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KINETIC AND THERMODYNAMIC ADSORPTION STUDIES OF METHYLENE BLUE ONTO ZEOLITE FROM AQUEOUS SOLUTION

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ABSTRACT
Zeolite was synthesized via hydrothermal method from sodium metasilicate and sodium aluminate solutions. The prepared sample was characterized by Fourier transform infrared (FTIR) spectroscopy, Scanning electron microscopy (SEM) and X-ray diffraction (XRD).The adsorption of methylene blue dye onto zeolite was studied. The adsorption experiments were carried out in batches and the effect of parameters such as concentration, pH, adsorbent dosage, temperature and contact time were investigated. The experimental data were fitted into the Langmuir and Freundlich Adsorption Isotherm. The result was fitted into pseudo- first order and pseudo- second order kinetic models. The thermodynamic parameters were also evaluated. The results revealed that maximum adsorption of methylene blue dye was achieved at a concentration of 20 mg/L and pH of 8.9. The adsorption process followed a Langmuir adsorption isotherm model with a correlation coefficient value of 0.9911. The negative value of standard enthalpy of adsorption, ΔH^o calculated as -9.4 $kJmol^{-1}$ revealed the exothermic nature of the adsorption process, the negative value of standard entropy of adsorption, ΔS^o evaluated as -20.6 $Jmol^{-1}K^{-1}$showed that no significant change occurs in the internal structures of zeolite during the adsorption process and the negative value of Gibbs free energy, ΔG^o obtained as -3.28 $kJmol^{-1}$indicated the spontaneity of the adsorption process.

Keywords: Zeolite, Adsorption, Kinetics, Thermodynamic parameter, Methylene blue.

INTRODUCTION

Dyes have been extensively used in industries, such as textile, plastic and food to color their products. The discharge of dyes into water bodies by these industries is a threat to the environment due to their persistent nature. Besides, they are carcinogens and mutagens, while they appear inert and non-biodegradable when released into water streams (Ozer *et al.,* 2007).

Dye molecules possess diverse structures, which enables them to be reclassified in several ways; either based on their chemical structures or either application with specific types of fiber (Mahammedi and Benguella, 2016). Methylene blue (MB) is a cationic thiazine dye whose presence in surface and underground water is harmful to human beings and aquatic life because it is toxic to the reproductive system, neural tissue and skin (Wei *et al*., 2015). Therefore, the removal of methylene blue from industrial effluent is essential. Various physicochemical techniques have been investigated for dye removals such as biological treatment, adsorption, coagulation, reverse osmosis, ozonation, ultrafiltration, precipitation and electrochemical processes (Allouche and Yassaa, 2018). Adsorption was found to be the most effective process for the treatment of wastewater in terms of simplicity of design, ease of operation and insensitivity to toxic substances (Tong *et al*., 2010). Activated carbon is the most commonly used adsorbent due to its high adsorption capacity. However, because of its high cost and difficulty of regeneration, cheaper and more effective adsorbents such as zeolite (Zhiming *et al.,* 2018), clays like kaolin (Gougazeh and Buhl, 2013) and bentonite (Almeida *et al*., 2009) are alternative low-cost adsorbents. Different zeolites have been used for the removal of pollutants in wastewater because of their properties and characteristics (Donat *et al*., 2004). Zeolites are crystalline, microporous hydrated aluminosilicate of alkaline or alkaline earth metals. The aluminum ion (Al^{3+}) occupies the position in the center of the tetrahedron of four hydrogen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative ion in the lattice. The net negative charge is balanced by the exchangeable cations in the solution (Barer, 1987).
This study investigates the effectiveness of zeolite for the adsorption of methylene blue dye from aqueous solution and the mechanism of the adsorption process.

MATERIALS AND METHODS

Sodium metasilicate solution (Na_2SiO_3), sodium hydroxide, sodium aluminate ($NaAlO_2$), methylene blue, pH meter, Thermometer, Magnetic stirrer and Thermostatic shaker bathe. All the reagents used were of analytical grade.

Hydrothermal Synthesis

Sodium hydroxide (40 g) was dissolved in 300 ml of de-ionized water. This solution was divided into two portions. To the first portion of the solution, sodium aluminate (12.8 g) was added. To the second portion, sodium metasilicate (10.6 g) was added. These mixtures were stirred. The two portions were poured simultaneously into a Teflon container, resulting in the

formation of a creamy gel. The Teflon container was sealed in an autoclave and heated at 90^0 C for 90 minutes. It was then cooled and the precipitate was collected by filtration. The white precipitate obtained was washed with deionized water and the resulting product was dried in an oven at 30^O C.

Characterization of the Adsorbent

The particle size and surface morphology of zeolite were analyzed by scanning electron microscopy (SEM) using SEM QUANTA 250 with an acceleration voltage of 20.00 kV and a working distance of 10.0 mm. The sample was placed on a disk holder and sealed by a carbon tape for it to be fixed, the image was captured by an Everhart–Thornley detector with high vacuum mode and circular backscatter detector for contrast. Fourier Transform Infrared (FTIR) Spectroscopy was used to characterize the functional groups present on zeolite using Bruker Alpha FTIR spectrometer. The preparation of the sample was done using KBr pellet technique by mixing a small quantity of zeolite with spectroscopic grade KBr that has been grinded and pressed into a pellet. The Pellet was dried in an oven overnight and inserted into the instrument after which a spectrum was obtained. X-ray powder diffraction patterns were obtained using a Philips APD-3720 diffractometer with Cu Kα radiation, operated at 40 kV, 40 mA.

Batch Adsorption Results

Adsorption experiments were carried out using the batch method in a mechanically agitated shaker. The ranges of the experimental parameters were selected as follows; initial concentrations of methylene blue (1 mg/L to 100 mg/L), pH (1-11), contact time (10 to 300 minutes) and temperature (295k to 335k). The pH of the solution was adjusted with HCl and NaOH. The beakers were placed in a shaker and then shaken with a speed of 150rpm for 2 h. The mixtures were filtered and supernatant was analyzed with a UV-Visible spectrophotometer. The adsorption capacity of methylene blue was measured and calculated from the difference between the initial and final concentration of the methylene blue adsorbed (mg/g) using the formula:

$$Q = \frac{V\,(c_i - c_f)}{w} \quad (1)$$

Where Q = Quantity of solute adsorbed from solution of volume, V (cm^3), C_i = initial concentration before adsorption (mg/dm^3), C_f = Concentration after adsorption (mg/dm^3) V = Volume of the adsorbate used in litres and W = mass of the adsorbent in gram.

Adsorption isotherm and kinetics models

Adsorption isotherm was used to study the mechanism of adsorption and to interpret the relationship between the concentration of the adsorbate and the adsorption capacity of the adsorbent (Wang *et al*., 2010; Naushad, 2014). They provide information about the adsorption capacity of adsorbents are also used to differentiate the adsorptive capacities of the adsorbent for various pollutants. The data obtained in this study by varying the initial concentration was fitted into Langmuir and Freundlich adsorption isotherms.

Langmuir Adsorption Isotherm

The Langmuir isotherm assumes that adsorption occurs at specific homogeneous sites within the adsorbent and has been applied to monolayer adsorption (Wang *et al*., 2005). The nonlinear form of Langmuir isotherm is given below;

$$Q_e = \frac{Q_m\ k_L C_e}{1 + k_l C_e} \quad (2)$$

Where: Q_m is the maximum specific uptake corresponding to sites saturation (mg/g), k_L is the adsorption equilibrium constant (l/mg) (Donmez and Aksu, 2002) and Ce is the equilibrium concentration of adsorbate in solution (mg/L).
Equation (2) can be rearranged and linearized to give the following expression

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K} + \frac{C_e}{Q_m} \quad (3)$$

The dimensionless separation factor (R_L) of the equilibrium parameter is used to determine the favorable nature of the adsorption process.

$$R_L = \frac{1}{1 + K_L C_o}$$

The values of R_L shows the type of isotherm to be irreversible ($R_L = 0$), favorable

($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) (Hamdaoui., 2006).

Freundlich Isotherm

The Freundlich isotherm is an empirical equation applied to describe the adsorption on heterogeneous surfaces with different affinities. According to this model, stronger binding sites are initially occupied. The empirical equation is expressed by equation (4).

$$Q_e = K_f C_e^{1/n} \quad (4)$$

Q_e is the quantity of solute adsorbed at equilibrium, K_f is a constant that indicates the adsorption capacity of the adsorbent and n determines the affinity between the adsorbent and adsorbate (Bayramoglou *et al*., 2005).

Adsorption Kinetics

To describe adsorption kinetics, the two most frequently used kinetic models of Pseudo-first-order and Pseudo-second-order kinetic were applied to test the experimental data respectively. The Pseudo-first-order is expressed as follows;

$$\frac{dq}{dt} = K_1\,(q_e - q_t) \quad (5)$$

Integration of equation (5) gives:

$$\ln((q_e - q_t) = \ln q_e - k_1 t$$

q_e (mg /g) is the adsorption capacity at equilibrium, q_t (mg /g) is the adsorption capacity at time t and K_1 (min^{-1}) is the rate

constant for Pseudo-first-order model. The plot of ln (qe $-qt$) against t should give a linear relationship from which K_1 and qe can be obtained from the slope and intercept of the plot, respectively.

The Pseudo-second-order equation is presented as follows:

$$\frac{dq}{dt} = K_2 (q_e - q_t)^2 \quad (6)$$

After the integration equation (6) becomes:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

Where k_2 (g/mg/min) is the rate constant of the pseudo-second-order. K_2 and qe can be obtained from the intercept and slope of a plot of $t/q\ t$ versus t

RESULTS AND DISCUSSION

3.1. Properties of Adsorbent

Fourier Transform Infrared, FTIR spectra of the prepared zeolite is illustrated in fig. 1. The bands at 450 to 1200 cm^{-1} are identified to be due to Si-O-Al, Si-O-Si, Si-O, Si-Al, and Al-O species (Thompson and Huber, 1982). A broad absorption band at 3445 cm^{-1} is attributed to the presence of the hydroxyl functional group.

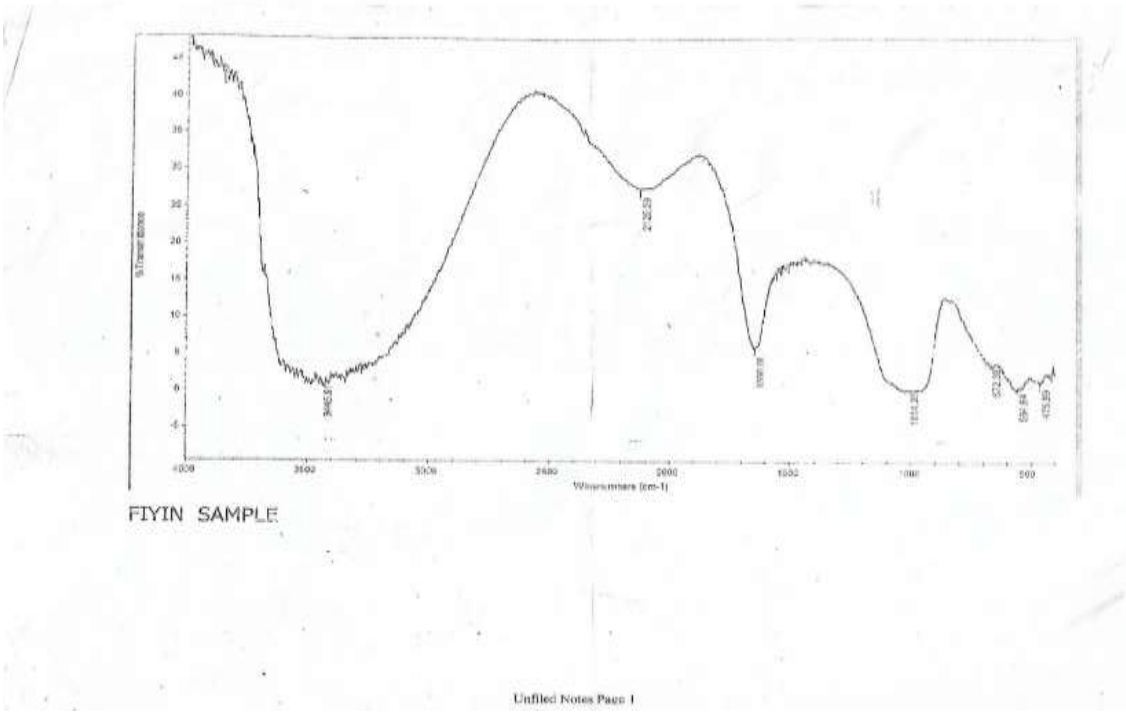

Fig 1: Fourier Transform Infrared Spectrum of the prepared Zeolite

Scanning electron microscopy (SEM)

The SEM micrograph depicted in fig 2. showed the morphology of the synthesized zeolite at different magnifications. The presence of many cubic crystals with well-developed crystalline face supports the presence of more sharp reflection peaks detected by X-ray diffraction pattern (Fig. 3)

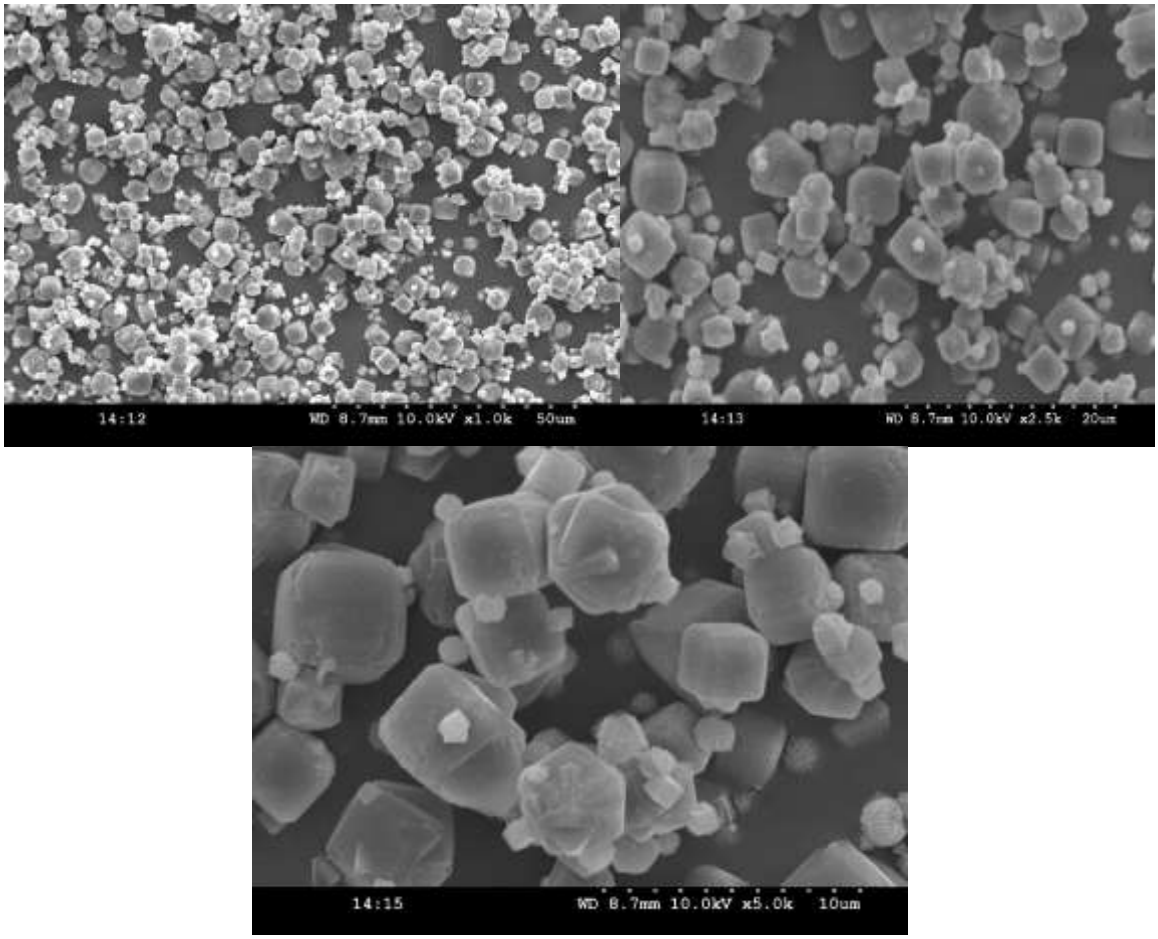

Fig 2: Scanning electron micrographs of Zeolite at different magnifications

Diffraction Analysis

The x-ray diffraction patterns of zeolite is illustrated in Fig.3.The crystalline phases of the prepared product correspond to the main peaks of zeolite A at 2θ values of 7.2º, 10.3º, 12.6º, 16.2º, 21.8º, 24º, 26.2º, 27.2º, 30º, 30.9º, 31.1º, 32.6º, 33.4º and 34.3º that were reported by (Treacy and Higgins, 2001). The sharp diffraction peaks reflect the crystalline nature of the adsorbent.

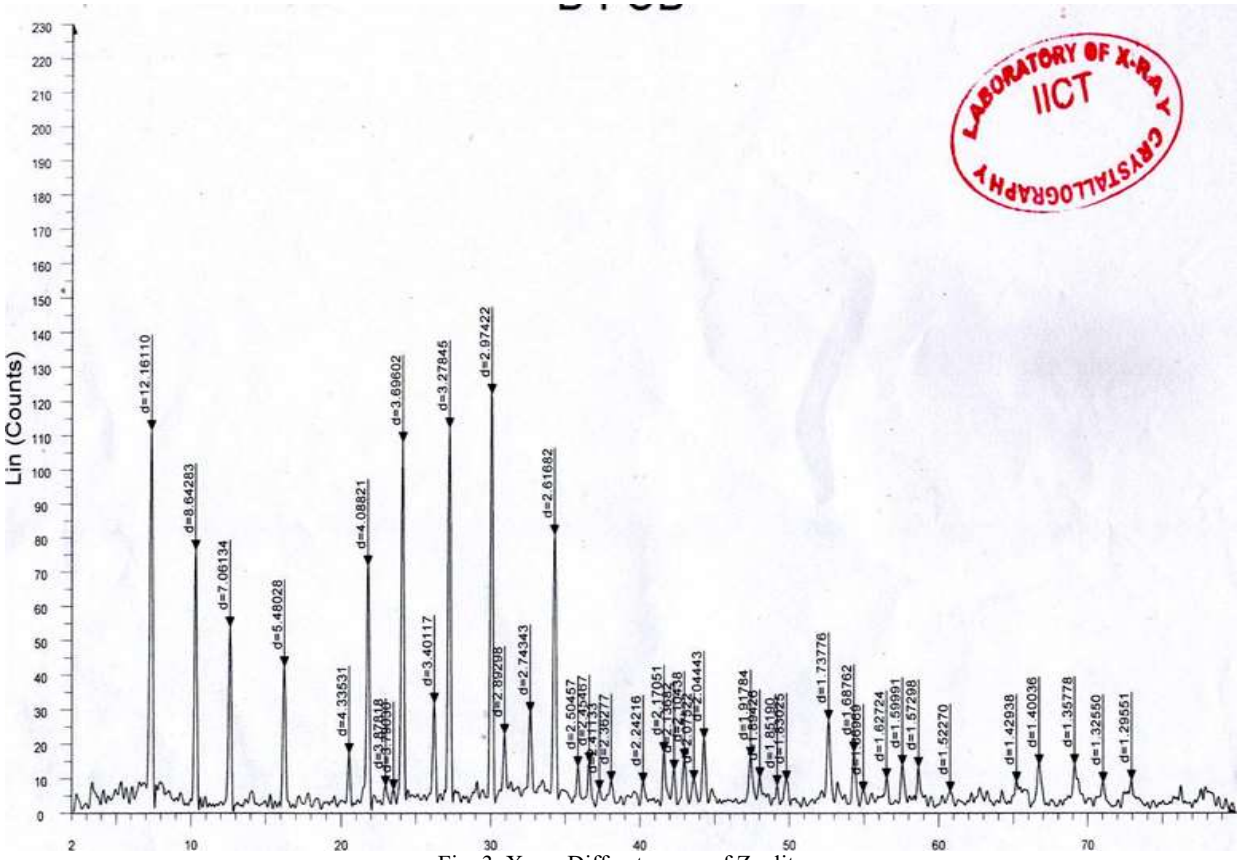

Fig. 3. X-ray Diffractogram of Zeolite

Effect of Initial Dye Concentration

The effect of initial dye concentration on the adsorption capacity of zeolite is shown in fig. 4. At the initial stage, it was found that the rate of removal of methylene blue increases with an increase in initial dye concentration. This was because the initial concentration of methylene blue essential driving force provided by to overcome all the mass transfer hindrance. Also, the increase in adsorption capacity of zeolite with an increase in the concentration of methylene blue can be due to higher interaction between zeolite and the adsorbate. The rate of uptake of dye was found to be fast at the initial stage of the contact time until an equilibrium point is reached with no further changes. This is similar to what was reported by Kashefialasl *et al.,* 2010)

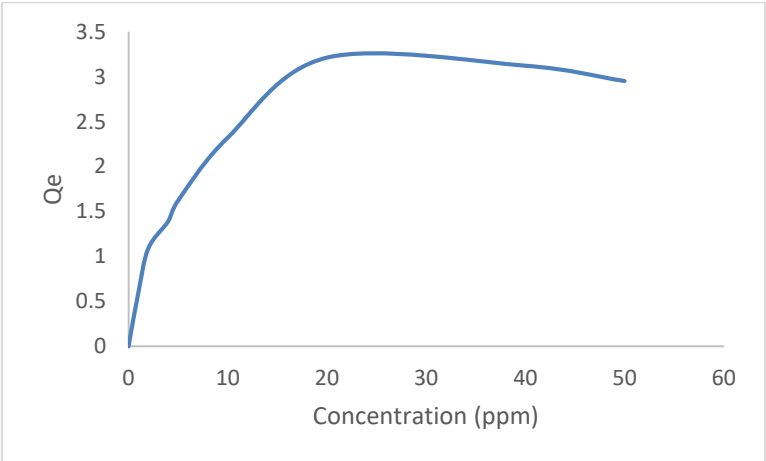

Fig 4 : Effect of Initial Concentration on Adsorption of Methylene blue

Effect of Contact Time

The rate of removal of methylene blue onto the synthesized zeolite was studied at different time intervals using 0.02 g dosage of zeolite. As depicted in fig 5 maximum adsorption was achieved in 30 minutes, after which a further increase in contact time had no significant effect on the adsorption capacity. This

can be attributed to the availability of many vacant sites for adsorption at the initial stage, and after the end of this time, the vacant surface sites left are difficult to be occupied because of the repulsive forces between the solute molecules on the solid and bulk phases.

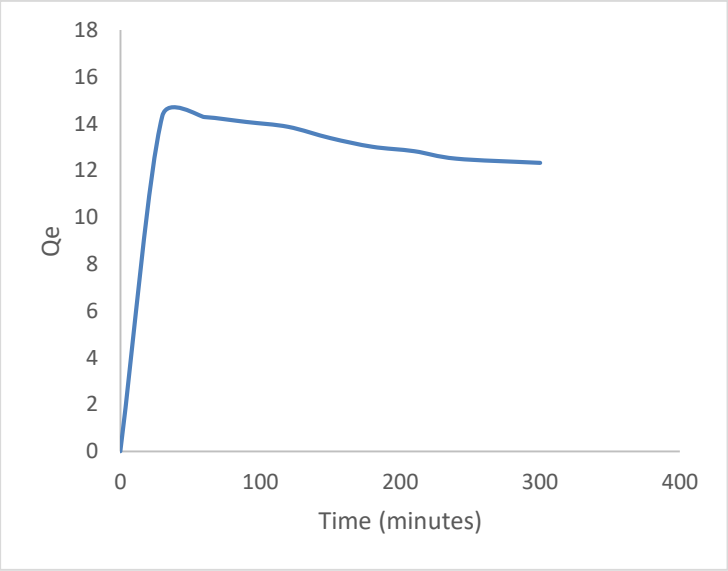

Figure 5: Effect of Contact Time on Adsorption of Methylene blue

Effect of pH

The pH of the solution is one of the most essential factors affecting the adsorption process. The effect of pH on the adsorption of methylene blue was carried out in the pH range of 1 to 11. It can be observed in fig. 6 at the adsorption capacity increases with increase in pH which was followed by a steady decrease at pH 8. The lower adsorption of methylene blue in the acidic medium may be attributed to the presence of excess H^+ competing with dye cations for the available active adsorption sites (Vadivelan and Kumar, 2005; Bestani *et al*., 2008). Also, the increase in pH of the aqueous solution result in a rise in density of negative charge at the adsorbent surface (Kashefialasl *et al*., 2016). Hence, the increase in negative charge on the zeolite surface enhances the adsorption of methylene blue. Similar results have been reported by Shahryari *et al.,* 2010) in the adsorption of methylene blue onto carbon nanotubes.

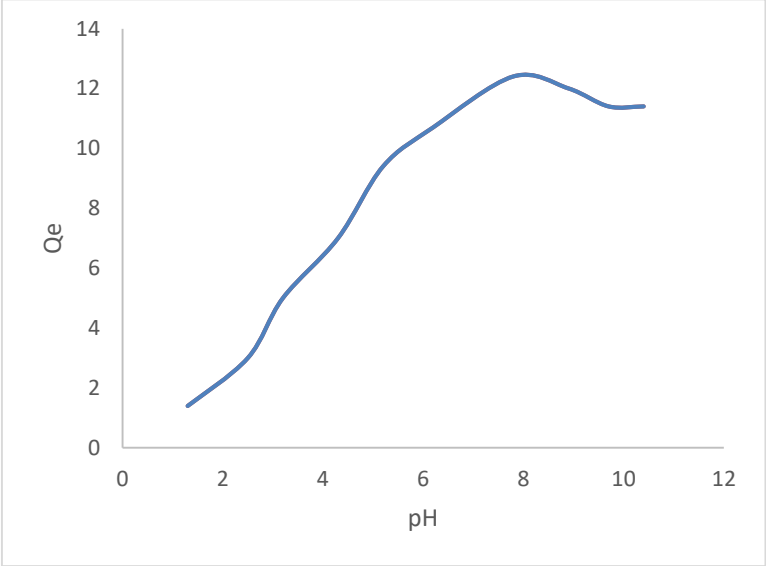

Fig 6. Effect of pH on Adsorption of Methylene blue

Effect of temperature

Fig. 7 depicts the influence of temperature on the adsorption of dye onto zeolite. The adsorption capacity was found to decrease with an increase in temperature. This showed that the mobility of dye molecules decreases with the temperature and it can be explained based on the fact that an increase in temperature led to a decrease in the boarder layer around the adsorbent. Hence, the transmission of adsorbate from the solution to active sites of adsorbent will be difficult resulting into a decrease in removal efficiency (Kashefialasl *et al*., 2010).The fall in adsorption

capacity can also be attributed to a decrease in kinetic energy of the adsorbent particles. The unfavorable effect of temperature on adsorption efficiency reflects the exothermic nature of the adsorption process (Rao *et al*., 2006; Cheng *et al*., 2012).

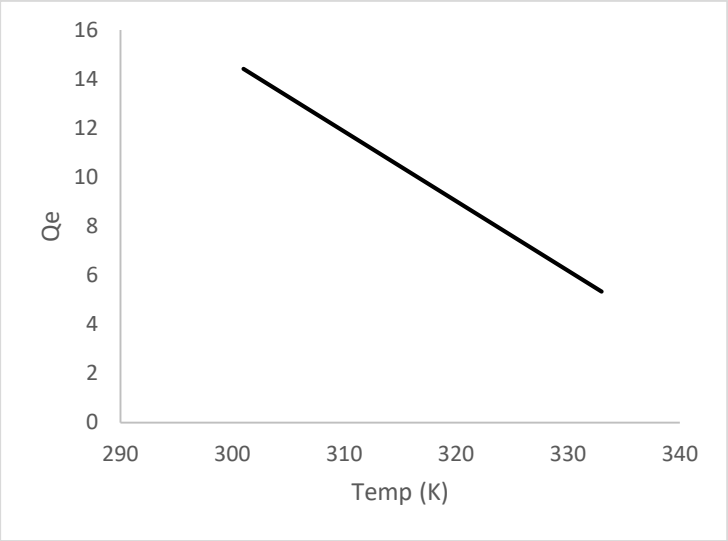

Fig.7: Effect of Temperature on Adsorption

Adsorption Isotherms Studies

Adsorption isotherms are used to calculate the theoretical adsorption capacity of the adsorbent **(**Tchobanoglous and Burton, 1991). In this study, Langmuir and Freundlich's models were tested to study the adsorption behavior of the adsorbate. The results showed that the adsorption of Methylene blue onto zeolite fits well with the Langmuir model than the Freundlich model. Hence, monolayer adsorption occurred. The calculated value of the dimensionless factor R_L , from the Langmuir isotherm which was between 0 and 1 indicates favorable adsorption between methylene blue and zeolite (Tamirat *et al*., 2014).

In the Freundlich isotherm model, if the value of n = 1, the adsorption is linear. If the value of constant n< 1, it indicates that the adsorption process is unfavourable (Tamirat *et al*., 2014). Hence, the value of n which was above unity suggested that the adsorption of methylene blue on zeolite was favorable.

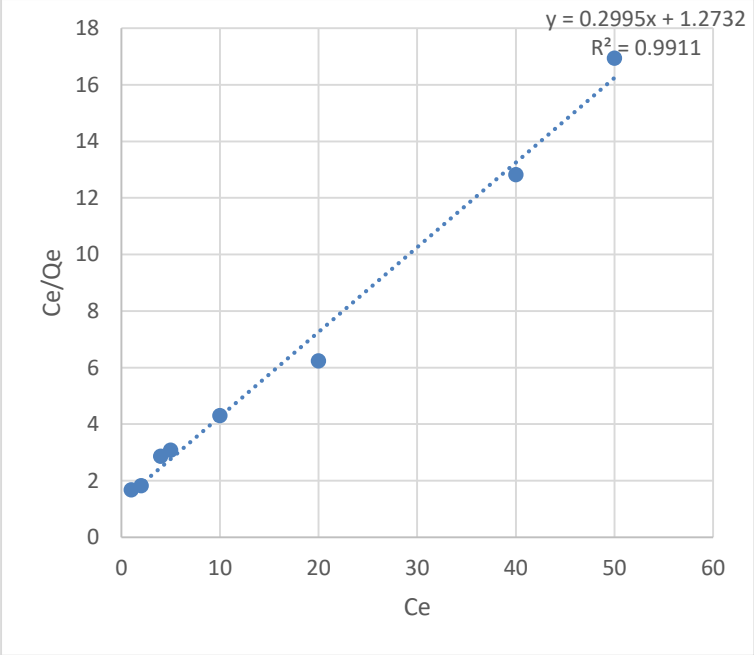

Fig. 8: Langmuir isotherm for Adsorption of methylene Blue onto Zeolite.

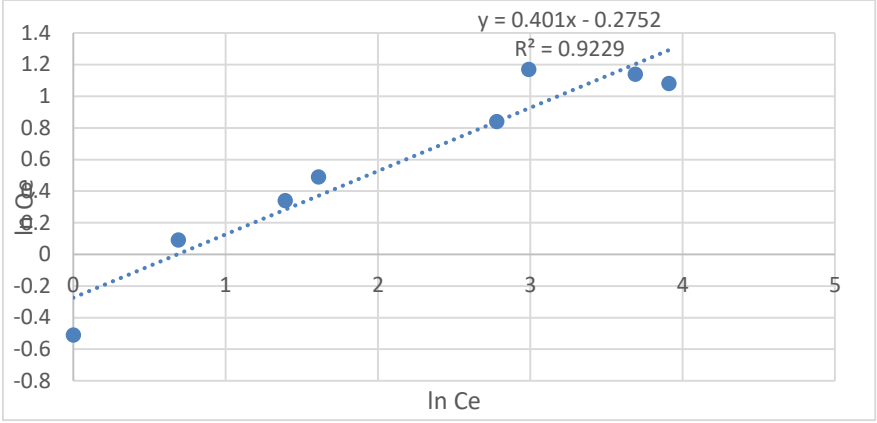

Fig. 9: Freundlich Isotherm for Adsorption of methylene Blue onto Zeolite.

Adsorption Thermodynamics

The thermodynamic parameters, such as enthalpy (ΔHº), entropy (Δ*S*º) and free energy (ΔGº).These parameters can be evaluated from the equations below:

$$K_c = \frac{F_e}{1-F_e} \qquad (2)$$

$$\ln k_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad (3)$$

$$\Delta G = -\text{ RT ln } (K_c)$$

F_e is a fraction of methylene blue dye adsorbed at equilibrium. R (J/Kmol) is Universal Gas Constant and T (K) is the absolute temperature. Values of ΔH and ΔS can be obtained from slope and intercept of the linear plot of log Kc against on l/T. According to the results obtained, the negative value of standard enthalpy of adsorption (ΔH^o) indicated the exothermic reaction of adsorption of methylene blue on zeolite while the negative value of standard entropy of adsorption (ΔSº) showed that no significant change occurs in the internal structures of zeolite during the adsorption process. The negative value of Gibbs free energy (ΔGº) indicated the spontaneity of the adsorption process.

Adsorption Kinetics Result

The kinetics of adsorption of methylene blue onto zeolite was analyzed using pseudo-first-order and using pseudo-second-order kinetic models. The result showed that the adsorption process fits in well into the pseudo-second-order model than the pseudo-first-order model. The correlation coefficient, R^2, for the pseudo-second-order kinetic model which was almost equaled to unity signifies the applicability of the model.

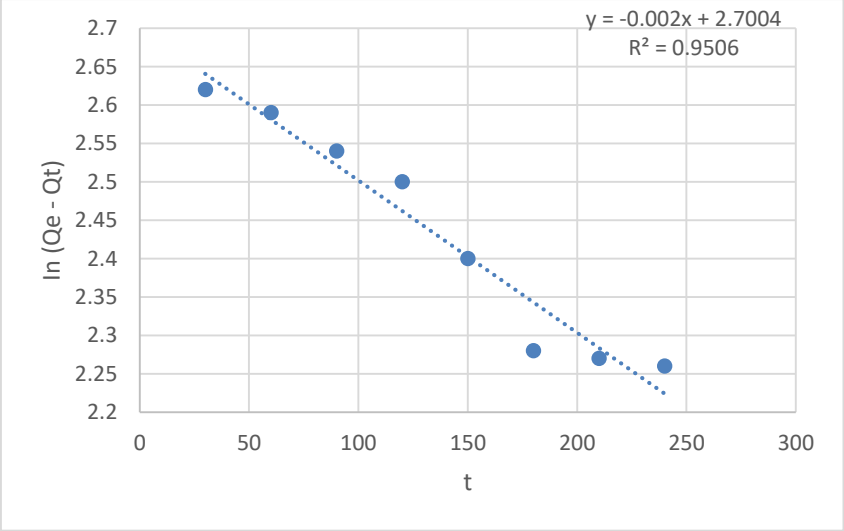

Fig 10: Pseudo-first Order Model for the adsorption of Methylene Blue

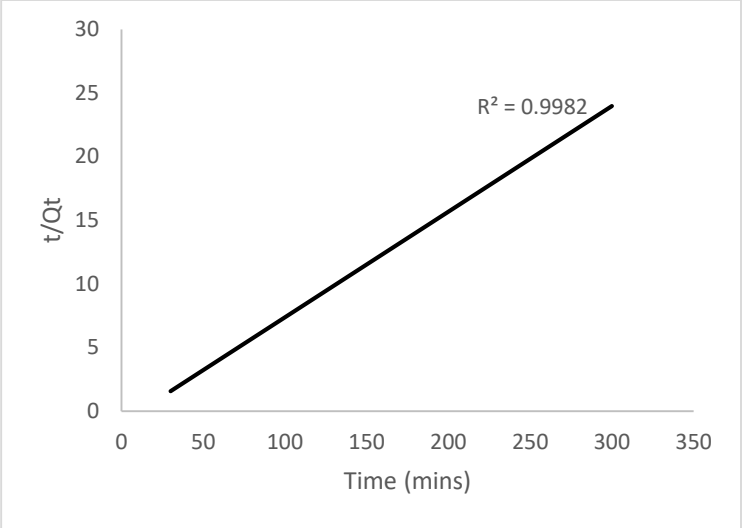

Fig 11: Pseudo-second Order Model for the Adsorption of Methylene Blue

CONCLUSION

Kinetic and thermodynamic studies investigated the adsorption of methylene blue from aqueous solution onto zeolite, in batch studies, the adsorption was highly dependent on various operating parameters: contact time, pH, initial dye concentration and temperature. The kinetics of the adsorption was found to follow the pseudo-second-order model. The experimental results were analyzed by Langmuir and Freundlich adsorption isotherms. Langmuir isotherm has a better fitting model than Freundlich as the former has a higher correlation regression coefficient.

This present work has successfully shown that zeolite is an effective low-cost adsorbent for the removal of methyl blue from aqueous solution.

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