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Adsorptive Removal of Bromophenol Blue Dye from Aqueous Solution using Acid Activated Clay

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Abstract

Sulphuric Acid Activated River Niger (SAARC) adsorbent was prepared and used for the treatment of simulated wastewater. The merits of the chemical activation were evident on the characterization results. The morphology of the clay suggested that it belongs to the kaolinite family. Experiments conducted show the percentage of Bromophenol blue (BB) dye adsorbed on SAARC significantly depends on pH, adsorbent dosage, contact time, temperature and dye concentration. Langmuir model best fitted the experimental data compared to the results obtained for Freundlich, Temkin and Dubnin-Radushkevich isotherm models. The Dubinin-Radushkevich isotherm , E, depicts that the adsorption process is physisorption in nature. The experimental data were better described by the pseudo-second order and the power function kinetics models. The feasibility and spontaneity, exothermic nature and decreased randomness at the solid-solution interface were confirmed by the negative values calculated for Gibb's free energy (ΔG∘), enthalpy change (ΔH∘) and entropy change (ΔS∘) respectively. The results obtained corroborate the potential suitability of the prepared sulphuric acid activated River Niger Clay (SAARC) as an adsorbent.

Keywords: Adsorption, Isotherm, Kinetics, Bromophenol blue dye, River Niger Clay

1.0 Introduction

The pollution of water resources with industrial effluents containing organic compounds and toxic substances is a matter of great concern. Environmental contamination has been pointed as one of the greatest problems of modern society, mainly due to the population explosion and the increased industrial activity (Zhang *et al*., 1998; Colpini *et al*., 2008). Generally, effluents from textile industries, paper printing and photography contain residues of dyes and chemicals. However, the textile industry stands out because it produces large amounts of effluents which can cause serious environmental problems since they contain coloured compounds resulting from dyes unfixed to fibers during the dyeing process (Colpini *et al*., 2008).

Textile industry is one of the largest industries in the world (Beltra *et al*., 2008). There are a number of dye substances which could be highly polluting if released into the environment. Therefore, it is important to reduce the dye concentration in the wastewater before discharging it into the environment. Discharging large amounts of dyes into water resources, accompanied by organics, bleaches, and salt, can affect the physical and chemical properties of fresh water (Erdem *et al*., 2004). These dyes and their degradation products may be carcinogens and toxic (Teng and Lin, 2006), hence the removal of dyes from wastewater becomes an important issue in the environmental protection.

Due to their complex structure and synthetic origin, they cannot be easily removed by conventional physical, chemical or biological effluent treatment processes such as flocculation-coagulation, ozonation and aerobic or anaerobic digestion (slokar and Marechai, 1998). These processes are expensive and may lead to the generation of sludge or by-products (Hutzinger, 1980**)**. Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, simplicity of design, use of operation and insensitivity to toxic substances (Meshko *et al*., 2001; Choi *et al*., 2001). Adsorption has been used extensively in industrial process for separation and purification. The removal of coloured and colourless organic pollutants from industrial waste water using adsorbents is considered as an important application of adsorption process (Al-qodah, 2000).

Activated carbon has been the most widely used adsorbent because of its high capacity for the adsorption of organic species and dye (Malik, 2003). However, due to the difficulty and expense in regeneration, clays are considered as alternative low cost adsorbent. Since some clay derivatives can be easily prepared and regenerated, they are proposed as an inexpensive removal technique (Ho *et al*., 2006).

Natural clays are hydrophilic and, therefore, inefficient for the adsorption of organic compounds in water (Alkan *et al*., 2005). When subjected to chemical treatments, such as for example, with Sulphuric or phosphoric acid, surface properties of the clay can be greatly changed presenting a hydrophobic and organophilic character, which exhibits a high affinity for organic compounds. These modified clays have been widely used in waste water treatment process (Gok *et al*., 2010; Bertagnolli *et al*., 2011; Almeida et al., 2012).

In this work, the prime objective is to study the level of treatment measured by the percentage of BB dye adsorbed from aqueous solution on SAARC. The effects of the process variables, pH, adsorbent dosage, contact time, temperature and dye concentration for the adsorption were examined. Adsorption isotherms using models such as Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherms were evaluated. Kinetic models will be evaluated in order to identify potential adsorption process mechanisms. Also, the thermodynamic parameters, Gibb's free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were evaluated.

2.0 **Materials and Methods**

2.1 Materials preparations

Clay sample, a material of abundant regenerative resource, was sourced from River Niger in Onitsha, Anambra state. The sample was washed with clean water, dried for three days, size-reduced and sieved to 300 µm particle size with mechanical shaker. 90g of the sample was introduced into a beaker containing 900ml of 2.5M H_2SO_4 solution then agitated in a constant temperature magnetic stirrer at a temperature of 98^o C for 2hours (Onu *et al.*, 2014). The resulting mixture was filtered and washed repeatedly with distilled water to reduce to neutral pH. The sample was then dried in an electric oven at a temperature of 110˚C. The dried activated clay sample was finally crushed and size reduced to 75µm then stored in an air tight container.

Stock solution of the dye, BB (Molecular formula: $C_{19}H_{10}Br_4O_5S$, Molar mass: 669.96 g.mol^{-1}, Wavelength: about 590nm), was prepared by dissolving 500mg of BB dye in 1litre of distilled water (500mg/L). The resulting solution was kept in a dark coloured glass bottle. Lower concentrations of the dyes were prepared by diluting the stock solution to the desired concentrations using distilled water. Sulphuric acid and other chemicals were of analytical grade and used without further purification.

2.2 Adsorbent Characterization

Scanning electron microscopy (SEM) was used to view the surface morphology of the samples. The Clay elemental analysis was evaluated using Varian AA240 Atomic Absorption Spectrophotometer (AAS) according to the method of American Public Health Association (APHA 1998). The following physic-chemical properties of the samples were also evaluated:

2.2.1 Determination of Surface Area

Sears' method was used for the determination of the surface area of sulphuric acid activated and raw clay samples (Dada *et al*., 2012). It involves agitating 1.5g of the activated clay samples in 100ml of diluted hydrochloric acid at a pH of 3 and then adding 30g of sodium chloride while stirring the suspension. The volume was then made up to 150ml with deionised water. The solution was titrated with 0.1M NaOH to raise the pH to 4.0, and then to pH 9.0. The volume, V required to raise the pH from 4.0 to 9.0 was recorded. The surface area was then calculated by the equation below:

$$S=32V-25 \qquad (1)$$

Where, S = surface area of the clay sample, V = volume of NaOH needed to raise the pH of the sample from 4.0 to 9.0

2.2.2 Determination of pH

5g of raw clay was added to 50ml of distilled water. The mixture was stirred vigorously using magnetic stirrer without heat and then allowed to settle. The pH of the clay suspension was then measured using pH meter. The same procedure was repeated for sulphuric acid activated clay sample.

2.2.3 Determination of Moisture Content

This was done by weighing 2g of the clay sample into a crucible of a known weight. This was placed in the oven and heated for 2hours at constant temperature of 105°C. The sample was re-weighed and the weight recorded as W_3.The difference in the mass constitutes the amount of moisture content of the adsorbent (Dada *et al*, 2012). The percentage of moisture was calculated from equation (2):

$$\%MC = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \qquad (2)$$

where, W_1= Weight of crucible, W_2= Initial weight of crucible with sample, W_3= Final weight of crucible with sample.

2.3 Batch Adsorption Studies

2.3.1 Effect of pH

The effect of pH on the adsorption capacity was studied over pH 2-10. Five 250ml-stoppered glass Erlenmeyers flasks containing 100ml of the adsorbate at 100mg/L initial concentration, 30 ± 2°C at various pH values under investigation were prepared. In each of the flasks, 1g of 75µm particle size of SAARC was fed. pH adjusters (NaOH and HCl) were used to alter the pH of the solution to a desired pH. The content of each flask was agitated at 120rpm stirring speed. After a period of 120 minutes, the adsorbent was then filtered off the solution. The concentration of the supernatant solution was measured using a UV-vis spectrophotometer. The % of BB dye adsorbed was calculated from equation (3):

$$\%Ads = \frac{C_o - C_e}{C_o} \times 100 \qquad (3)$$

where C_o and C_e are initial and equilibrium concentrations of the aqueous solution respectively

2.3.2 Effect of Adsorbent Dosage

At various adsorbent dosages (0.3, 0.5, 0.8, 1.0, 1.5 and 2.0grams), the effect adsorbent dosage on adsorption process at room temperature, 75µm, 150mins, 120rpm and initial dye concentration of 100mg/L was evaluated.

2.3.3 Effect of Contact Time and Temperature

The effect of contact time (10, 20, 30, 40, 50, 60, 70, 80 and 90 minutes) and temperature (30^oC - 60^oC) on the % of BB dye adsorbed at 75µm, 120rpm was also studied.

2.3.4 Effect of Initial Dye Concentration and Temperature

The effect of concentration (100, 150, 200, 300 and 500mg/l) and temperatures (30^oC - 50^oC) on the % of BB dye adsorbed at 75µm, 150mins, 120rpm was studied.

3.0 Results and Discussion

3.1 Physic-chemical Parameters of the Clay Sample

Moisture content, pH and Surface area of the sulphuric acid activated clay (SAARC) and raw clay (RC) samples are shown in Table 1. The results presented show higher surface area for SAARC when compared to the value recorded for RC. This difference in surface area may be as a result of possible burning-off of volatile matter and other impurities during the activation process. On a general note, the larger the specific surface area of an adsorbent, the better its adsorptive performance. The lower moisture content of SAARC compared to RC is an indication that extensive porosity was introduced by the activation process.

Table 1: Physic-Chemical Parameters of the clay Sample

Property	Clay	
	SAARC	RC
pH	5.47	6.38
Moisture (%)	8.5	6
surface area(cm^2)	114.5	29.4

3.2 Atomic Absorption Spectrophotometer (AAS)

The result of AAS analysis is tabulated in Table 2. It shows the concentration (ppm) of different elements present in the clay sample. It is observed from the result that River Niger clay contains Aluminium, Silicon, Iron, Zinc, Magnesium, and Manganese in major quantities and elements like Potassium, Copper, Sodium, and Calcium in minor quantities. The result also indicates that the element with highest concentration is Silicon.

Table 2: The AAS Characterization Result of River Niger clay

Element	Concentration (ppm)
Si	458.4375
Al	258.4375
Fe	48.629
Ca	2.067
Mg	30.226
Na	1.003
K	4.567
Zn	43.317
Mn	157.205
Cu	2.458

3.3 Scanning Electron Microscopy (SEM) Analysis of Clay Samples

Figures 1 and 2 show the SEM microphotographs of RC and SAARC. SEM micrograph presents the morphology, crystalline structure and surface topography of the adsorbent. The SEM analysis of some clay indicates coarse and loosely packs with some well-formed flakes and irregular and hexagonal edges (Kaolinites). Others may appear as plates of variable thickness and size with relatively well defined edges (Illites) or showing some elements of curling layers in the particles (Smectite) (Bajwa, 2002). This suggests that clay minerals could be identified by exploiting the morphological features of the clay. Based on this, the coarseness and loose packs observed in the SEM microphotograph suggests the presence of Kaolinite. The result also showed that activated clay is more loosely packed and coarser than natural clay.

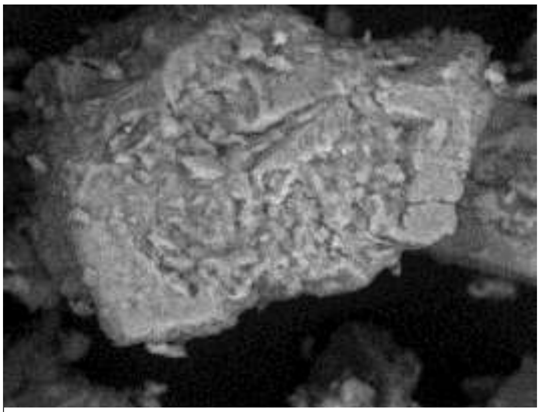

Fig 1: SEM micrograph for RC

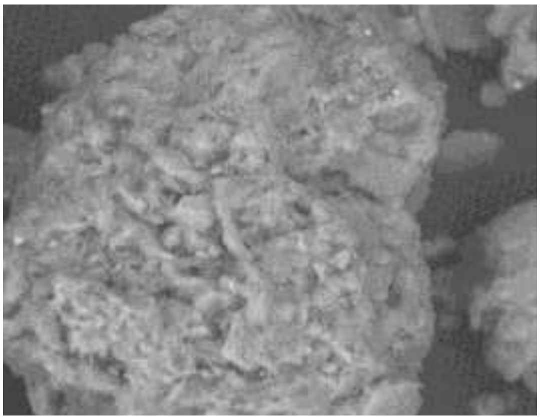

Fig 2: SEM micrograph for SAARC

3.4 Effect of adsorption system variables

3.4.1 Effect pH

The adsorption of BB dye from aqueous solution onto the activated clay sample is primarily influenced by the surface charge of the adsorbent and the degree of ionization of the adsorptive sites (Bayramoglu *et al.*, 2009). The pH of the solution may change the surface charge of the adsorbent, degree of ionization of the adsorbate molecule and extent of dissociation of functional groups on the active sites of the adsorbent (Ramachandran *et al,* 2011). The range of pH was adjusted between 2 – 10 to investigate the effect of pH on the adsorption of BB dye on SAARC at a fixed initial concentration 100mg/l. Figure 3 shows the effect of pH on the adsorption of BB dye on SAARC. It is observed that there is a decrease in percentage of BB dye adsorbed with increase in pH. The lower values recorded at basic pH range may be as a result that as pH value of the system increases, the surface charge of the adsorbents becomes more negatively charged hence electrostatic repulsion subsists between the dye molecules and surface charge of the SAARC thus the poor adsorbance was recorded (Okoye, *et al*., 2016). The maximum percentage uptake of BB dye was recorded at pH 2.

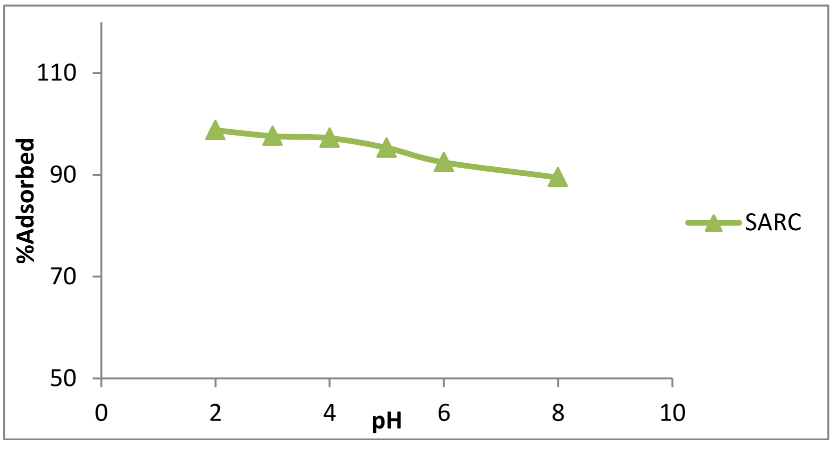

Fig 3: Effect of pH on percentage of BB dye adsorbed on SAARC

3.4.2 Effect of dosage

Figure 4 shows the percentage of BB dye adsorbed at different amounts of SAARC (0.3 – 2g). The trend of the graph shows increase in percentage of BB dye adsorbed as the adsorbent dosage was increased. The increase in adsorbent mass increased the contact surface of adsorbent particles which means more active sites, therefore, adsorption efficiency was increased (Pankaj and Harleen, 2011). Increase in dosage beyond 1g did not show any significant difference on the percentage of BB dye adsorbed. Therefore, 1g was selected as the optimum adsorbent dosage.

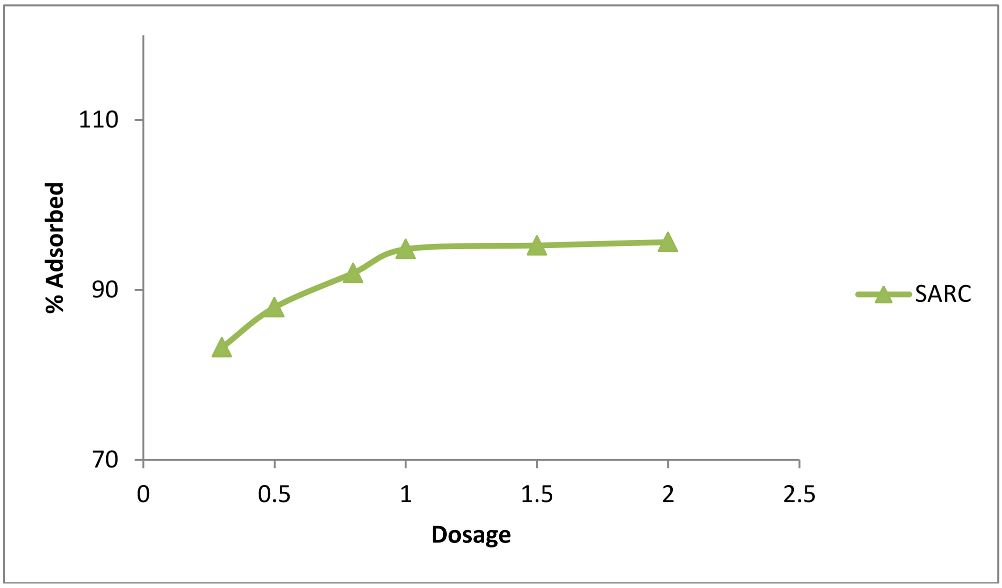

Fig 4: Effect of Dosage on percentage of BB dye adsorbed on SAARC

3.4.3 Effect of Temperature and Contact time

The effect of temperature on the adsorption of BB dye on the adsorbent was studied over temperatures 30°C, 40°C, 50°C and 60°C and contact times between 10 and 90 minutes at initial concentration of 100mg/l. The results obtained are represented in Figure 5. The results show a decrease in percentage of BB dye adsorbed with increase in temperature. This shows that adsorption of BB dye on SAARC is controlled by an exothermic process, hence, favoured by lower temperatures. A similar result was reported for Indigo carmine adsorption on silk (Jiwalak *et al*, 2010). The trend followed by Fig 5 show that the percentage of BB dye adsorbed initially increased rapidly with increase in contact time until the 60th minute. Increase in the percentage of dye adsorbed almost became constant at further increase in time. This result might be due to a large number of vacant surface sites available for adsorption during the initial stage of the treatment time. As the process progressed, less remaining vacant surface sites were available which resulted in almost constant adsorption efficiency (Jiwalak *et al*, 2010). However, in their explanation Gulipali *et al*, 2011 reported that the decrease in rate of adsorption at later time is due to repulsive forces between the solute molecules on the solid phase and in the bulk liquid phase.

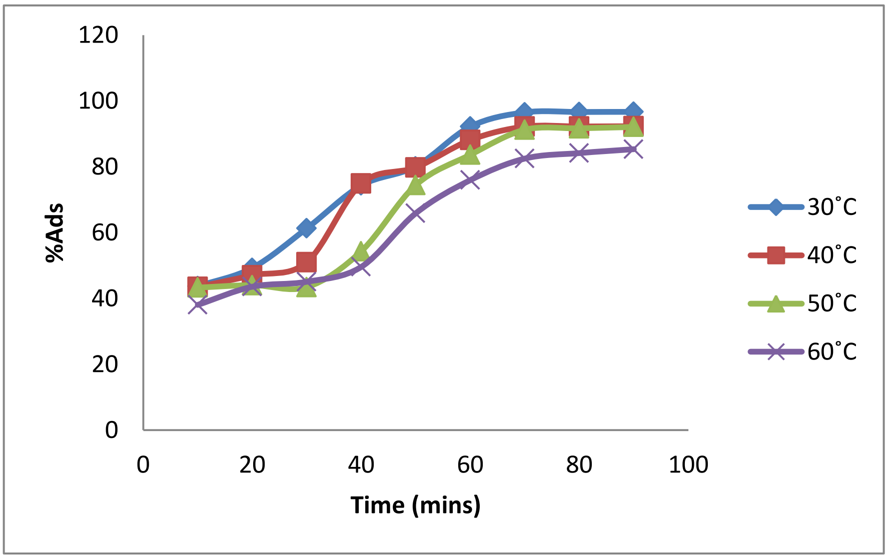

Figure 5: Effect of temperature and contact time on the percentage of BB dye adsorbed on SAARC

3.4.4 Effect of initial dye concentration and Temperature

The effect of initial dye concentration on adsorption process was studied at initial concentrations 100 – 500mg/l. The results presented in Figure 6 show that BB dye removal efficiency decreased with increase in initial dye concentration examined at various temperatures. This may be as a result that at higher adsorbate concentrations, the adsorptive sites became saturated therefore leaving some unadsorbed dye molecules in the supernatant solution. Bharathi and Ramesh (2013) stated that increasing concentration, the available adsorption sites become fewer and hence the percent removal of dye is dependent upon the initial concentration.

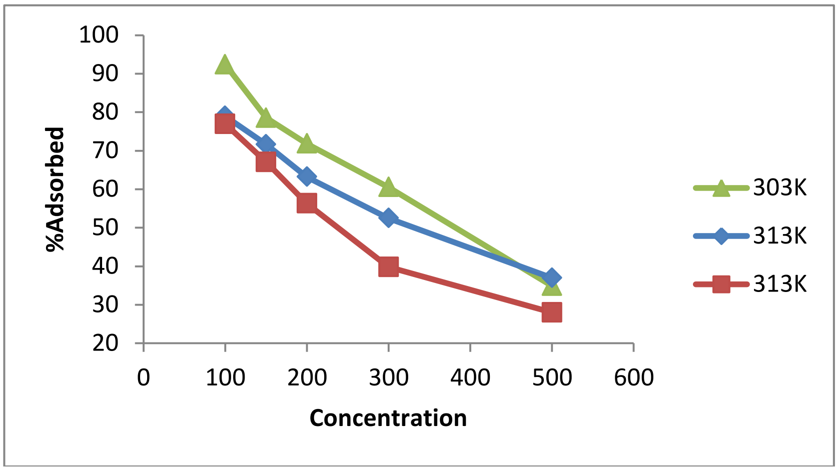

Figure 6: Effect of temperature and initial dye coon the percentage of BB dye adsorbed on SAARC

3.5 Adsorption Isotherm

Adsorption isotherms also referred to as equilibrium data are fundamental requirements for the design of adsorption systems (Bayramoglu *et al.*, 2009). The equilibrium data evaluates the capacity of the adsorbent to remove dye under the investigated conditions. Adsorption equilibrium defines a condition where the amount of solute adsorbed on the adsorbent is equal to the amount desorbed. Rao *et al*, 2006 stated that by plotting solid phase concentration against liquid phase concentration graphically, it is possible to depict the equilibrium adsorption isotherm. There are many theories relating to adsorption equilibrium. This current research considered Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherm models.

3.5.1 Langmuir Isotherm

The Langmuir model assumes that the uptake of adsorbate molecules occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed molecules[35]. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based upon these assumptions, Langmuir model is represented by the following equation:

$$q_e = \frac{\mathrm{Q_0 K_L C_e}}{\mathrm{1+K_L C_e}} \tag{4}$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation 4 into linear form (equation 5).

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{Q_o K_L} \tag{5}$$

where Ce is the equilibrium concentration of adsorbate (mg/L^{-1}); q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g); Q_o is the maximum monolayer coverage capacity (mg/g) and K_L is Langmuir isotherm constant (L/mg). From the intercept and slope of the graph (fig 7) Ce/qe against Ce, the Langmuir isotherm constant and maximum monolayer coverage capacity were derived. The coefficient of determination for the plots lie between 0.980 and 0.999. Considering the values recorded for the coefficient of determination at all temperatures, the Langmuir Isotherm model best described the adsorptive behaviour under investigation. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter (Dada *et al*, 2012).

$$R = \frac{1}{1+(1+K_L Co)} \qquad (6)$$

The Langmuir separation factor (R_L) indicates if the isotherm is unfavourable (R_L>1), linear (R_L=1), favourable (0<R_L<1) or irreversible (R_L=0) (Hameed et al, 2008; Ramachandran *et al*, 2011). The R_L values obtained lie between 0 and 1. This indicates that the adsorption process is favourable. Lower values of R_L within the range, 0< R_L <1, depict more favourability of the adsorbate on the adsorbent (Zengyu, et al., 2009). The result in Table 3 also shows that the separation factor was lowest at 30°C, implying that the adsorption process was more favourable at low temperature.

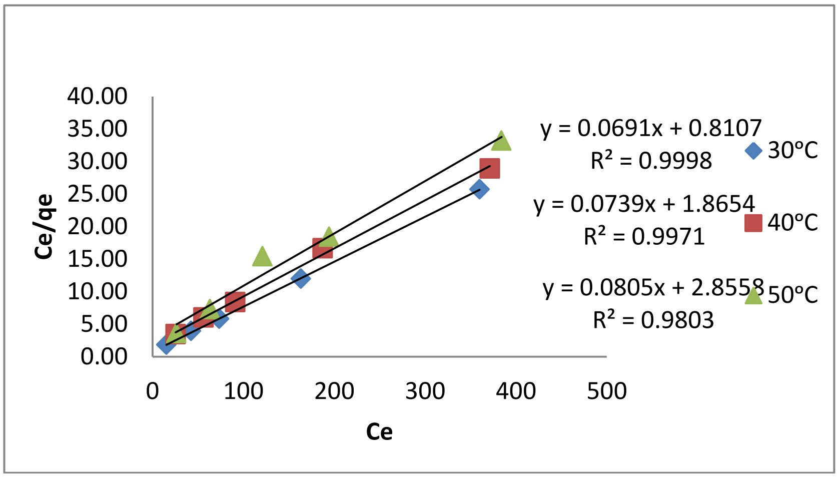

Figure 7: A plot of Langmuir Isotherm for BB dye adsorption on SAARC

3.5.2 Freundlich Isotherm

This is commonly used to describe the adsorption characteristics for the heterogeneous surface (Hutson and Yang, 2000). These data often fit the empirical equation proposed by Freundlich (equation 7):

$$Q_e = K_f C_e^{\frac{1}{n}} \qquad (7)$$

Where K_f is the Freundlich isotherm constant (mg/g); n is adsorption intensity; Ce is the equilibrium concentration of adsorbate (mg/L) and Qe = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g). Linearizing equation 7, we have:

$$logQ_e = K_f + \frac{1}{n} logC_e \qquad (8)$$

The Freundlich isotherm describing BB dye adsorption was illustrated in Figure 8. The Freundlich constants calculated from the linear equations were summarised in Table 3. The values of the exponent (1/n) was computed from the slope of equation 8. Arami *et al*, (2008) stated that 1/n values indicate the type of isotherm to be irreversible (1/n = 0), favourable (0<1/n<1), unfavourable (1/n>1). The values of 1/n which ranges from 0.110 – 0.165 were obtained from table 3. These values fall within the range 0 <1/n<1 implying that the adsorbents are good for adsorption. The values of the coefficient of determination show that Freundlich isotherm model did not fit properly the experimental data at temperature 60°C. However, at temperatures 30°C and 40°C, the R^2 values recorded were close to unity.

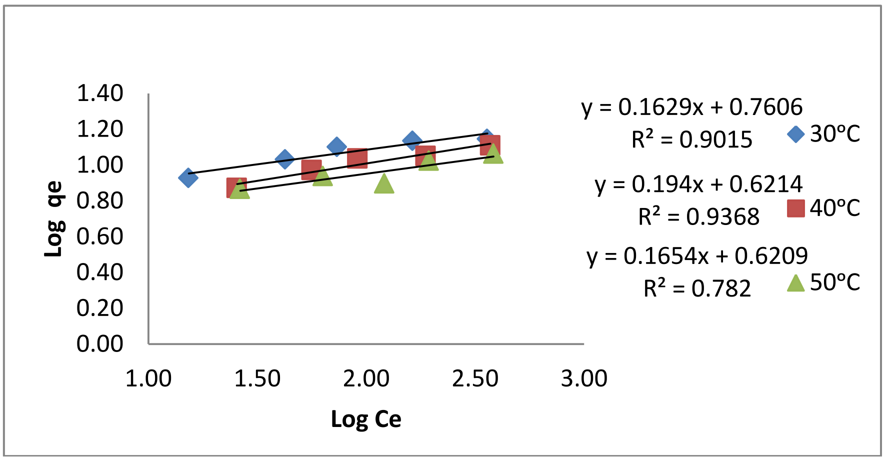

Figure 8: A plot of Frendlich Isotherm for BB dye adsorption on SAARC

3.5.3 Temkin Isotherm

The model is given by the following equations (9 – 12) (Dada *et al*, 2012):

$$q_e = \frac{RT}{b} ln(A_T C_e) \qquad (9)$$

$$q_e = \frac{RT}{b} lnA_T + \frac{RT}{b} lnC_e \qquad (10)$$

$$B = \frac{RT}{b} \qquad (11)$$

$$q_e = BlnA_T + BlnC_e \qquad (12)$$

A_T represents Temkin isotherm equilibrium binding constant (L/g); b_T is Temkin isotherm constant; R is universal gas constant (8.314J/mol/K); T is Temperature at 298K and B is Constant related to heat of sorption(J/mol). The Temkin isotherm for BB dye adsorption on SAARC was shown in figure 9. The isotherm parameters and the coefficient of determination, R^2, are listed in Table 3. The values of R^2 indicate that the adsorption of BB dye on the SAARC do not follow at higher temperatures, 40°C and 50°C, the Temkin isotherm model.

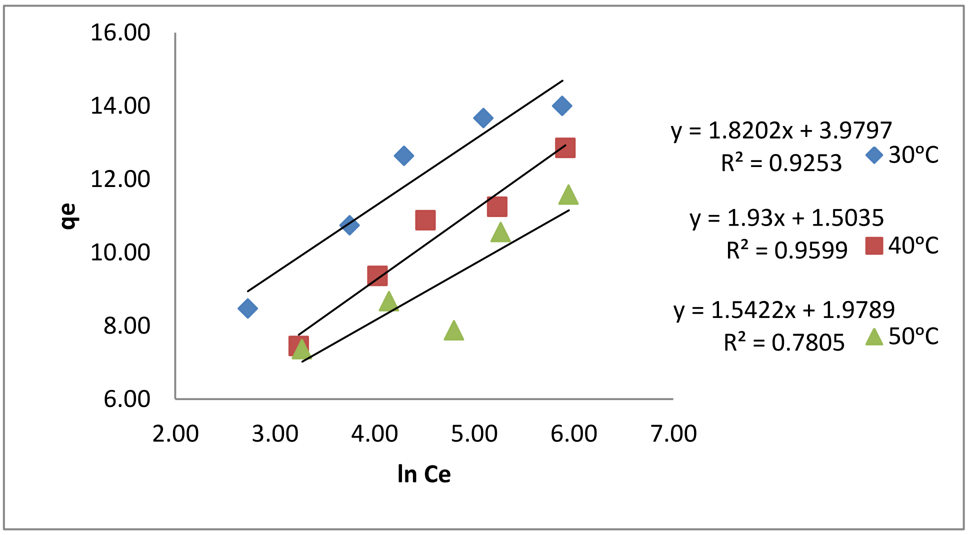

Figure 9: A plot of Temkin Isotherm for BB dye adsorption on SAARC

3.5.4 Dubinin-Radushkevich Isotherm

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface (Gunay *et al*, 2007, Dabrowski, 2001).

$$q_e = q_m exp(-\beta\varepsilon^2) \quad (13)$$

$$lnq_e = lnq_m - \beta\varepsilon^2 \quad (14)$$

where qe, qm and β are amount of adsorbate in the adsorbent at equilibrium(mg/g); theoretical isotherm saturation capacity (mg/g) and Dubinin–Radushkevich isotherm constant (mol^2/kJ^2) respectively. The approach was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy, E per molecule of adsorbate can be computed by the relationship (Dada *et al*, 2012):

$$E = \frac{1}{\sqrt{2\beta}} \quad (15)$$

ε is the Polanyi potential which is related to the equilibrium concentration as follows:

$$\varepsilon = RTln\left(1 + \frac{1}{C_e}\right) \quad (16)$$

where R, T and Ce represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively.

The experimental data showed poor agreement with Dubinin-Radushkevich isotherm as is evident in the low R^2 values obtained (Table 3). The value of E calculated is seen in Tables 3. Based on this energy of activation one can predict whether an adsorption is physisorption or chemisorption. If the energy is < 8KJ/mol, the adsorption is physisorption and if the energy is 8-16 KJ/mol, the adsorption is chemisorptions in nature (Ramachandran *et al*, 2011). From Table 3, the value of E obtained in this research work is below 16KJ/mol thereby implying that adsorption is physisorption in nature.

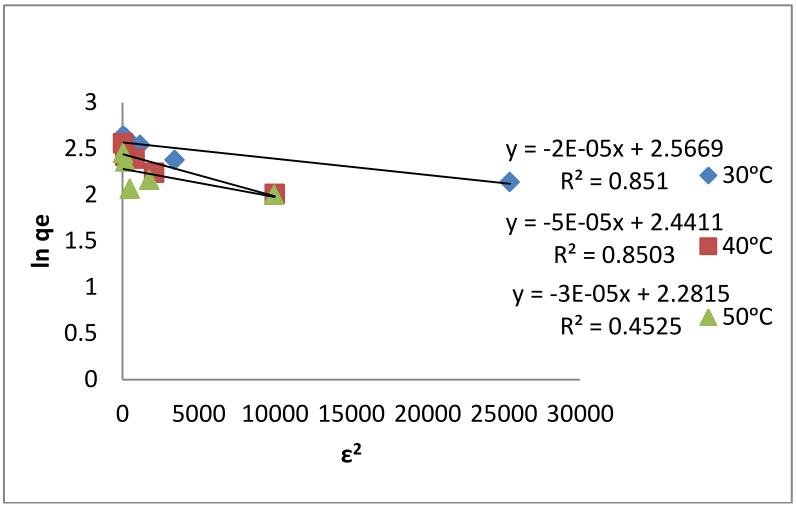

Figure 10: A Plot of Dubinin-Radushkevich Isotherm for BB dye adsorption on SAARC

Table 3: Isotherm data for BB dye adsorption on SAARC

Temp	Langmuir				Freundlich		
	Q_o	K_L	R_L	R^2	1/n	K_f	R^2
30°C	14.493	0.085	0.095	0.999	0.162	0.760	0.901
40°C	13.699	0.039	0.169	0.997	0.194	0.621	0.936
50°C	12.500	0.028	0.208	0.980	0.165	0.620	0.782

Temp	Temkin			Dubnin-Raduskevich			
	B	A_T	R^2	β	q_m	E	R^2
30°C	1.820	8.902	0.925	8E-06	13.014	0.250	0.851
40°C	1.930	6.008	0.959	5E-05	11.485	0.100	0.850
50°C	1.542	3.607	0.780	1E-05	9.786	0.224	0.452

3.6 Adsorption Kinetics

3.6.1 Pseudo-first Order Kinetic model

Equation 17 represents the linear form of pseudo-first-order equation:

$$\log(q_e - q_t) = \log q_e - t\frac{K_1}{2.303} \qquad (17)$$

Where k_1 (min^{-1}) is the pseudo- first-order adsorption kinetic parameter; q_t is the amount adsorbed at time t (min); and q_e denotes the amount adsorbed at equilibrium, both in mgg^{-1}. The experimental data obtained for the adsorption of BB dye on SAARC was fitted to the pseudo-first order kinetic model equation. Figure 11 are plots of Log (qe-qt) against time, t at various temperatures. K_1 and q_e at different temperatures were derived from the slope and the intercepts of the plots and tabulated in table 4. The results show low coefficient of determination values for BB dye on SAARC. This implies that the adsorption kinetics of BB dye cannot be well described by the pseudo-first order model.

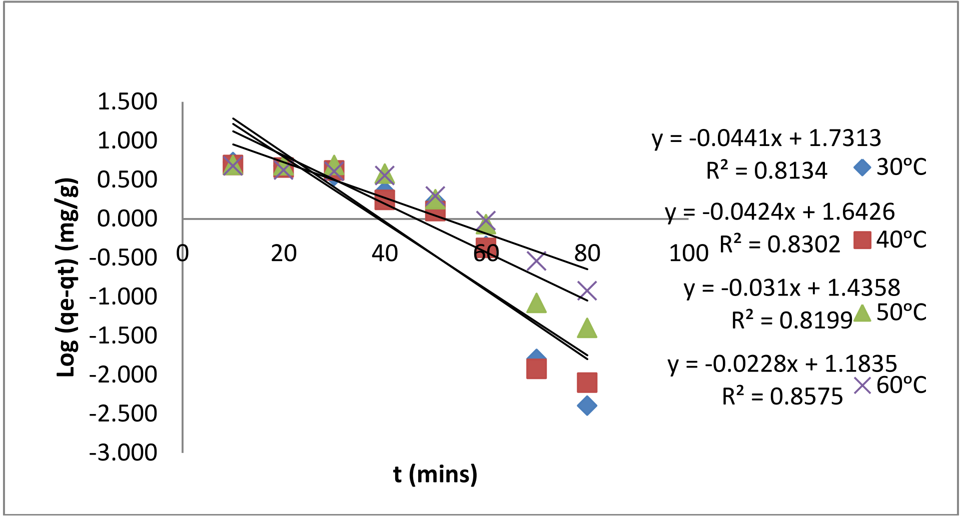

Figure 11: A plot of pseudo-first order kinetic model for adsorption of BB dye on SAARC

3.6.2 Pseudo-second order kinetic model

The pseudo - second-order equation based on the adsorption capacity at equilibrium may be expressed by the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e} \qquad (18)$$

where k_2 ($g\ mg^{-1}\ min^{-1}$) is the pseudo-second - order adsorption kinetic parameter. From the slope and intercept of the (t/q_t) as a function of t, k_2 and q_e can be obtained. The values obtained are presented in Table 4. Figure 12 are plots of t/q_t vs t at various temperatures. The results show higher R^2 values for adsorption BB dye on SAARC. From table 4, it is observed that the coefficient of determination values are close to unity, thus defined the adsorption process.

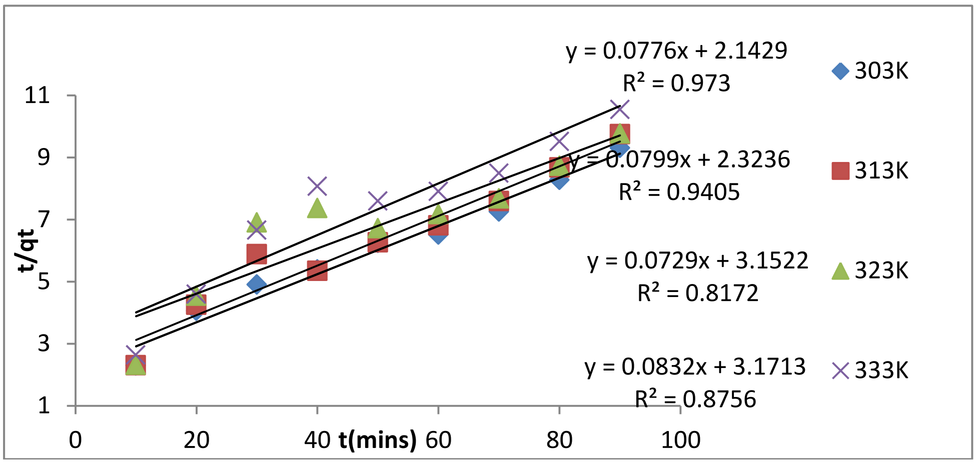

Figure 12: A plot of Pseudo-second order kinetic model for the adsorption of BB dye on SAARC

3.6.3 Power Function Kinetic Model

The fractional power function model is a modified form of the Freundlich equation and may be expressed by equation 19 or its linear form as given in equation 20 (Ho and Mckay, 2002).

$$q_t = at^b \qquad (19)$$

$$logq_t = \log a + \ blog\ t \qquad (20)$$

where q_t is the amount adsorbed at time t, while a, and b are constants with b < 1. The function ab is also a constant, being the specific sorption rate at unit time, i.e. when t = 1. Figure 13 show the plots of log (qt) against log (t) at various temperatures. The plots show R^2 values ranging from 0.817- 0.962. Generally, the coefficient of determination values recorded were close to unity therefore described the experimental data obtained for the process.

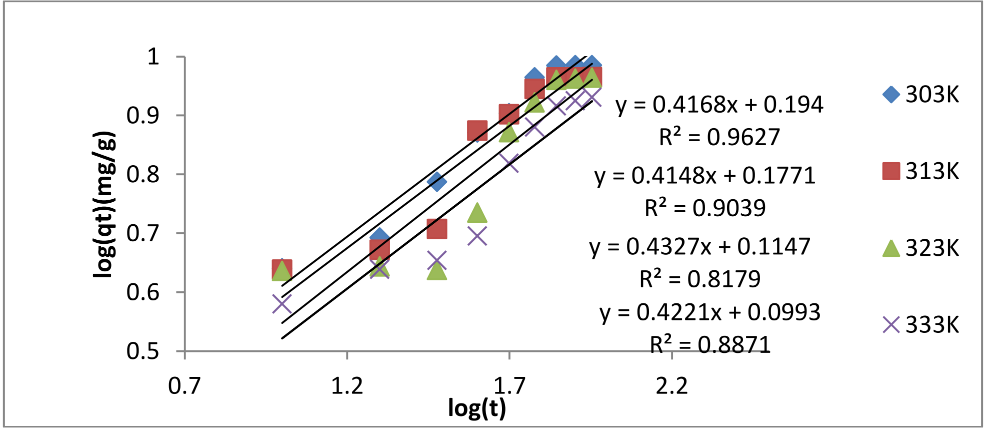

Figure 13: A plot of power function kinetic model for the adsorption of BB dye on SAARC

Table 4: Kinetics parameters for adsorption on BB dye on SAARC

Temp (°C)	Pseudo-first order			Pseudo-second order			Power function		
	qe	K_1	R^2	qe	K_2	R^2	a	B	R^2
30	53.8270	0.1013	0.813	12.9870	0.0359	0.973	1.5631	0.416	0.962
40	43.8531	0.0967	0.830	12.6582	0.0340	0.940	1.5031	0.414	0.903
50	27.2270	0.0714	0.819	13.8889	0.0228	0.817	1.3002	0.432	0.817
60	15.2405	0.0507	0.857	12.0482	0.0262	0.875	1.2560	0.422	0.887

3.7 Thermodynamic Parameters

Equations (21) **(**Rameshraja *et al.*, 2012) and (22) were employed to determine the thermodynamic parameters (Gibbs free energy change, ΔGº, enthalpy change, ΔHº and entropy change, ΔSº).

$$\Delta G^{\circ} = -RTlnK \qquad (21)$$

$$\Delta G = \Delta H - T\Delta S \qquad (22)$$

Where R (universal gas constant) = 8.314J/molK, *K* (L/mol) is the dependency of the equilibrium association constant (K = K_L, Langmuir constant) and T is the solution temperature.

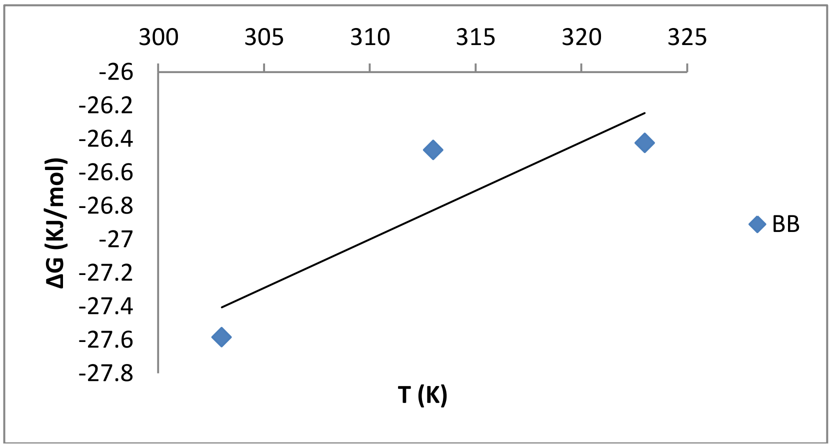

Figure 14: Thermodynamic plot for the adsorption of BB on SAARC

The thermodynamic parameters derived were presented in Table 5. A negative Gibbs free energy value indicates that the process is feasible (Singh et al, 2011 and Jiwalak et al, 2010). The negative ΔH values obtained confirm the exothermic nature of the process. According to Oliveira *et al.* 2008, negative ΔS value confirms the decreased randomness at the solid-solute interface during the adsorption process.

Table 5: Thermodynamic Parameters for the adsorption of BB dye on SAARC

Adsorbent	Temp (K)	ΔG (KJ/mol)	ΔH(KJ/mol)	ΔS(J/mol)
	303	-27.54		
SAARC	313	-26.47	-44.98	-59.20
	323	-26.42		

3.8 Conclusion

Adsorbent was produced from chemical activation of River Niger clay. From the results obtained, the adsorbent, SAARC, was effective in the treatment of aqueous BB dye solution at various operating conditions evaluated. The characterization results of the raw and activated clay samples show improvements on the properties of the activated clay. The process variables, pH, adsorbent dosage, contact time, temperature and dye concentration had significant effect on the level of treatment achieved using the adsorbent (SAARC). Considering the coefficient of determination recorded, the Langmuir isotherm model within the range of temperatures examined, best fitted the experimental data; also, the Pseudo second-order and the power function models better described the kinetics of the removal of BB dye onto SAARC. The negative values obtained for Gibbs free energy, enthalpy and entropy reveals that the process was feasible and spontaneous, exothermic and decreased randomness at the solid-solute interface.

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