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Adsorption and Thermodynamic Studies on the Removal of Congo Red Dye from Aqueous Solution by Alumina and Nano-alumina

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Abstract Removal of Congo red dye from aqueous solution by adsorption onto alumina and nano alumina was investigated using batch adsorption process. The adsorption was studied at different concentrations and at various temperatures. Experimental results indicated that adsorption of the dye unto nano alumina surface followed better defined pattern than that of alumina. Adsorption pattern of nano alumina at different temperatures revealed that the nano adsorbent is more sensitive to temperature than the classical alumina. Adsorption capacity obtained from experiment correlated strongly with theoretical adsorption capacity obtained from the Langmuir isotherms. However, from calculated standard free energies of adsorption, Langmuir separation factors and thermodynamic parameters, nano-alumina is a better adsorbent than alumina.

Key Words: *Waste water, contamination, dye, adsorption*

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List of symbols

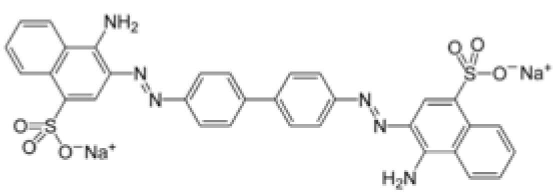
q_e	Equilibrium amount of dye adsorbed
C_0	Initial concentration of the dye
C_e	Equilibrium concentration of the dye
V	Vvolume of solution and m is the mass of the adsorbent
k_c	Equilibrium constant
ΔG^*	Standard free energy change
ΔH^*	Standard enthalpy change
ΔS^*	Standard entropy change
R	Universal gas constant
q_e	Amount of adsorbate adsorbed per unit mass of the adsorbent (mg/g)
b	Langmuir adsorption constant
q_m	Theoretical monolayer saturation capacity
R_L	Langmuir separation factor
K_{ads}	Langmuir constant

1.0 Introduction

Dyes of various types are used in some industries including textile, paper, printing, plastic, leather, cosmetic and paint industries (Wanyonyi and Onyari, 2014). However, their discharge to water bodies may impact serious mutagenic and carcinogenic effects (Fatombi *et al*., 2019). Colour can obscure the penetration of light to the aquatic system, which will lead to retardation of photosynthesis and the consequence reduction of oxygen content of water, and, aquatic flora and fauna (Kaur *et al*., 2013; Sharma *et al*., 2019). Dye industrial effluent must therefore be treated in order to reduce contamination risk. Although several treatment methods (such as photochemical degradation, biological degradation, coagulation, chemical oxidation and adsorption) are available, adsorption process has been established to be one of the best options because it is cost effective, easily accessible and can be made environmentally friendly (Litefti *et al*., 2019).

Several adsorbents have been successfully utilized for the removal of dyes from aqueous solution including plant materials (Abass and Trari, 2015; Ahmed and Kumar, 2010; Lafti *et al*., 2018; Odoemelam *et al*., 2018). However, the use of nano materials has greatly increased the efficiency of adsorption processes because nano materials have some unique properties that enhance their adsorption capacity compared to material of comparable composition. For example, nano materials have large pore volume, large surface area and their surface mostly exert unsaturation. This work seeks to investigate and compare the adsorption potential of alumina and nano-alumina for Congo red dye. Banerjee *et al*. (2017) used nano alumina to remove Orange G dye from aqueous solution and found that nano adsorbent was very effective. Nadafi *et al*. (2014) concluded that nano alumina is a good adsorbent for the removal of reactive red 120 dye from aqueous solution, Al-Rubayee *et al*, (2016) found that nano-alumina is a good adsorbent for alizarin yellow R and methylene blue dyes. Similar findings were reported by Chu *et al*. (2019) for some cationic dyes. Literature is scanty on the use of nano-alumina for the removal of Congo red dye from aqueous solution and on the comparative studies of nano alumina and alumina for the removal of Congo red dye from aqueous solution. Therefore, this study is aimed at investigating the effectiveness of alumina and nano alumina in removing Congo red dye from aqueous solution.

The chemical structure of Congo red dye is given below,



1.0 Materials and methods

2.1 Chemicals/reagents

Reagents used were $AlCl_3.6H_2O$, liquid ammonia, NaOH, HCl, ethanol and Congo red dye. They were supplied by the Akwa Ibom State University and were used without further purification. Stock solution of Congo red dye was prepared by dissolving 1g of the dye in 1000 ml of double distilled water. Serially concentrations of 10, 20, 30, 40 and 50 mg/L were obtained through dilution.

2.2 Synthesis of nano alumina

The sol gel method of precipitation in ethanol was used for the synthesis (ref). 0.6 M of $AlCl_3.6H_2O$ was prepared as a precursor solution. Liquid ammonia (1 M) was added dropwise to the solution and $Al(OH)_3$ was precipitated out as a gelatinous white precipitate. The resultant solution was washed with ethanol and dried in the oven at 90 °C. The dried sample was calcined in a muffle furnace maintained at 600 °C and at a heating rate of 10 °C/minute. The calcination converted the $Al(OH)_3$ to Al_2O_3 which was milled and sieved. A yield of 87 % was obtained.

2.3 Batch adsorption process

Batch adsorption process as reported elsewhere was used to study the effect of concentration, contact time, adsorbent dosage and temperature (Odoemelam *et al*. 2018). Amount of dye adsorbed at equilibrium was calculated using the following equation (equation 1)

$$q_e = \frac{C_0 - C_e}{C_0} \times \frac{V}{m} \quad (1)$$

where C_0 is the initial concentration of the dye , C_e is the equilibrium concentration of the dye, V is the volume of solution and m is the mass of the adsorbent.

2.4 Determination of concentration of Congo red dye

All spectrophotometric analyses were carried out using 721,P/N:A003 UV-visible spectrophotometer. In spectrophotometric analysis, wave length of maximum absorption of Congo red dye was measured. The measured wavelength was used as a reference wave length for all analysis and determination of the concentrations using extrapolation method according to Beer-Lambert's law of spectrophotometry.

3.0 Results and discussions

3.1 Effect of concentration

Fig. 1 shows the calibration curve for the absorption of the dye. The development of calibration curve forms the bases for spectrophotometric analysis. This is often done in accordance with Beer-Lambert's law which states that absorbance is directly proportional to the product of molar absorptivity, path length and concentration, thus

$$A = \varepsilon l C \quad (2)$$

Consequently, a plot of A versus C is expected to be linear with intercept equal to zero. From this plot (Fig.1), estimation of concentrations of the dye at a measured absorbance was achieved through extrapolation to the concentration unit.

Figs. 2 and 3 show plots for the variation of equilibrium amount of dye adsorbed unto alumina and nano alumina with concentration at various temperatures respectively. Fig.2 reveals that the amount of dye adsorbed depends on the concentration of the adsorbate. Adsorption of Congo red dye unto nano alumina is observed to converge at higher concentration. Such separations and convergence were not observed for the adsorption of the dye unto alumina indicating that nano modification influences the adsorption capacity of alumina. A close examination of Figs 2 and 3 indicate that nano modification increases values of equilibrium amount of dye adsorbed. This is attributed to increase in surface area of adsorption unto nano alumina compared to alumina.

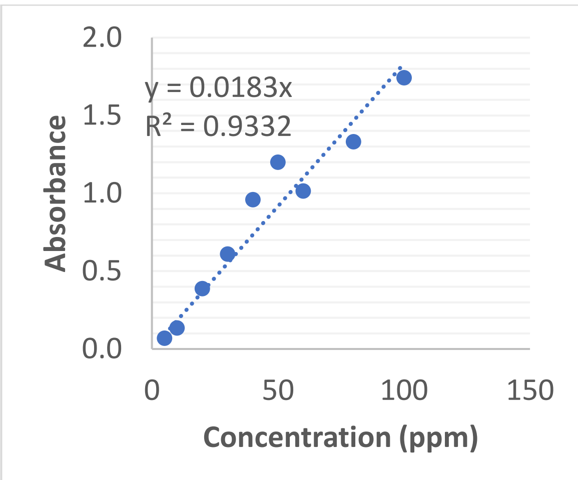


Fig.1: Calibration curve for Congo red dye

Since the available adsorption site is fixed, it is observed that as adsorption begins, the amount of dye molecules diffusing toward the surface of the adsorbent increases which led to increase in the amount of dye adsorbed. However, a stage is reached where further diffusion does not lead to adsorption. This may be attributed to continuous occupation or deactivation of the adsorption site leading to the development of the peak and deep respectively. However, the adsorption site may further be activated, resulting in further increase in adsorption, hence, the rise. In the case of nano alumina, the equilibrium amount of dye adsorbed increases with increase in concentration indicating that increase in the number of dye molecules diffusing unto the alumina surface increases the tendency for adsorption. At first, the adsorption was observed to trace different paths at different temperatures but as the concentration of the adsorbate increases, the four lines converge (even at all temperatures).

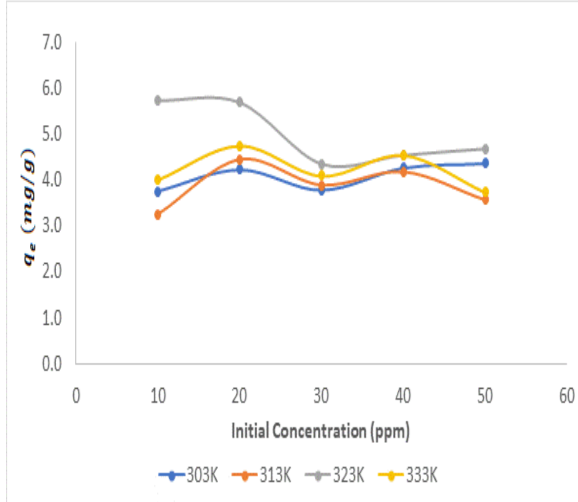


Fig. 2: Variation of equilibrium amount of dye adsorbed by alumina with initial concentration at various temperatures

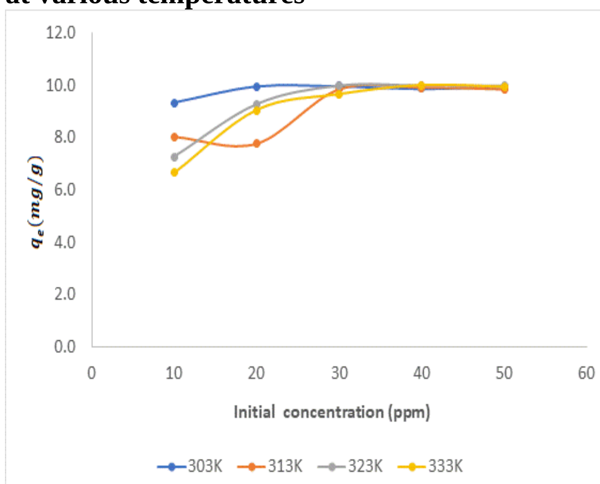


Fig. 3: Variation of equilibrium amount of dye adsorbed by nano alumina with initial concentration at various temperatures

This implies that there may exit a point where further increase in temperature may not affect the adsorption of the dye unto nano alumina. Such separations and convergence were not observed for the adsorption of the dye unto alumina indicating that nano modification influences the adsorption capacity of alumina. A close examination of Figs 2 and 3 indicate that nano modification increases values of equilibrium amount of dye adsorbed. This is attributed to increase in surface area of adsorption in nano alumina compared to alumina.

3.2 Effect of temperature

Temperature can influence the rate of adsorption in two ways. Therefore, increase in temperature may increase or decrease the extent of adsorption of a dye unto the surface of the adsorbent. Figs..4 and 5 present plots for the variation of equilibrium amount of dye adsorbed with temperature for alumina and nano alumina respectively. In alumina, a slight drop in adsorption was observed with increase in temperature and was succeeded by a rise and further drop (except at dye concentration of 40 ppm). The rise may be associated with activation of the adsorption site while the fall in q_e maybe attributed to deactivation. Activation can populate the adsorption site while deactivation can depopulate or reduce adsorption efficiency. However, in nano alumina the adsorption line is neatly ordered and are generally pointed toward decrease in adsorption with increase in temperature.

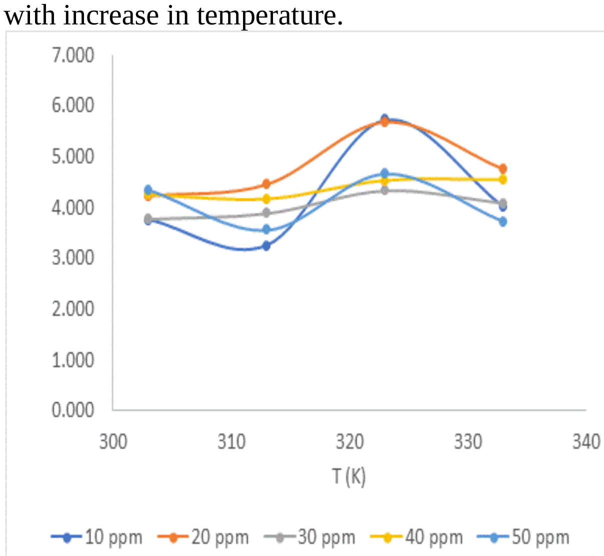


Fig. 4: Variation of equilibrium amount of dye adsorbed by alumina with initial temperature at various concentrations

This is expected because the molecules in nano alumina is more ordered than those in alumina. Also, nano alumina seems to be more sensitive to changes in temperature than alumina because of reduced molecular dimension.

Adsorption isotherm can furnish sufficient information on the adsorption behavior of the dye unto alumina and nano alumina. Consequently, adsorption data were tested for various adsorption isotherm and was found to fit the Langmuir adsorption model (equation 8)(Nagy *et al.*, 2017)

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (8)$$

C_e denotes the equilibrium concentration of adsorbate (mg/l), q_e stands for the amount of adsorbate adsorbed per unit mass of the adsorbent (mg/g), b is the Langmuir adsorption constant which is related to affinity between the adsorbate and the adsorbent and q_m represents the theoretical monolayer saturation capacity.

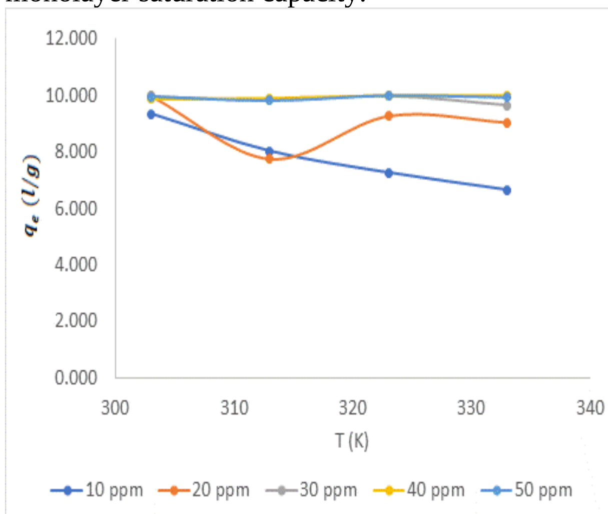


Fig. 5: Variation of equilibrium amount of Congo red dye adsorbed by nano alumina with initial temperature at various concentrations

3.3 Thermodynamic and adsorption study

The equilibrium amounts adsorbed(q_e) and equilibrium concentration (C_e) are related to the equilibrium constant according to the following equation,

$$k_c = \frac{q_e}{C_e} \qquad (3)$$

Also, from thermodynamics,

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (4)$$

Therefore,

$$-2.303RTlogk_c = \Delta H^* - T\Delta S^* \qquad (5)$$

$$-Tlnk_c = \Delta H^* - T\Delta S^* \qquad (6)$$

$$lnk_c = \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \qquad (7)$$

Therefore, a plot of lnk_p *versus* $\frac{1}{T}$ is expected to be linear with slope and intercept equal to $\frac{\Delta H^*}{R}$ and $\frac{\Delta S^*}{R}$ respectively. These plots are shown in Figs. 6 and 7 for the adsorption of Congo red dye unto alumina and nano alumina respectively. .

Thermodynamic parameters deduced from the plots are presented in Table 1. The results reveal that the adsorption of the dye is endothermic and occurred with positive values of entropy change.

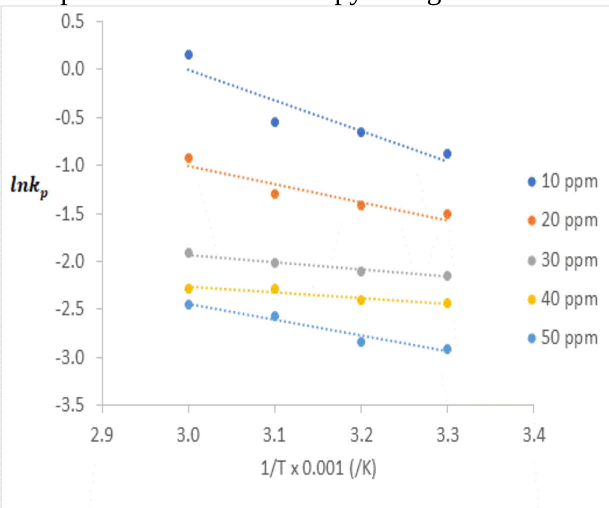


Fig. 6: Transition state plot for adsorption of Congo red dye unto alumina

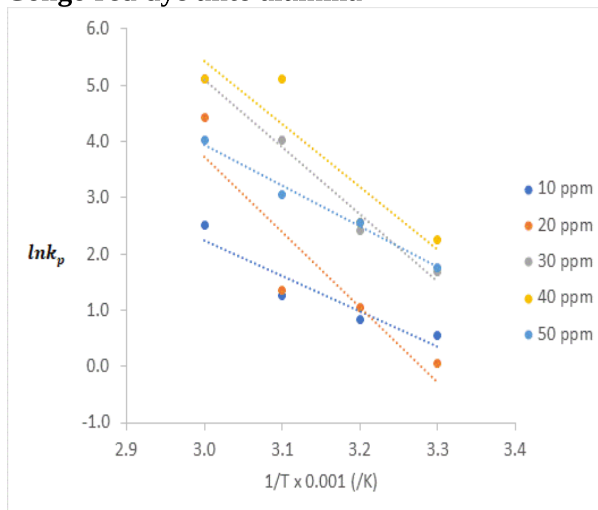


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Fig. 7: Transition state plot for adsorption of Congo red dye unto nano alumina

Table 1: Thermodynamic parameters for the adsorption of Congo red dye unto alumina and nano alumina

System	C (ppm)	Slope	Intercept	ΔH^* $J/mol)$	ΔS^* (J/mol)	R^2
Alumina	10	-3.1893	9.57	26.516	79.565	0.8622
Alumina	20	-1.8906	4.671	15.718	38.835	0.8877
Alumina	30	-0.7835	0.4231	6.514	3.518	0.9764
Alumina	40	-0.5538	-0.6073	4.604	-5.049	0.8934
Alumina	50	-1.6506	2.5065	13.723	20.839	0.9585
Nano alumina	10	-6.3199	21.193	52.544	176.199	0.8866
Nano alumina	20	-13.428	44.015	111.640	365.941	0.8442
Nano alumina	30	-11.924	40.864	99.136	339.743	0.9827
Nano alumina	40	-11.171	38.948	92.876	323.814	0.8428
Nano alumina	50	-7.2645	25.732	60.397	213.936	0.9857

The Langmuir isotherm for the adsorption of the studied dye unto the surface of alumina and nano alumina are provided in Figs. 8 and 9 respectively. Adsorption parameters were calculated from the slope and intercept of the plots (according to equation 8) and are recorded in Table 3. The slope gives the theoretical maximum adsorption capacity (q_m), which reveals that nano-alumina has better experimental and theoretical adsorption capacity for the dye than alumina.

The theoretical adsorption capacity of the studied adsorbent compares favourably with experimental data (R^2 = 0.9627). The Langmuir adsorption model also analysed the feasibility of adsorption through a dimensionless factor called separation factor (R_L) defined as (Badu *et al*., 2014),

$$R_L = \frac{1}{1 + b_{ads}(C_0)} \quad (9)$$

Adsorption is termed linear when $R_L = 1$, favourable when $0 > R_L < 1$ and unfavourable when $R_L > 1$.

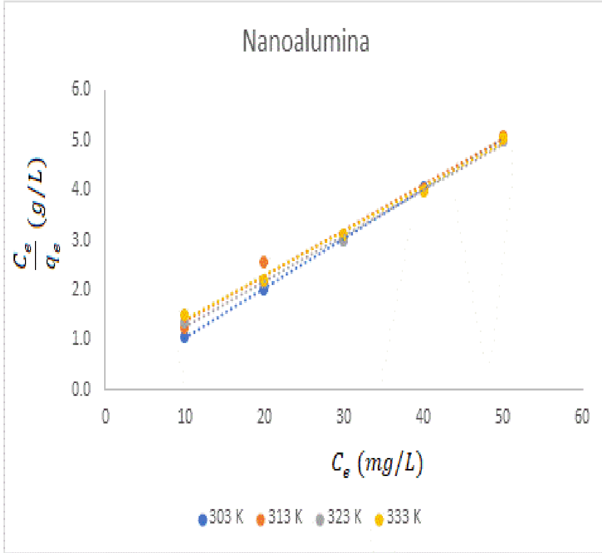

Fig. 8: Langmuir isotherm for the adsorption of Congo red dye unto the surface of nano alumina

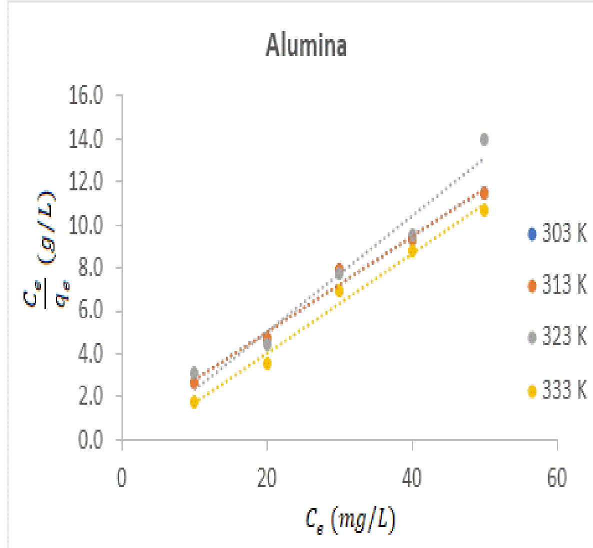

Fig. 9: Langmuir isotherm for the adsorption of Congo red dye unto the surface of alumina

Table 3: Langmuir parameters for the adsorption of Congo red dye onto the surface of alumina and nano alumina

Adsorbent	T (K)	Slope	Intercept	q_m $(mg/g$ (Theo)	q_m (mg/g) (Exp)	b_{ads}	K_{ads} (mg/g)	ΔG^0_{ads} (J/mol)	R^2
Nano alumina	303	0.0995	0.0476	10.05025	9.954	2.0903	21.0084	-7670.59	0.9997
Nano alumina	313	0.0913	0.4590	10.9529	9.835	0.1989	2.1786	-2026.41	0.9844
Nano alumina	323	0.0911	0.3768	10.97695	9.983	0.2418	2.6539	-2621.08	0.9967
Nano alumina	333	0.0885	0.5162	11.29944	9.926	0.1714	1.9372	-1830.74	0.9960
Alumina	303	0.2225	0.5567	4.494382	4.363	0.3997	1.7963	-1475.53	0.9872
Alumina	313	0.2225	0.5567	4.494382	3.564	0.3997	1.7963	-1524.23	0.9872
Alumina	323	0.2698	0.3243	3.706449	4.676	0.8319	3.0836	-3024.02	0.9679
Alumina	333	0.2321	0.6269	4.308488	3.735	0.3702	1.5952	-1292.83	0.9873

Calculated R_L values for nano alumina were 0.00948, 0.0914, 0.0764 and 0.1045 at 303, 313, 323 and 333 K. The corresponding values for the alumina were 0.0477, 0.0477, 0.0235 and 0.0513 respectively. Therefore, the adsorption of Congo red dye on alumina and nano-alumina is favourable. The standard free energy of adsorption of the dye unto alumina and nano alumina were also calculated using the Gibb Helmholtz equation (Eddy, 2009)

$$\Delta G^0_{ads} = -RTlnK_{ads} \quad (10)$$

where R is the gas constant, T is the temperature and K_{ads} is Langmuir constant defined as the product of the monolayer adsorption constant (b_{ads}) and the theoretical maximum adsorption capacity (q_m). Calculated values of the free energy (Table 3) were relatively low and pointed towards spontaneous physisorption mechanism. However, ΔG^0_{ads} for the nano-alumina were more negative than those obtained for the alumina, which indicated better adsorption.

4.0 Conclusion

Alumina and nano alumina are good adsorbents for the removal of Congo red dye from aqueous solution. Both adsorbents follow similar mechanism of physiosorption. Their adsorption is spontaneous, favourable and endothermic. However, nano-alumina has better adsorption capacity for Congo red dye than alumina.

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