFZA and FZA on adsorption of MB were also investigated as shown in figure 11 and 12. It could be deduced that the uptake of dye decreases as the adsorbent dosage increases for both UFZA and FZA. This is as a result of increment of fraction of active sites which are saturated with dye at smaller adsorbent dosages (Gunasekar, 2013 and Ho, 1999). It is also evident that the rate of adsorption increases with contact time and was more rapid at adsorbent dosage of 0.5g which is considered to be the critical dose, after which the adsorption rate decreases with increases in adsorbent dosage. This was reported in previous work (Tehran- Bagha, 2011) and can be attributed to the splitting effect of concentration gradient between the adsorbent and adsorbate (Nandi, 2009).

Effect of temperature on adsorption of MB

The effect of temperature was also studied on the adsorption of MB onto UFZA and FZA at temperatures of 30°C, 40°C & 50°C while other parameters were kept constant. These are represented on figure 9 & 10. As could be seen, the uptake of dyes increases with increasing temperature but decreases with contact time. This is also reported in previous reports (Gupta, 2003 and Shiau, 2004). The increase of dye uptake with temperature rise can be attributed to the increase in the mobility of the dye molecules as the temperature rises, thus, producing a swelling effect within the internal structure of zeolite A which enables large dye molecules to penetrate further (Acemioglu, 2004). This is a clear indication of chemisorptions mechanism for adsorption of MB by UFZA & FZA (Tsai, 2005).

Adsorption isotherms

The equilibrium relationship between the adsorbent and adsorbates were also evaluated by adsorption isotherms. There are several isotherms models used in analysing the experimental data and equilibrium of adsorption. Langmuir, Freundlich, and

Temkin equations were tested in this work and their equations are stated below;

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_a q_m C_e} \dots\dots\dots 1$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots\dots\dots 2$$

$$q_e = B \ln A_T + B \ln C_e \dots\dots\dots 3$$

where, $B = \frac{RT}{b_T}$.

Where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), q_m & b are the Langmuir constant related to the maximum adsorption capacity (mg/g) and energy of adsorption (L/mg), K_f is the Freundlich constant, T (K) is the absolute temperature, R is the universal gas constant (8.314J/molK). The plots of $1/q_e$ vs $1/C_e$, $\log q_e$ vs $\log C_e$ and q_e vs $\ln C_e$ are shown in the figure 13,14,&15;

The values of q_m , k_a , k_f , $1/n$, A_T , B_1 , & R^2 were evaluated from the slopes and intercepts of the plots and are tabulated as shown in the table 2; From the table, it could be deduced that Langmuir is more suitable because it has highest value of R^2 and for the FZA which has the lowest R^2 simply indicated that the UFZA is better than FZA in all cases.

Adsorption kinetics

In order to investigate the mechanism of sorption, the characteristic constant of adsorption were evaluated using pseudo- first order equation of Lagergren and pseudo- second order kinetic models and their equations are stated below;

$$\log(q_e - q_t) = \frac{1}{q_e} - \frac{k_2}{2.303} t \dots\dots\dots 4$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \dots\dots\dots 5$$

Where k_1 (1/min) is the Lagergren rate constant of adsorption, k_2 is the pseudo – second order rate constant in (g/mg.min). The linear plot of $\log (q_e - q_t)$ vs time and t/q_t vs time are shown elsewhere. The values of k_1 , k_2 , R^2 , & q_e were evaluated from the slopes and intercepts of the plots and are tabulated as shown in the table 3;

From the table above, it is evident that the sorption of MB onto UFZA and FZA conform to pseudo- second order kinetics.

Thermodynamics of Adsorption

Thermodynamic parameters such as Gibb’s free energy, ΔG , the enthalpy ΔH , and the entropy ΔS were also evaluated as they are the actual indicators for the practical applications of a process. The parameters were determined from the equations as discussed in the literature review while K was obtained from the equation stated below;

$$K = \frac{q_e(t)}{C_e(t)} \dots\dots\dots 6$$

Where K is the equilibrium constant, $q_e(t)$ mg/g is the adsorption capacity of MB at time t and $C_e(t)$ is the equilibrium concentration of MB at time t . A plot of $\ln K$ vs $1/T$ was plotted and shown in the figure 16 below

ΔH^0 & ΔS^0 were evaluated from the slopes and intercepts of the plots respectively while the ΔG^0 were calculated from the equations 2.7.1 in the literature review and they are tabulated in the table 4 below

The positive values of ΔH^0 indicate that the adsorptions of MB onto UFZA & FZA are endothermic reactions as supported by the increase in adsorption of MB with increase in temperature. Also, the positive values of ΔS^0 shows that

randomness increases at the solid- solution interface (Nuhoglu, Y., 2009). The negativity of ΔG^0 indicates that the adsorption process of MB is spontaneous and the increase in the negativity demonstrates that at higher temperature, the rate of adsorption of MB unto UFZA & FZA increases (Kalavathy, M.H., 2005).

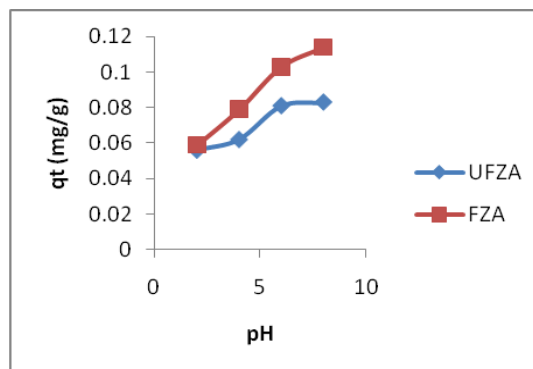


Figure 6. Effect of pH on adsorption of MB

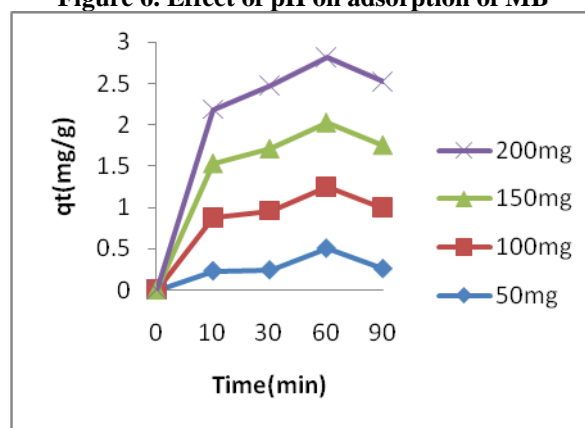


Figure 7. Kinetics of MB onto UFZA & FZA

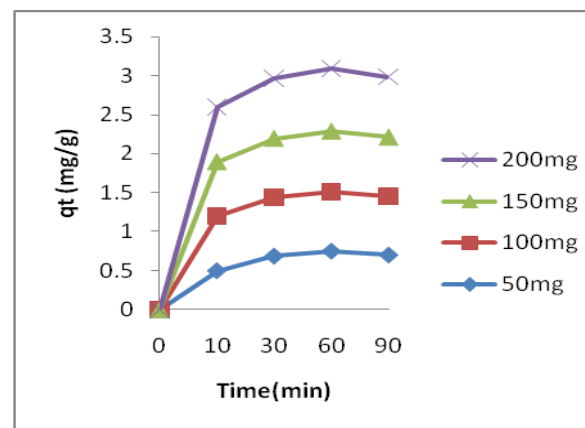


Figure 8. Kinetics of MB onto FZA

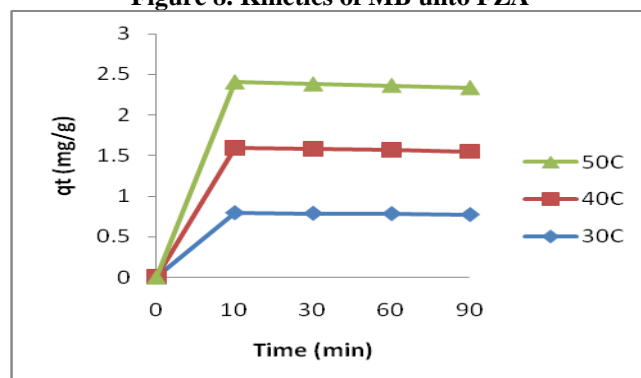


Figure 9. Effect of temperature on adsorption of MB onto UFZA at pH=7

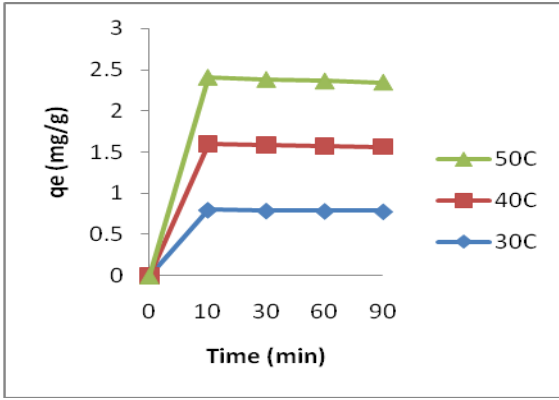


Figure 10. Effect of temperature on adsorption

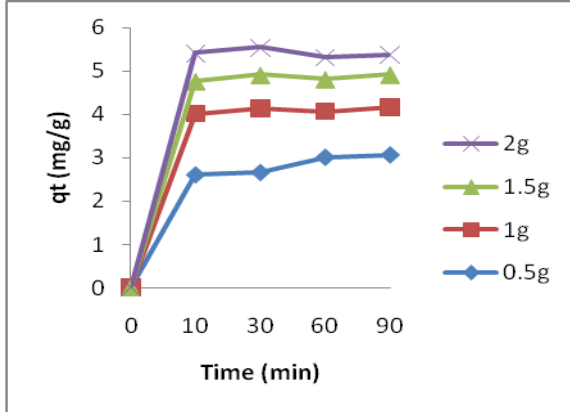


Figure 11. Effect of adsorbent dosage on Of MB unto FZA (pH=7, D= 2g/L) adsorption of MB unto UFZA at pH=7

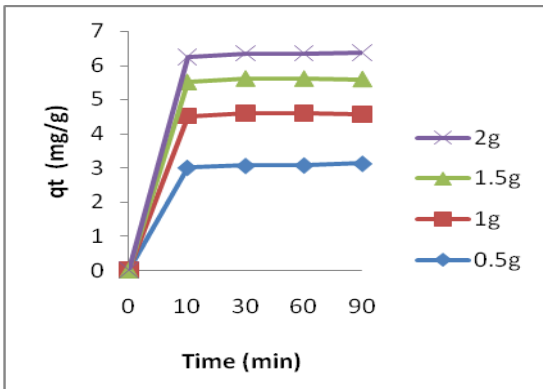


Figure 12. Effect of adsorbent dosage on Isothermal model

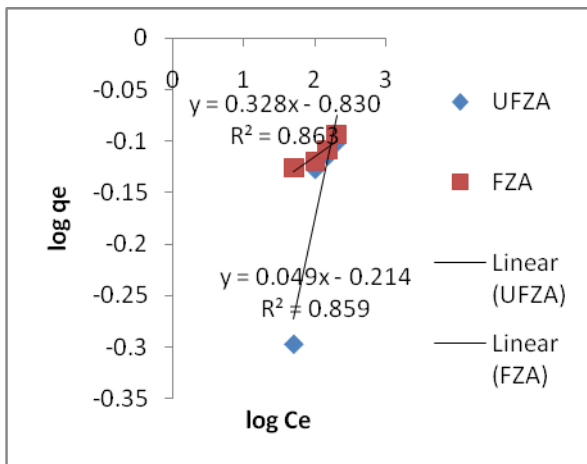


Figure 13. Linearized plot of Langmuir Adsorption of MB unto FZA (pH=7, D=2g/L)

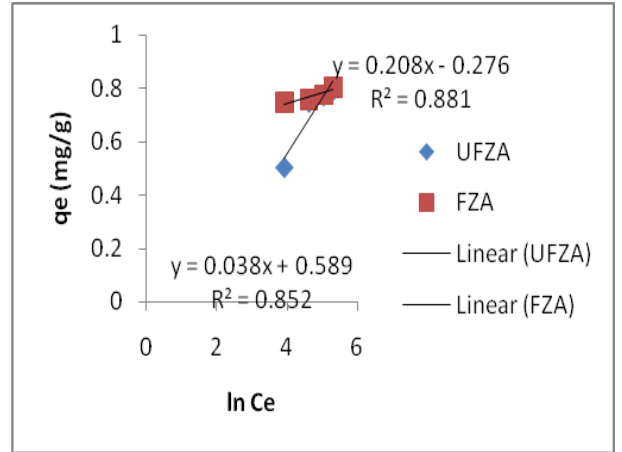


Figure 14. Linearized Freundlich plot

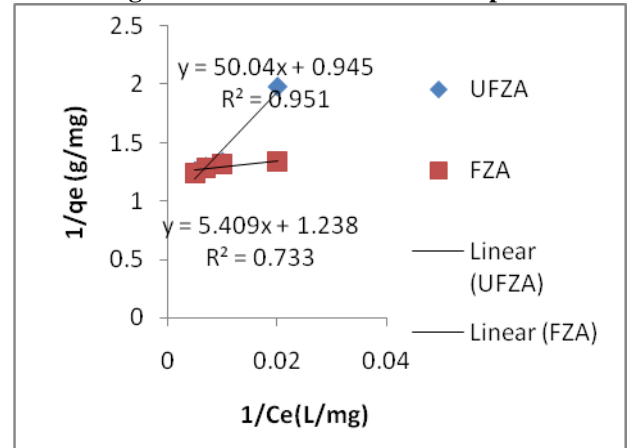


Figure 15. Linearized Temkin's plot

Table 2. Adsorption isotherm parameters

	UFZA	FZA
Langmuir		
qm (mg/g)	1.058	0.8075
K _L (L/mg)	0.019	4.368
R ²	0.952	0.7332
Freundlich		
K _f (L/g)	0.148	0.611
1/n	0.328	0.050
R ²	0.864	0.859
Temkins		
A _T (L/mg)	0.265	0.039
B ₁	0.208	
R ²	0.881	0.853

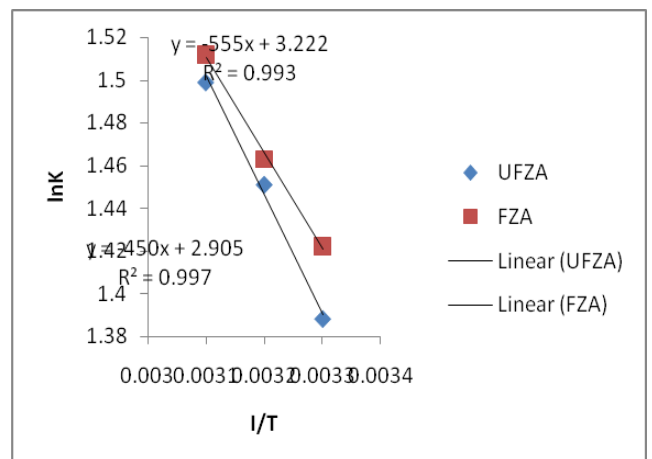


Figure 16 plots of ln K vs 1/T

Table 3. Adsorption kinetics values of MB on UFZA & FZA at 30°C, pH 7 and 200 rpm agitation speed

Dye (mg/L)	Pseudo first order				Pseudo second order					
	UFZA		FZA		UFZA			FZA		
	K_1 (1/min)	R^2	K_1 (1/min)	R^2	q_e	K_2 (g/mg min)	R^2	q_e	K_2 (g/mg min)	R^2
50	0.004	0.127	0.004	0.535	0.294	-3.946	0.816	0.741	0.441	0.994
100	0.002	0.670	0.001	0.526	0.754	0.888	1.00	0.760	2.289	1.00
150	0.002	0.533	0.001	0.494	0.768	1.190	0.999	0.769	2.490	0.999
200	0.002	0.498	0.001	0.467	0.784	1.125	0.999	0.789	2.038	0.999

Table 4 Thermodynamic parameters of adsorption of MB unto UFZA & FZA

ΔG^0 (kJ/mol)		ΔH^0		ΔS^0	
303K	313K	323K	(kJ/mol)	(J/K.mol)	
UFZA	-3.50	-3.771	-4.039	4.614	
26.79					
FZA	-3.599	-3.821	-4.062	3.741	
24.16					

Conclusions

Zeolite A was successfully synthesised from kaolin and functionalized for adsorption studies of MB. The result showed that synthesised zeolite A from kaolin can be conveniently functionalized with cationic surfactant for removal of MB. The raw kaolin, UFZA, FZA were characterized using XRF, XRD, SEM, FT-IR and BET Nitrogen adsorption. The adsorption of MB unto UFZA & FZA increases with increase in pH, temperature, initial concentration while it decreases with adsorbent dosage. Isothermal models indicated that a Langmuir model is most suitable and it conforms to pseudo- second order kinetics. The thermodynamic studies show that the adsorptions of MB unto UFZA & FZA are spontaneous and endothermic reactions.

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