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Equilibrium, Kinetic and Thermodynamic Study of Aniline Adsorption over Prepared ZSM-5 Zeolite

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Abstract

Aniline and its derivatives are common contaminants in various wastewaters and represent a serious worry for societies health and a challenge to ecologists due to their dangers effects on to the human health.

ZSM-5 zeolite was prepared from locally available materials (kaolin and rice husk) for adsorption of aniline from synthetic wastewater. Characterization of the prepared zsm-5, kinetics and thermodynamic of the adsorption process were investigated.

The characterization results of the prepared zsm-5 zeolite showed that the surface area was 270.1 m^2/g and pore volume 0.21828 cm^3/g. The silica to alumina ratio (Si/Al) was 166. 47 and the sodium content was 11 wt. %. The atomic force microscope (AFM) results showed that the average particle diameter of the prepared adsorbent was 70.71nm.

Langmuir isotherm better illustrated the adsorption process with maximum uptakes 8.3125 mg/g. Whereas, kinetics results of the adsorption process showed it the pseudo-second order in different operating temperatures.

The calculated values of ΔG showed that the adsorption process was spontaneous, while the ΔH results illustrated the process to be exothermic nature of this process with negative values of ΔS.

Key words: Adsorption, aniline, zsm-5, zeolite, wastewater, kinetics, thermodynamic.

Introduction

Aniline is one of the supreme common contaminants found in wastes from the various industrial wastewater such as pharmaceutical, pesticide, dyestuff, petrochemicals, tanneries, distilleries, textile, paper and pulp mills, electroplating, food processing and agrochemical industries [1]. Accordingly, the elimination of aniline from these effluents has become a social worry especially for the colored effluents. Color being a visible pollutant, The water contaminated with aniline is not only unfit for drinking purpose due to transformation of hemoglobin to methemoglobin, which has a lower affinity for oxygen than hemoglobin, therefore decreases blood's ability to transport oxygen, but is also not suitable for agriculture due

to its inhibitory action on photosynthetic process in plants [2], [3].

Numerous methods are used to treat wastewater containing aniline such as oxidation، extraction, membrane separation, biochemical decomposition, and adsorption [3], [5], [6].

Among all methods, the adsorption is the most effective way to remove aniline and such organics from wastewater. Adsorption technique does crop harmful byproducts, and the recycling of both the adsorbent and pollutants is possible. One challenge met by adsorption technology is the discovery of new adsorbents like activated carbons, polymer resin, clays, mesoporous oxides and zeolite, that effectively eliminate organic pollutants, such as aniline, from aqueous solutions.[1], [2], [3], [7].

In the design and optimization of adsorption processes, the adsorption isotherms and kinetics are of greatest importance to study. Adsorption isotherms are essential for the description of how adsorbate will interact with adsorbent and are in necessary optimizing the use of adsorbent. Thus, the correlation of experimental equilibrium data using either a theoretical or an empirical equation is essential for adsorption performance assessment. Adsorption kinetics involves the study of the rate at which pollutants are removed from aqueous solution onto adsorbent surface, which in turn controls the residence time of the adsorbate uptake at the solid-solution interface [8].

Aim of the Work

The aim of this research is the removal of aniline from wastewater by prepared ZSM-5 zeolite. Characterization results of prepared ZSM-5 zeolite adsorbent were discussed. The study the isotherm models of adsorption to identify the effect of temperature and time on the removal of aniline in a batch experiments was presented. Finally, the study of kinetics and thermodynamics of the aniline adsorption over prepared zeolite in the best selected conditions, was illustrated.

Adsorption Isotherms and Thermodynamics

Langmuir Isotherm

The Langmuir adsorption isotherm represented by Equation 1, Langmuir in (1918)

$$\frac{C_e}{q_e} = \frac{1}{q_o k_l} + \frac{C_e}{q_o} \quad \ldots(1)$$

Where, Ce is the equilibrium concentration (mg/L) of adsorbate (aniline) in the bulk; $q_e$is the amount of adsorbate (mg/g) adsorbed at equilibrium. $q_o$and 'k_l' are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively [2].

Freundlich Isotherm

Freundlich in 1906 represented the adsorption isotherm as shown in Equation 2:

$$\text{Log } q_e = \log K_f + \frac{1}{n} \log C_e \quad \ldots(2)$$

Where q_e and C_e have their usual meanings and the constants K_f and n are measures of adsorption capacity and intensity of adsorption, respectively [2].

Hill Isotherm

The Hill equation (in, 1910) was postulated to describe the binding of different species onto homogeneous substrates defined as:

$$q_e = \frac{q_{sh} C_e^{nh}}{K_D + C_e^{nh}} \quad \ldots(3)$$

Where K_D, nH, and qsH (mg/L) are Hill isotherm constants, Hill cooperatively coefficient of the binding interaction and Hill isotherm saturation uptake. The model assumes that adsorption is a cooperative phenomenon by which ligand binding at one site of the macromolecule may influence different binding sites on the same macromolecule [9].

Sips Isotherm

Sips (in 1948) combined the Langmuir and Freundlich isotherm type models to describe heterogeneous surface much better. Sips adsorption isotherm is given by the Equation 4:

$$q_e = \frac{q_m K_S C_e^{1/m}}{1+K_S C_e^{1/m}} \quad \ldots(4)$$

Where q_m (mg/g) is the maximum adsorbed amount of adsorbate per unit mass of adsorbent, K_s ((l/mg) ^1/m) is sips constant related to energy of adsorption, and parameter m could be regarded as the parameter characterizing the system heterogeneity [4].

Redlich–Peterson Isotherm

The Redlich–Peterson isotherm (in, 1959) is a hybrid isotherm featuring both Langmuir and Freundlich isotherms, which incorporates three parameters into an empirical equation given by:

$$q_e = \frac{K_R C_e}{1+a_R C_e^g} \quad \ldots(5)$$

Where K_R (L/g) and a_R (1/mg) are Redlich–Peterson isotherm constants, and g is the isotherm exponent. The model can be applied either in homogeneous or heterogeneous systems. It approaches the Freundlich isotherm model at high concentration and in accordance with the low concentration limit it approaches the ideal Langmuir condition [9].

Toth Isotherm

The Toth isotherm model (in, 1971) is another empirical equation developed to improve Langmuir isotherm fittings. It is useful in describing heterogeneous adsorption systems, and satisfies both low and high-end boundary of concentrations:

$$q_e = \frac{K_T C_e}{(a_T+C_e)^{1/2}} \quad \ldots(6)$$

Where K_T (mg/g), a_T (L/mg) is the Toth isotherm constants. The correlation presupposes an asymmetrical quasi-Gaussian energy distribution where most binding sites have an adsorption energy lower than the peak value [9].

Adsorption Kinetics [7], [12]

1- Pseudo_First Order Model

The psedo first-order kinetic model can be represented as follow:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \ldots(7)$$

Integration of Equation 7 for the boundary condition t=0 to t=t and qt=0 to qt=qt:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \ldots(8)$$

Where q_e (mg/g) and q_t (mg/g) are the amounts of adsorbed adsorbate at equilibrium and at time t respectively, and $k_1(min^{-1})$ is the rate constant of pseudo first order equation.

2- Pseudo_Second Order Model

The pseudo second_order kinetic model can be represented as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad \ldots(9)$$

Integration Equation 9 for the boundary condition t=0 to t=t and q=0 to q=q_t:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \quad \ldots(10)$$

Where q_e (mg/g) and q_t (mg/g) are the amounts of adsorbed adsorbate at equilibrium and at time t respectively, and k_2 (g/mg. min) is the equilibrium rate constant of pseudo second order model.

3- Intra_Particle Diffusion Model

The intra-particle diffusion kinetic model can be represented as follow:

$$q_t = k_3 t^{1/2} + c \quad \ldots(11)$$

Where q_t (mg/g) is the amount of solute on the surface of sorbent at time t, k_3 (mg/g.$min^{1/2}$) is the intra-particle diffusion rate constant and c (mg/g) is the intercept

Adsorption Thermodynamics

Adsorption thermodynamic is an important tool elucidating the adsorption behavior of an isolated system. Its original concept assumes that energy cannot be gained or lost, and entropy changes. The values of enthalpy change (ΔH), Gibbs free energy change (ΔG), and entropy change (ΔS) were computed using the following equation:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \ldots(12)$$

$$\Delta G = - RT \ln K_d \quad \ldots(13)$$

$$K_d = \frac{q_e * (\frac{w}{v})}{C_e} \quad \ldots(14)$$

Where R is the universal gas constant (8.314 J/mol. K), T is temperature (K), and K_d is the distribution coefficient for the adsorption [10].

Experimental Work

Material

The reactant materials used in this study were silica SiO_2 (purity 92%) molecular weight 60.08 g/mole as silica source, tetrapropylammonium hydroxide solution (TPAOH, $C_{12}H_{29}NO$, 20% aqueous solution, Merck) as direct template agent, sodium hydroxide (NaOH, 98 wt%, Merck) and kaolin as alumina source.

Zeolite Preparation

Kaolin was sieved to a particle size ≤ 75μm. 4g of NaOH was dissolved in 70 ml of distilled water and then divided in two portion. 29.8 g of SiO_2 were dissolved in one portion of sodium solution and stirred until clear solution was reached, after that was added 18.3 g of 20% of TPAOH to sodium silicate solution and stirred to 60 min. 1.7 g of kaolin (alumina source) was mixed with the another portion of sodium solution.

Silicate solution was slowly added to aluminate solution and stirred to 60 min. The mixture was placed in Teflon-lined stainless steel autoclave at 150 °C for 96 hr. The product obtained was filtered and washed with distilled water for several times until pH value dropped to 8.5 after that the product was dried in an electrical oven at 110˚C overnight and followed by calcination at 550 ˚C for 3 h.

Characterization and Analysis of Prepared ZSM-5 Zeolite

The prepared catalyst was characterized by using different instrumental analysis techniques such as: X–Ray Diffraction (XRD), Atomic Force Microscope (AFM), BET specific surface area and pore volume by ISO-9277-2010 method, sodium content by ASTM D-1428-64 method, and X-ray Fluorescence (XRF) for determine the silica content and silica to alumina ratio.

Experimental Procedure

Batch adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.05 g of ZSM-5 zeolite per 10 ml of solution containing 60 mg/L of the aniline. The mixture was agitated in a thermostatic orbital shaker at room temperature with an agitation speed of 150 rpm. The aniline concentration in the supernatant was determined using a double beam UV–Vis spectrophotometer (Shimadzu UV160-A, Japan) at 280 nm. Each experiment was carried out in triplicates under identical conditions and an average value was determined. qe (mg/g), was calculated by: [9]

$$q_e = \frac{(C_o - C_e) * V}{W} \quad \ldots(15)$$

Where Co and Ce (mg/L) are the liquid phase concentration of aniline at initial and equilibrium, respectively. V (L) is the volume of the solution, and the W (g) is the mass of adsorbent used [9].

Results and Discussion

X-ray diffraction pattern was determined for prepared zsm-5 zeolite as shown in Figure 1. The comparison between lattice spacing of prepared zsm-5 zeolite with standard synthetic one is shown in Table 1. The comparison in the lattice spacing shows that the prepared zsm-5 zeolite is approximately comparable with the standard.

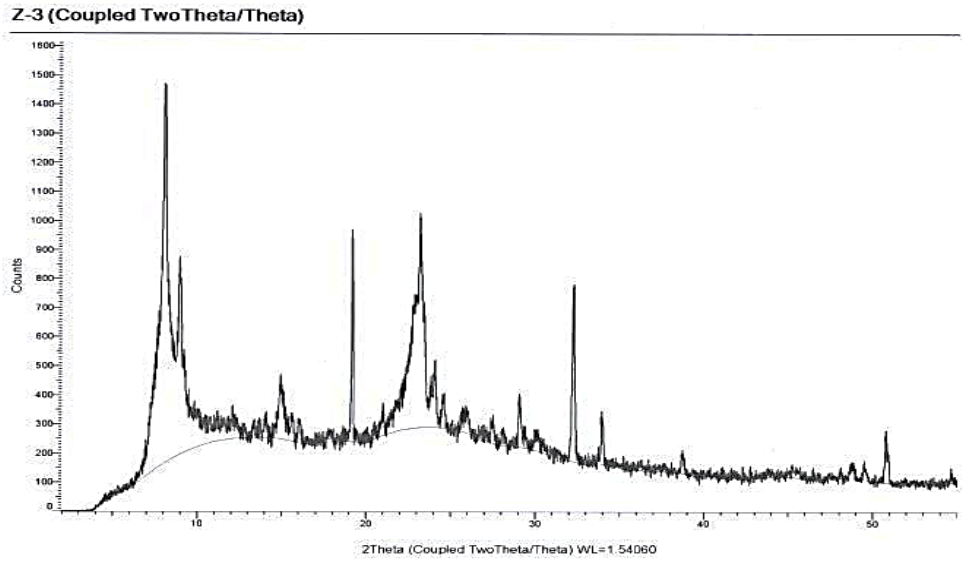

Fig. 1: XRD pattern of prepared zeolite-ZSM_5

Table1: Comparison of lattice spacing between prepared ZSM-5zeolite and standard synthetic ZSM-5zeolite

Prepared zsm-5 zeolite		Standard zsm-5 zeolite	
Angle (2ɵ) deg.	**d, spacing (Å)**	**Angle (2ɵ) deg.**	**d, spacing (Å)**
7.453	11.85116	7.93	11.153
8.06	10.95828	8.01	11.033
8.95	9.86504	8.90	9.939
9.133	9.675	9.14	9.673
14.945	5.92300	14.99	5.909
15.612	5.67156	15.63	5.669
16.045	5.51930	16.07	5.517
19.157	4.62933	19.24	4.613
20.981	4.23063	20.94	4.242
23.200	3.83080	23.19	3.836

The silica to aluminum ratio (Si/Al) of ZSM-5 zeolite was equal to 166.47 according to XRF analysis which lie in the range of Si/Al ratio of standard ZSM-5 zeolite (10_∞). Also, these results were in a good agreement with Sari et al., [11] who mentioned that the ratio of silica to alumina in ZSM-5is about 177. The BET surface area and pore volume of ZSM-5 zeolite were 270.1 m^2/g and 0.21828 cm^3/g respectively with sodium content equal to 11 wt. %. The AFM analysis was shown that the ZSM-5 zeolite have average nano particle equal to 70.71 nm.

Adsorption Isotherm

The adsorption isotherms illustrate the interaction between the adsorbates and adsorbents. Adsorption equilibrium is established when an adsorbate has been contacted with the adsorbent for enough time, and the adsorbate concentration in the bulk solution is in balance with the interface concentration [13]. The fitting of adsorption data isotherm models is a main step to find the appropriate model that can be used for design purposes. In this work, experimental equilibrium data for aniline adsorption on zsm-5 zeolite, calculated from Equation 15, fitted to the Langmuir and Freundlich isotherms, Equations 1 and 2 respectively. Results are represented in Figures 2 and 3. The results of this fitting, as summarized in Table 2, show that Langmuir isotherm has the highest R^2 value as compared to that Freundlich isotherm. The Langmuir model correlates the equilibrium data with R^2 (correlation factor) values of 0.9987 for aniline, suggesting the monolayer adsorption of aniline on zsm-5 zeolite. These results are in good agreement with [3]. For the Langmuir isotherm, the values of R_L (separation factor) are 0.0311 for aniline, which indicate the favorability of aniline adsorption on zsm-5 zeolite. Also, Table 2 shows that the Langmuir isotherm gives maximum adsorption capacity of 8.3125 mg/g for aniline.

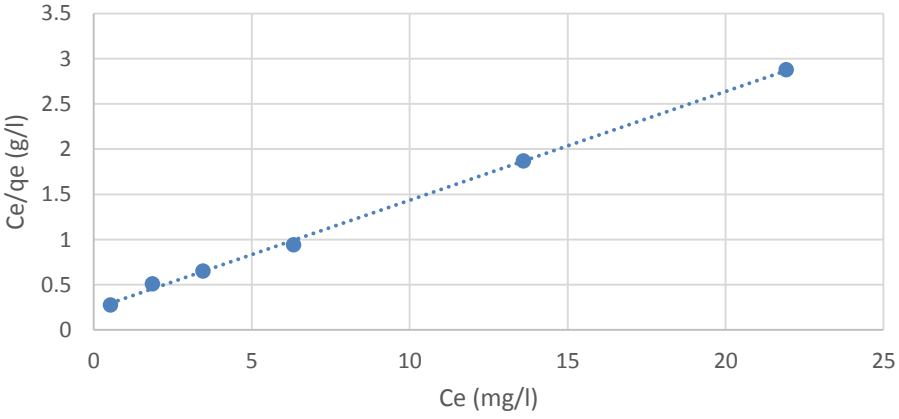

Fig. 2: Langmuir adsorption isotherm of aniline on zsm-5 zeolite

Table 2: Isotherm parameters for aniline adsorption on zsm-5 zeolite

Isotherm	Parameter	Temperature (k) 303
Langmuir	q, max(mg/g) K_L (l/g) R^2 R_L	8.3125 0.5196 0.9987 0.0311
Freundlich	K_F ((mg/g)(l/g))1/n n R^2	-0.3480 2.6371 0.9228

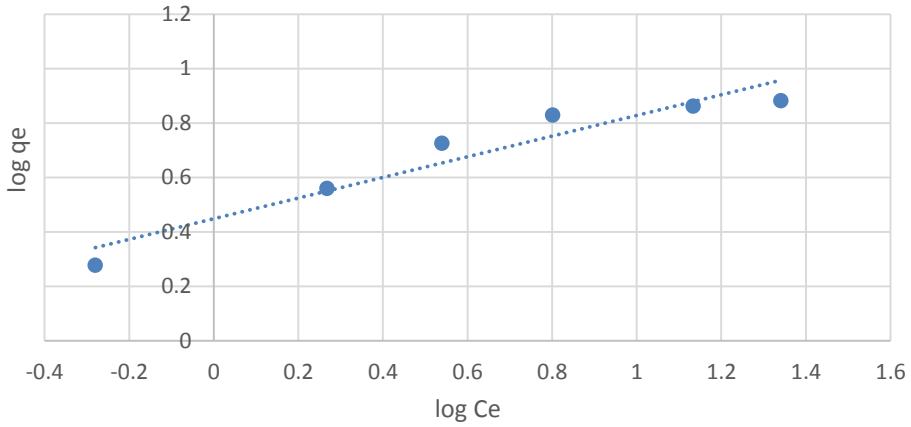

Fig. 3: Freundlich adsorption isotherm of aniline on zsm-5 zeolite

Adsorption Kinetics

Two kinetic models: pseudo-first order and pseudo- second order models, Equations 8 and 10, where used to correlate the experimental kinetic data of aniline on zsm-5 zeolite at different temperature. The pseudo-first order equation is of low R^2 values as compared to the pseudo- second order equation, as shown in Table 3. High deviation between the experimental and calculated adsorption capacity can be seen from this table. On the other hands, the linear plot of t/q_t versus t Figures 5 for pseudo-second order equation has high R^2 values compared to pseudo- first order model. The results of this tables show that the adsorption kinetics data are better represented by pseudo- second order and the values of K_2 increased with increasing solution temperature taking the values 0.02196, 0.0245 and 0.0280 for aniline at 303, 313 and 323 K respectively. On the contrary, the values of q_e decreased with increasing temperature to 8.0515, 7.61035 and 7.0028 for aniline at 303, 313 and 323 K respectively. These results are in agreement with those reported by [1] and [7] for the adsorption of aniline.

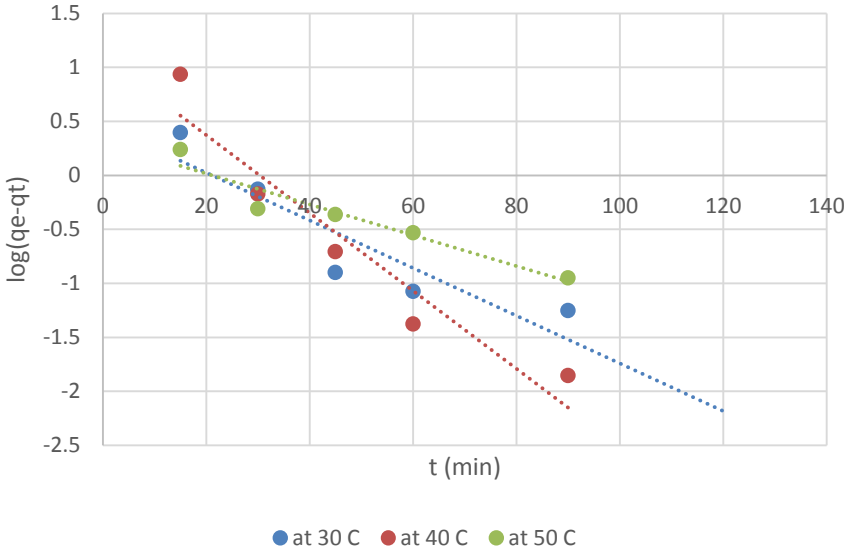

Fig. 4: Pseudo- first order kinetic for aniline on zsm-5 zeolite at different temperature

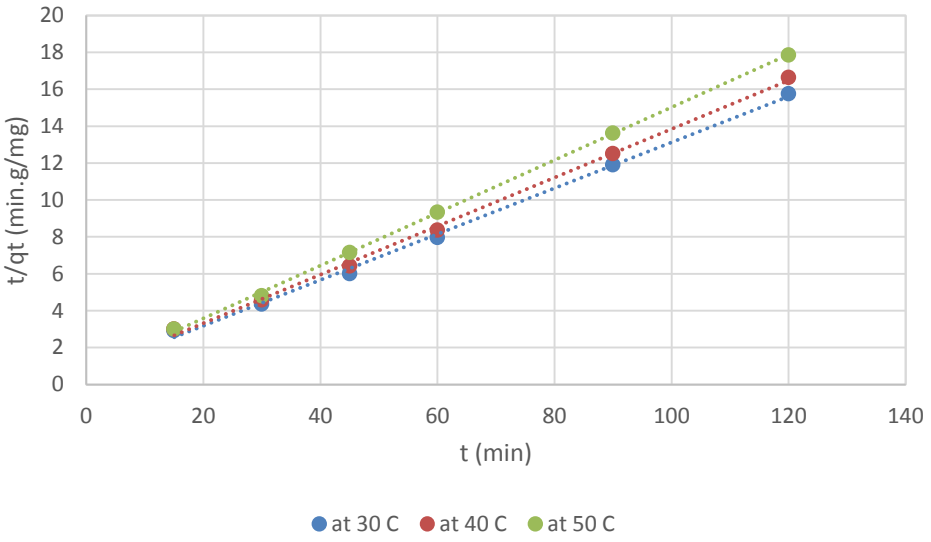

Fig. 5: Pseudo- second order kinetic for aniline on zsm-5 zeolite at different temperature

Table 3: Rate constant for aniline adsorption on zsm-5 zeolite

Temperature (K)	**Pseudo- first order model**			
	$q_{e,\,exp}$ (mg/g)	$q_{e,\,cal}$ (mg/g)	K_1 (1/min)	R^2
303	7.6154	2.9289	0.0509	0.8309
313	7.2098	12.3851	0.0829	0.9163
323	6.7203	2.0003	0.0329	0.9204
Temperature (K)	**Pseudo- second order model**			
	$q_{e,\,exp}$ (mg/g)	$q_{e,\,cal}$ (mg/g)	K_2(g/mg.min)	R^2
303	7.6154	8.0515	0.02196	0.9977
313	7.2098	7.61035	0.0245	0.9983
323	6.7203	7.0028	0.0280	0.9996

Adsorption Thermodynamics

According to Eqs. 12 - 14. The values of ΔH, ΔS, and ΔG were determined from the slope and intercept by plotting $\ln kd$ versus $\frac{1}{T}$ as shown in Figure 6. Table 4 summarizes the thermodynamic parameters at different temperatures for the adsorption of aniline onto zsm-5 zeolite. The negative ΔH values -12630.6288 J/mole illustrate the adsorption process to be exothermic in nature. The ΔS values -37.0480 J/mole revealed decreasing randomness at the solution/solid interface during the adsorption of aniline onto zsm-5 zeolite. Generally, the absolute magnitude of the change in free energy for physical adsorption is smaller than that of chemisorptions [15]. The obtained Gibbs free energy (-ΔG) values were 1390.74, 1063.98, 647.876 (J/mol) at different temperatures 303, 313 and 323 K, respectively. The ΔG values were negative indicating that the adsorption process occurred spontaneously. Because ΔG decreased with the increase of temperatures, it confirmed that adsorption more likely occured at lower temperatures. These results are in agreement with those reported [14].

Table 4: Thermodynamics parameter for adsorption aniline on zsm-5 zeolite

ΔH(J/ mole)	ΔS(J/mole)	-ΔG(J/mole)		
		303 k	313 k	323 k
-12630.6288	-37.0480	1390.74	1063.98	647.876

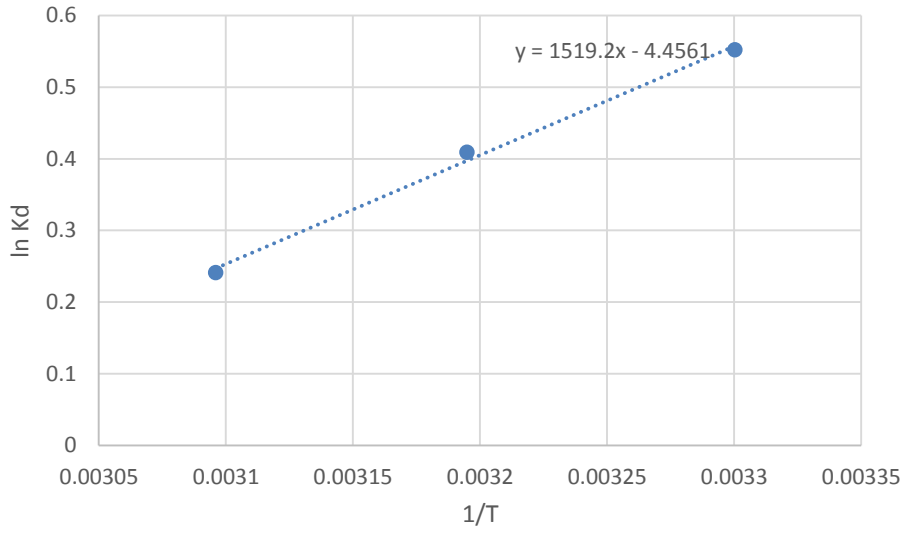

Fig. 6: Thermodynamic of adsorption aniline on zsm-5 zeolite

Conclusions

According to the results obtained from this study, the following conclusions are obtained:

1. The characterization results, i.e silica to alumina ratio (Si/Al) 166. 47, surface area of 270.1m^2/g, pore volume 0.21828 cm^3/ g and sodium content 11 wt% for prepared zsm-5 zeolite were in good with standard zsm-5 zeolite, Therefore is possible to say that the prepared catalyst obtained from locally kaolin and rice husk in this work is zsm-5 zeolite.
2. The average diameter of particles of prepared zsm-5 zeolite determined by AFM was 70.71 nm, and this means that this catalyst is nano type catalyst.
3. Maximum aniline uptakes, as calculated from Langmuir isotherm model was 8.3125 mg/.
4. The kinetics data were fitted to pseudo- second order kinetic model.
5. The thermodynamic parameters, ΔG values were negative from 1390.74 to 647.876 J/mol at different temperature, ΔH values was -12630.6288J/mole and ΔS values was -37.0480 J/mol K.

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