Special Conference Edition, November, 2018

http://dx.doi.org/10.4314/bajopas.v11i1.3S

Bayero Journal of Pure and Applied Sciences, 11(1): 17 - 26
ISSN 2006 – 6996

KINETICS AND THERMODYMICS STUDIES FOR THE REMOVAL OF BROMOCRESOL PURPLE USING RAW BENTONITE CLAY AND ACTIVATED CARBON FROM *Vachellia nilotica* POD AS ADSORBENTS

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ABSTRACT
The adsorption of Bromocresol purple (BCP) onto Raw Bentonite Clay (RBC) and activated carbon from Vachellia nilotica (AVNP) was investigated using batch adsorption process. The adsorbents were characterized using Fourier transform spectrometer (FTIR) and Scanning Electron Microscope (SEM). The study of adsorption Kinetics and Thermodynamics were carried out. The pseudo –second order kinetic exhibits the best fit with the experimental data with R^2 values close to 1 and experimental values q_e (mg/g) 7.197 and 5.169 for RBC and AVNP are more closer to the calculated q_e 7.246 and 5.263.The negative values of Gibbs free energy change, ΔG of -5.98 to -7.75 and -2.77 to -4.36kJ/mol for RBC and AVNP respectively shows the process to be spontaneous. Positive values of enthalpy, ΔH, confirm the endothermic character of the adsorption process. Lower ΔH values of 11.01 and 11.98kJ/mol for adsorption of dye onto raw bentonite clay and activated carbon respectively, suggests that the adsorption is physical in nature..
Keywords: Bromocresol purple, Raw Bentonite clay, activated Vachellia nilotica pods kinetics, thermodynamic

INTRODUCTION

The use of synthetic chemical dyes in various industrial processes, such as food, paper, plastic, textile, e.t.c. is one of the most problematic water pollution causes. Discharge of waste-water into natural streams and rivers from the industries using dyes poses severe environmental problems because they are usually very recalcitrant to microbial degradation (Kadhim 2012; Bendaho *et al.*, 2015). Dyes in surface waters are of barrier effect on the sun light penetration and aeration of water body, and thus reduce photosynthetic activity (Arivoli *et al.*, 2015). For thse reasons, several methods are used for eliminating the excess of coloured organic pollutants from processes or waste effluents including biological treatments, however unsatisfactory results were achieved by these techniques.

Environmental contamination has been pointed as one of the greatest problem of modern society many due to the population explosion and increase in industrial activities (Farida *et al.,* 2015a). There are many processes available for treatment of dyes: chemical oxidation, flotation, adsorption, electrolysis, chemical coagulation, photo catalysis and biodegradation (Akinola and Umar, 2015; Brahim *et al.*, 2014). Among all these, adsorption has been found to be an efficient method for the removal of dyes from aqueous solutions because it produces high quality treated effluent and also allows kinetic and equilibrium measurements without the use any highly sophisticated instruments (Ghanbarnezhad *et al.*, 2014).

Adsorption is a process where pollutants are adsorbed on the solid surface. Basically, it is a surface phenomenon and adsorption takes place by physical forces but, sometimes, weak chemical bonding also participate in adsorption process (Sadanand and James, 2016). Different adsorbents have been used for removal of various materials from aqueous solutions, such as dyes, metal ions and other organic material. These include perlite, activated carbon, bentonite, silica gels, fly ash, lignite peat, silica e.t.c (Ishaq *et al.*, 2014).

Clays are hydrophilic in nature because of the presence of inorganic cations of bentonite. Thus, clay does not adsorb aliphatic and relatively hydrophobic compounds (Banik *et al.*, 2015). Natural clay is also considered an appropriate adsorbent due to its low cost and is nontoxic to ecosystem (Srinivasan,, 2011) and has high removal efficiency. In addition, importantfeatures such as large specific area, Bronsted and Lewis acidity and chemical stability (Patricia *et al.*, 2013).

Dye molecules have two major components: the chromophore groups, responsible for making the colour such as -C=C- and -N=N-, and the auxochrome groups, as for example: $-NH_2$, -OH, -COOH and $-SO_3H$, which render the solubility of the molecules and give affinity for the fibers (Farida *et al.*, 2015a). Dyes are mainly classified into cationic, anionic and non-ionic dyes (Farida *et al.*, 2015b; Bentahar *et al.*, 2016).

In this research raw bentonite clay (RBC) and activated carbon were used to remove bromocresol purple (BCP). The influence of adsorption parameter such as contact time adsorbent dose, initial dye concentration, temperature, point of zero charge and pH were studied. The adsorption kinetics and thermodynamics was evaluated.

MATERIALS AND METHODS

The pods of *a Vaheilianilotica was* collected from Central Bank of Nigeria quarters Hotoro GRA (Kano) and authenticated at the Department of plant science, Bayero University, Kano Nigeria. The Bentonite used in this investigation was obtained locally from Yobe at Potiskum. The different characterization techniques employed include: UV-Vis spectroscopy, (Cary 50, version 3.0), Scanning electron microscopy (SEM, Leica stereoscan-440 intertaced with phoenix EDX), Fourier Transform Infrared Spectroscopy FTIR (Cary 630 agilent technologies).

Preparation of raw bentonite clay

The raw bentonite clay was sieved with 75nm mesh size to remove large particles and dirt the raw bentonite clay was then stored in a plastic container and labeled (RBC).

Preparation of the Activated *Vachelia nilotica* pods Adsorbent (AVNP):

The sample was screened and washed with distilled water to remove dirt impurities, then air dried for 3 days. 250 g of the sample was impregnated in 75% H_2SO_4 for 24 hours. Then activated pods were carbonized in a furnace at 650^oC for one hour (Abdullah *et al.*, 2017). It was then washed again with de-ionized water until the pH being in the range of (6.8 ± 0.2). It was dried in an oven at 110^oC for 30 minutes then cooled, powdered, sieved with 75nm mesh size and stored in a plastic container and labeled (AVNP) this methods was reporteded by Sivakumar *et al.*, 2012 and Arivoli *et al.*, 2015).

Preparation of the Dye Stock Solution and Working Solution

1.11g of 90% Bromocresol purple (BCP), was accurately weighed using analytical weighing balance and dissolved to 1.0L of distilled water to prepare 1000mg/L of the aqueous dyes solution (stock solution). The working solutions, 2, 4, 6, 8, and 10mg/L of the dye were all prepared by serial dilution.

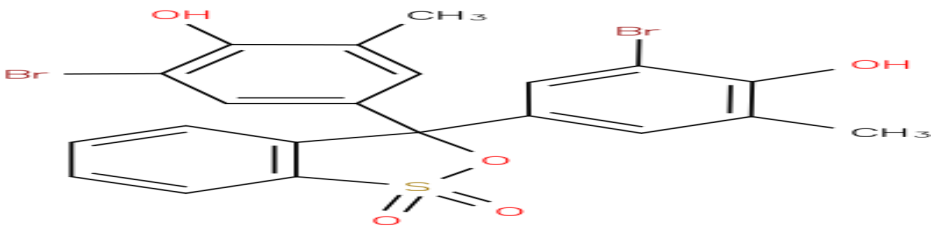


Figure 1: Structure of Bromocresol purple (BCP)

Batch Experimental studies

Adsorption experiments were carried out batch wise. 0.1g of adsorbents was added to sample bottles of 100 ml capacity; in each experiment 50 ml of dye solution of desired concentration was used. The bottles were subsequently capped and placed on an incubator shaker at a speed of 200 rpm at 29^oC with contact time (5-120minutes). Afore said conditions of batch experiments were kept constant during the optimization of various parameters effects on the dyes adsorption capacity of the adsorbents. The effects of temperature, pH, contact time, initial dye concentration and adsorbents dosage on adsorption capacity of the adsorbents were studied. After the batch experiment, the solution was filtered and then centrifuged for 10 minutes at 4000rpm and the supernatant was analyzed at 431nm wavelength for Bromocresolpurple using UV/VIS spectrophotometer. The amount of Bromocresol purple adsorbed and the adsorption efficiency (%R) of activated carbon and raw bentonite clay was calculated using Equations (1) and (2):

$$\% \ R = \frac{C_O - Ce}{C_O} \times 100 \quad (1)$$

$$qt = \frac{C_O - C_e}{C_O} \times \frac{V}{M} \quad (2)$$

Where C_0 is the initial concentration of dye in solution (mg/L), and Ce is the final dye concentration in aqueous solution after phase separation (mg/L), qt(mg/g) is the amount of biosorption per gram of adsorbent at any time t, V is the volume in L while m is mass of adsorbent in g (Farida *et al.*, 2015b).

RESULTS AND DISCUSSION

Characterization of adsorbents

Characterization of the adsorbent before and after adsorption was characterized by FTIR and SEM techniques.

Surface Morphological Studies

The surface morphology of natural clay and activated carbon were analyzed using scanning Electron Microscopy (tgSEM) both before and after adsorption of BCP molecules from aqueous solution. Figure 2(A & B) shows the SEM micrograph of raw bentonite clay (RBC) before adsorption and after adsorption of dye while figure 2 (C & D) shows the SEM micrograph of activated carbon (AVNP) surface before and after adsorption of BCP. SEM image of RBC before adsorption indicates that the material is composed of irregular shapes which provide a large surface area for the adsorption. After the adsorption of BCP, the structures become saturated as reported by Tahir *et al*. (2013). Similarly, for AVNP the image shows different structural features with uneven surface before adsorption. After adsorption the adsorbed molecules remain as aggregates on the adsorbents as shown in figure 2 (D).

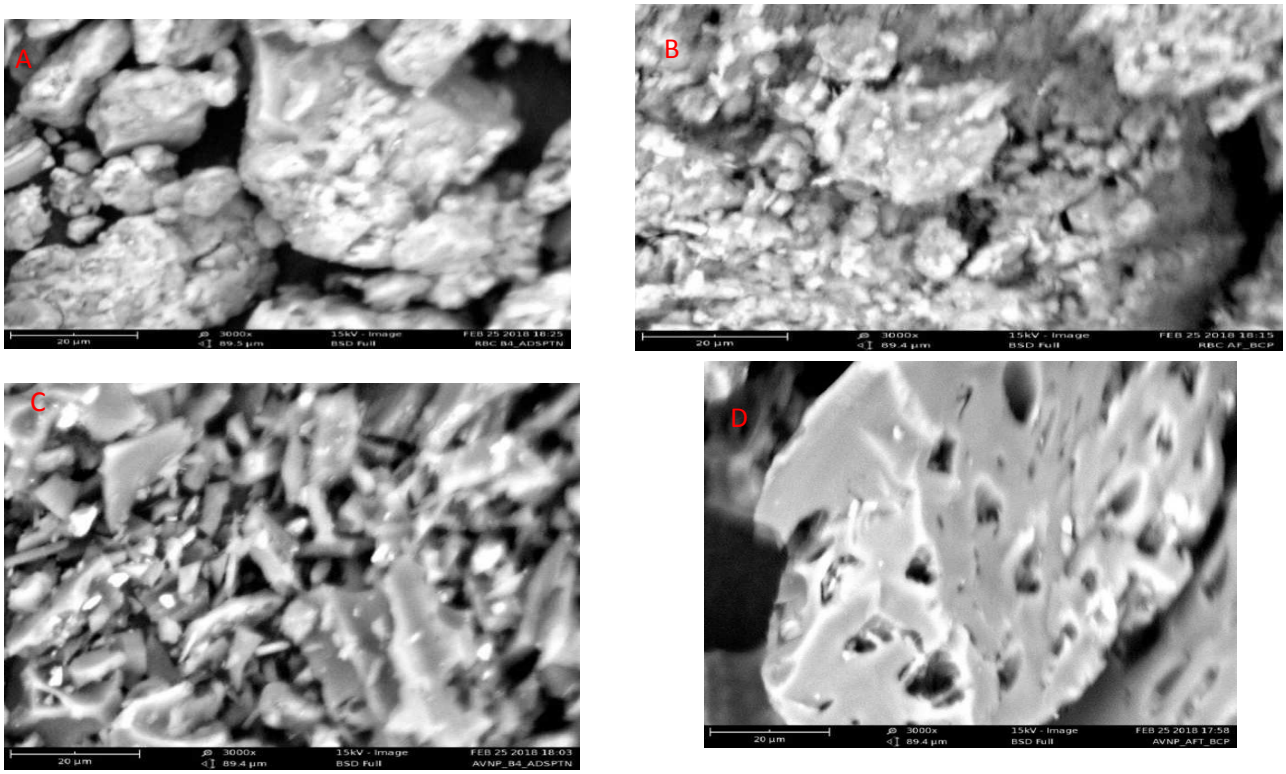


Figure **2 :**(A& B). SEM image of RBC before and after adsorption of bromocresol purple
:(C& D). SEM image of AVNP before and after adsorption of bromocresol purple

Interpretation of FTIR Results

In order to identify the major functional groups present on RBC and AVNP. A FTIR spectrum was recorded in mid IR region in the range of 4000 to 650 cm^{-1} by (Cary 630; Agilent Technologies), FTIR spectra for the adsorbents displayed a number of peaks pertaining to different functional groups. These were summarized in Tables 1 and 2 respectively. After adsorption peaks shifted to different frequency level or disappeared, indicating the possible involvement of those peaks for uptakes of dyes as shown in Table 1 and 2 through weak electrostatic interaction or Van der Waals forces as observed by Banerjee and Chattopadhyaya (2015). Similarly, the slight change in wave numbers show very small energy difference. Therefore there is a possibility of physical adsorption.

Table 1: Position and assignments of the IR vibration bands observed in the range of 4000-650 cm^{-1} of RBC before and after adsorption of bromocresol purple (BCP)

IR peak	Frequency (cm^{-1})		Differences	Assignment
	Before adsorption	After adsorption		
1	2121	2125	+4	C≡C (stretching
2	1994	2002	+8	O-H asymmetric stretching
3	1815	1819	-4	C=O in carboxylic, aldehydes, ketones, esters and lactones
4	1629	1640	+11	H-O-H bending
5	1000	992	+8	Si-O stretching
6	914	914	0	Bending vibration of (Al-Al-OH)
7	698	695	+3	-C-C- group

Table 2: Position and assignments of the IR vibration bands observed in the range of 4000-400 cm-1 of AVNP before and after adsorption of bromocresolgreen(BCG)

IR peak	Frequency (cm^{-1})		Differences	Assignment
	Before adsorption	After adsorption		
1	3413	3178	-235	O-H stretching in hydrogen bond
2	2843	2575	-263	Alkane (C-H Stretching
3	2125	2169	+44	C≡C (stretching)
4	1875	1875	0	C=O in carboxylic, aldehydes, ketones, esters and lactones
5	1585	1586	+1	C=C in aromatics or C=O stretch
6	1123	1033	-90	O-H asymmetric stretching
7	754	877	+123	=O in carboxylic, aldehydes, ketones, esters and lactones

Effect of contact time of BCP and BCG onto RBC

In the contact time effect on removal of Bromocresol purple onto bentoniteclay and activated carbon was evaluated. The result showed that the rate of adsorption of bromocresol purple onto the clay was rapid and then became slower near the equilibrium. The maximum adsorption capacity of bromocresol purple dye was attained after about 80min of shaking time .The percentage removal is 82.27% this is similar to the result reported by Farida *et al.*, (2015a). Similarly, adsorption capacity increasing with contact time and reached to the equilibrium approximately in 45minutes with maximum removal percentage of about 56.9 % for Bromocresol purple onto activated as shown in figure 3. The rapid removal of BCP dye is observed at the beginning of the contact time due to the percentage of large number of binding sites available for adsorption as reported by Arivoli*et al.*, (2015).

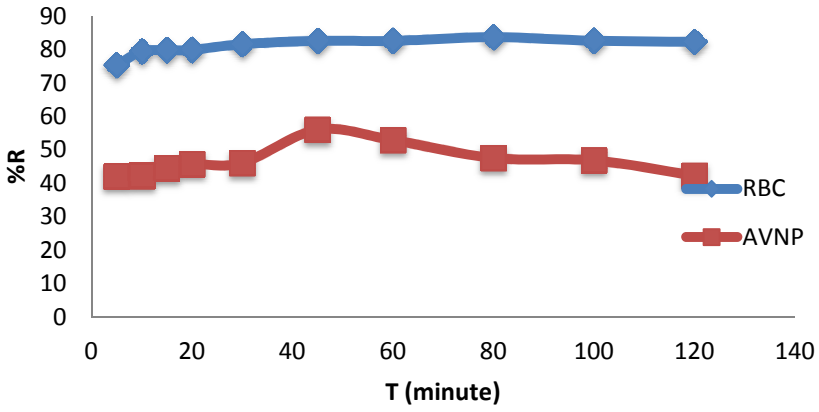


Figure 3: Effect of contact time on the removal of BCP onto Adsorbents

Effect of adsorbent dosage

The effect of adsorbents dosage on the percentage removal of Bromocresol purple dyes using an initial dye concentration of 20mg/L was examined. The studied adsorbent dosages were (0.1-3.0g) for the adsorbents. The percentage removal of Bromocresol purple increases 58.9% to 84.35% as RBC dosage increases from 0.1 to 3 g as shown in figure 4. This can be attributed to availability of more binding site as the dose of raw bentonite clay increases. This is in consistence with the results obtained by Omidi-Khaniabadi *et al., (*2017). However, for activated carbon AVNP percentage removal of the dyes decreases with increase in adsorbent dosage from 0.1 to 3g. This may be attributed to the fact that as the amount in grams of adsorbent is increased the total surface area available for the adsorption of the dyes reduces as a result of overlapping or aggregation of adsorption sites (Julius and Joseph, 2013).

Effect of pH

Initial pH of BCP solutions were adjusted to ,2,4.6, 8,10 and 12 for 100mg/l concentration contact time 80min and 45min, adsorbent dosage 2.5 g and 0.1 g speed 200rpm , temperature 29°C for the adsorption of dye onto raw bentonite clay and activated carbon respectively.

Effect of pH on the removal of Bromocresol purple onto raw bentonite clay and activated carbon is shown in Figure 5. It was observed that increase in the pH (from 2 to 12) caused a slight increase in percentage removal of Bromocresol purple onto raw Bentonite clay (RBC) and activated carbon (AVNP) i.e. from 93.96% to 96.71% and b also 66.32% to 88.42% respectively. The percentage removal is not significantly affected by pH for removal of bromocresol purple onto RBC this is similar to the result obtained by Intidhar *et al.*,(2018) on adsorption of Anoinic acid dye on Kenaf Core Fibre (KCF).

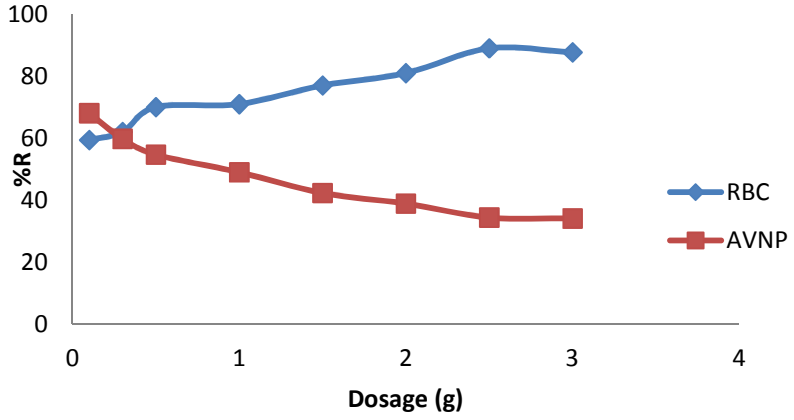


Figure 4: Effect of RBC and AVNP dosage on the adsorption of Bromocresol purple

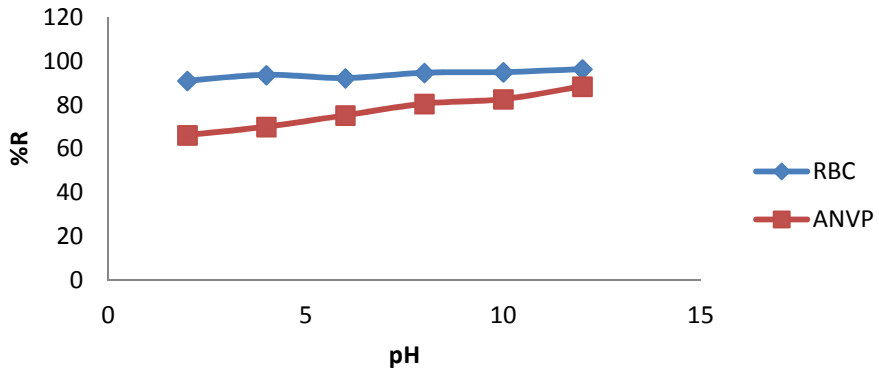


Figure 5: Effect of solution pH on extent of BCP adsorption onto RBC & ANVP

Effect of temperature

The effect of temperature on the adsorption at constant dye concentration was studied by varying the temperature from 25 to 55 ° C. The percentage removal of Bromocresol purple onto RBC and activated carbon increased slightly from 92.5% to 94.9% and 73.65% to 80.1% respectively as shown in Figure 6. It was observed that adsorption process is slightly endothermic as similar reported by Al-Khatib *et al*. (2012). The increase in temperature results in the movement of the adsorbate molecules into the adsorbents and slightly enhances adsorption of dyes. This may also be explained by the fact that increasing temperature lead to swollen of the adsorbents which facilitate the penetration of dye molecules into the internal structure as reported by Kindu *et al*. (2012).

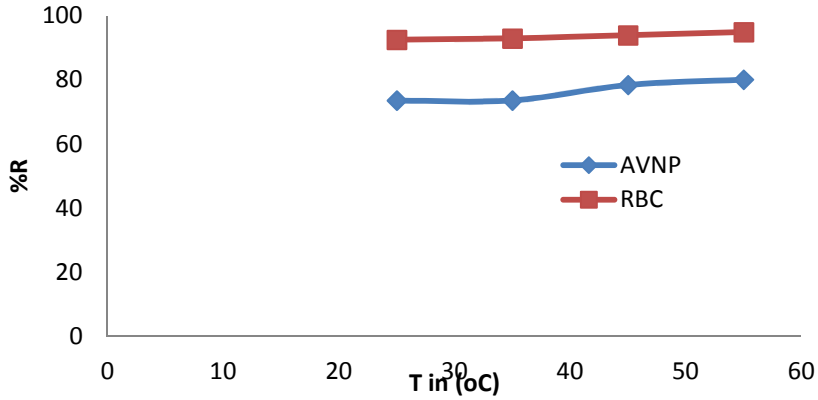


Figure 6: Effect of Temperature on the adsorption of BCP onto RBC & ANVP

KINETIC STUDIES

Studies of the adsorption rate are important for the design of batch adsorption systems. The modeling of kinetics data aids in the selection of the optimum operating conditions. The mechanism of adsorption was investigated by pseudo-first order, pseudo-second kinetic model respectively (El Haddad, 2012; Al Othman *et al*., 2011).

Pseudo-first-order model

The pseudo-first-order equation is given by equation 3:

$$1og(q_e - q_t) = logq_e - (k_f/2.303)t \quad (3)$$

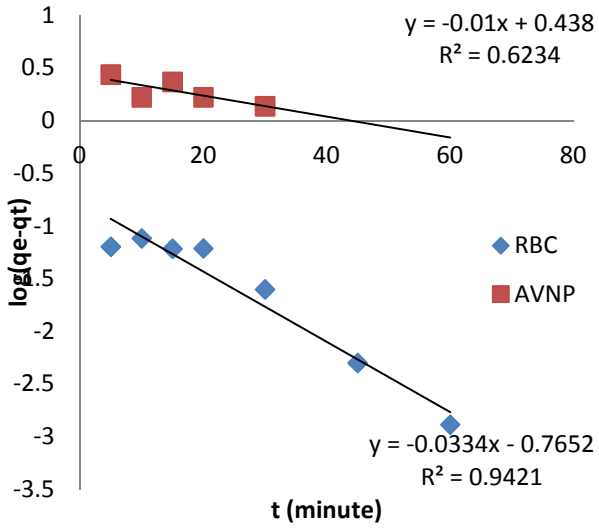
Where qt is the amount of dye (adsorbate) adsorbed at time t per unit mass of adsorbent (mg.g-1), qe the adsorption capacity at equilibrium (mg.g^{-1}), k_f the pseudo-first-order rate constant (min^{-1}), and t the contact time. Based on the pseudo first-order expression (Lagergren model) by plotting the values of log ($q_e - q_t$) against *t* give a linear relationship that q_e and $k_1$values can be determined from the intercept and slope of the obtained line, respectively (Patil *et al*.,2011; Jirekar *et al*., 2014). The low R^2 values and also qe calculated and qe experimental are far from each other, this indicate that the process do not follow pseudo first order.

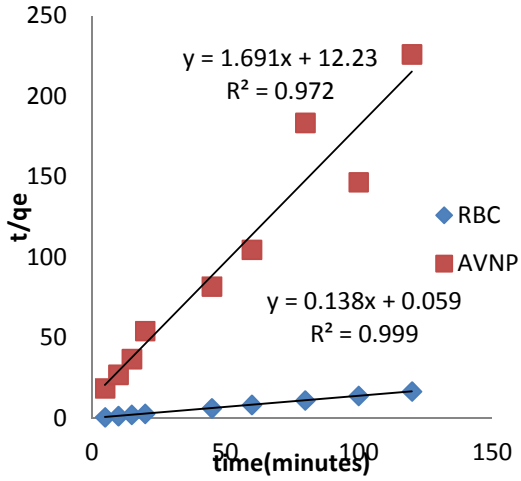
Pseudo-second order equation

Pseudo second order integrated rate equation is defined by equation (4):

$$t = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \quad (4)$$

Values of k_2 and equilibrium adsorption capacity (q_e) were calculated from the intercept and slope of the plots of $\frac{t}{qt}$ vs. t, respectively. The values of R^2 for the pseudo-second order kinetic model were higher than that of the other model as shown in Table 3. However, the calculated value of adsorption capacity, qe is closer to the experimental values for adsorption of the dye onto the adsorbents. The values of experimental qe for adsorption of onto RBC and AVNP are 7.426 and 5.263mg/g respectively. These results implies that the adsorption was better described by the pseudo-second order kinetic, indicating that the adsorption mechanisms of dyes depended on the adsorbates and adsorbents as reported by Bentahar *et al*. 2016; Intidhar *et al* . 2017). Figure 7a and 7b depict the pseudo-first order and pseudo –second order plots for adsorption of BCP onto both adsorbents.





a) Figure 7: (a) Pseudo-first-order kinetic model plot (b) Pseudo-second-order kinetic model plot

Table: 3. The Kinetic Parameters for the Adsorption of Rh-B dye onto ANSC

Kinetics	Parameters	RBC	AVNP
	Q_{exp}(mg/g)	7.197	5.169
PSEUDO-FIRST-ORDER	k_f(min^{-1})	0.076	0.983
	Qe(mg/g)	0.172	1.000
	R^2	0.942	0.623
PSEUDO-SECOND-ORDER	k_f(g/mgmin	0.322	0.179
	Q_{cal}(mg/g)	7.246	5.263
	R^2	0.999	0.972

Thermodynamic Studies

Thermodynamic parameters such as change in free energy (ΔG) (kJ/mol), enthalpy (ΔH) (kJ/mol) and entropy (ΔS) (J/K/mol) were determined using vant-hoffs equation (Al Othman *et al.*, 2011).

$$lnK = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

Where K is the equilibrium constant, T is the absolute temperature in Kelvin, and R is the universal gas constant (8.314Jmol^{-1}K^{-1}). The ΔH and ΔSvalues were obtained from the slope and intercept of the Vant Hoff's plots (lnK vs. 1/T) for the dyes adsorption from aqueous solution onto Bentonite clay and activated carbon. The values of ΔH are 11.01 and 11.98 kJ/mol, respectively. The positive values of ΔH show the endothermic nature of adsorption which governs the possibility of physical adsorption. In physical adsorption as temperature of the System, increases, the extent of dye adsorption increases, there is no possibility of chemisorptions as explained by Arivoli *et al.* (2015). Evaluated parameters of ΔH°, ΔS°, and ΔG° determined from the slope and intercept of linear plot of lnK against 1/T (Figure 8) are presented in Table 4. The negative Values of ΔG (Table 4) show that the adsorption is highly favorable and spontaneous.

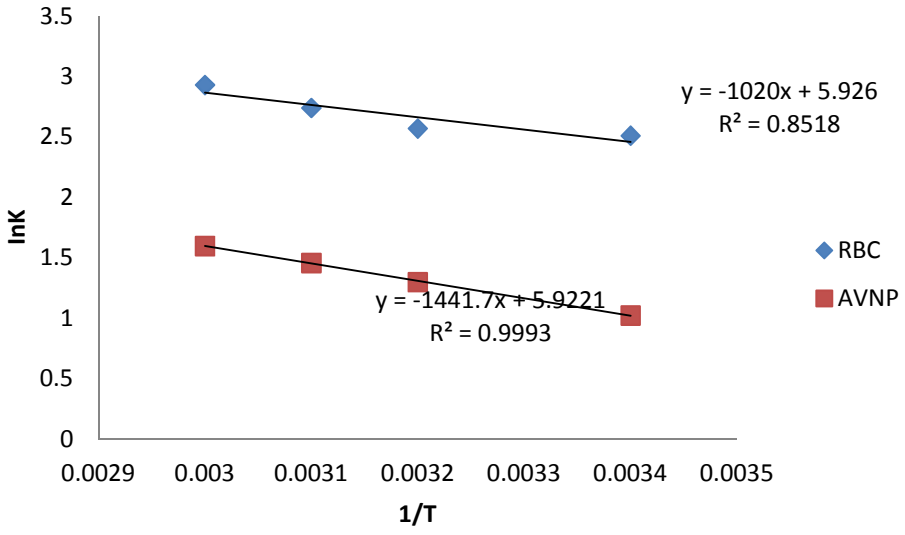


Figure: 8. Thermodynamic study of adsorption of bromocresol purple onto Raw bentonite clay (RBC) and activated carbon (AVNP)

Table: 4. Thermodynamic Parameter for the Adsorption of BCP dye onto RBC and AVNP

Adsorbents	ΔH(kJ/mol)	ΔS(kJ/molK)	ΔG(kJ/mol) $\Delta G = \Delta H - T\Delta S$			
			298K	308K	318K	328K
RBC	11.011	0.057	-5.981	-6.613	-7.180	-7.751
AVNP	11.982	0.049	-2.770	-3.274	-3.861	-4.363

CONCLUSION

In the present study raw bentonite clay (RBC) and activated carbon from *Vachellia nilotica* (AVNP) pod were selected as a cheap and readily available adsorbents for the removal of bromocresol purple BCP. Bentonite and activated carbon are excellent adsorbents for BCP adsorption; good yields were obtained with the two adsorbents. The investigation of the adsorption kinetics revealed that it was best described by the pseudo-second order model, while the thermodynamics study suggested that the adsorption of bromocresol purple on raw bentonite clay and activated *Vachellia nilotica* pods was a spontaneous and endothermic process. The values of ΔH indicates that the adsorption process is physical adsorption. The two adsorbents show excellent removal efficiency for the anionic dye in aqueous solutions but raw bentonite clay is more efficient.

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