Kinetics And Thermodynamics Study Of Bromophenol Blue Dye On Activated River Niger Clay

Okoye, C. C
Okey-Onyesolu, C. F
Nwokedi, I. C.

Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria

Abstract: The possibility of the usage of phosphoric acid (H₃PO₄) activated River Niger clay (PAARC) developed from a cheap, eco-friendly material of regenerative resource (River Niger Clay) to serve as an adsorbent for the treatment of Bromophenol Blue (BB) dye wastewater was investigated. Physic-chemical analyses results depict improvement on the properties of PAARC compared to the raw River Niger clay. pH, adsorbent dosage, solution temperature, contact time and concentration had significant effect on the percentage of BB dye adsorbed onto PAARC. The adsorption kinetic data was modeled using the pseudo first-order (PFO), pseudo-second order (PSO) and Elovich kinetic models. Results from sum of square error and root mean square error analyses show that the kinetics of the adsorption process can best be described by the pseudo-second order kinetic model. The positive Gibbs free energy (∆G°), negative enthalpy change (∆H°) and negative entropy change (∆S°) thermodynamic values calculated reveal non-spontaneous, exothermic and decreased randomness at the solid-solute interface during the adsorption process.

Keywords: Adsorption, PAARC, Bromophenol Blue dye, Kinetics, thermodynamics.

I. INTRODUCTION

The pollution caused by industrial wastewater has become a common problem for most of the countries. Wastewater from the textile, cosmetics, printing, dying, food coloring, and paper making etc., are polluted by dyes. The number of dyes presently used in textile industry is about 10,000. The annual production of these dyes is over 7×10⁵ tons (Ahmad et al., 2009; Bellir et al., 2010).

Quite often large amounts of coloured wastewater are generated in industries which use dyes to impart a desired colour to their products (food, paper, rubber, textile, plastics), and are discharged into natural streams with undesirable consequences to the environment and to human health. Aside from unpleasant aesthetic aspects, the presence of dyes in natural streams can cause serious harm to the aquatic life by increasing toxicity and chemical oxygen demand, and by hindering photosynthetic phenomena through reduction of light penetration (Oliveira et al., 2008). The complex aromatic structures of dyes make them more stable and more difficult to biodegrade (Jayalakshmia et al., 2013).

Removal of colour from effluents is one of the major environmental problems (Verma and Mishra, 2010). The convensional biological treatment process is not very effective in treating a dyes wastewater, due to low biodegradation of dyes. It is usually treated by either physical or chemical processes. However, these processes were very expensive and could not be effectively used to treat the wide range of dyes waste (Velmurugan et al., 2011). Adsorption process is an efficient and economic process for removing dyes, pigments and other colorants, particularly for its initial low cost, simplicity, ease of operation and insensitivity towards toxic substances (Bellir et al., 2010; Meshko et al., 2001; Choi et al., 2001). Thus, adsorption has been found to be more effective method for the treatment of dye containing wastewater. The most efficient and commonly used adsorbent
is commercially activated carbon which is expensive and has regeneration problems (Verma and Mishra, 2010). Sequel to this challenge, various attempts have been made by researchers to develop low cost alternative adsorbents from agro wastes, natural ores, industrial wastes, etc. In this research, River Niger clay, a natural ore of abundance resource was considered for investigation. According to Ho et al., 2006, some clay derivatives can be easily prepared and regenerated, thus are considered as an alternative low cost adsorbent and proposed as an inexpensive removal technique.

The objective of this research is to examine the adsorption efficiency of acid activated River Niger clay for the removal of BB dye from aqueous waste by adsorption technique. The impact of adsorption process variables, pH, adsorbent dosage, contact time, solution temperature and dye concentration on the percentage of BB dye adsorbed was studied. Kinetic models were evaluated in order to identify potential adsorption process mechanism. The thermodynamic parameters, standard Gibb’s free energy (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were evaluated.

II. MATERIALS AND METHODS

A. ADSORBATE

Dye stock solution of 500mg/L was prepared by dissolving 500mg of BB dye in 1litre of distilled water. Experimental solutions of desired concentrations were prepared by diluting the stock solution with distilled water. All reagents used for the research were of analytical grade. The physic-chemical properties of the BB dye are presented in Table 1.

B. ADSORBENT PREPARATION

Clay sample was collected from River Niger located in Onditha, Anambra state, Nigeria. As earlier reported in Okoye et al., 2018, 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 phosphoric acid solution then agitated in a constant temperature magnetic stirrer at a temperature of 98°C for 2hours. The resulting mixture was filtered and washed repeatedly with distilled water to reduce to a near 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.

C. 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). Physic-chemical properties of the samples: surface area, pH, moisture content were examined according to the method earlier reported by Okoye et al., 2018.

D. Adsorption study

Effects of pH, adsorbent dosage, contact time and solution temperature, initial dye concentration and temperature on the percentage of dye adsorbed were studied using a batch technique. The adsorption experiments were performed in 250ml Pyrex glass beaker placed on a magnetic stirrer with hot plate by mixing a pre-determined mass of the prepared adsorbent and 100ml of the aqueous dye solution of known concentration. The content of the reactor was agitated at constant speed for set residence time at constant temperature. Each process parameter was varied while keeping other parameters constant to ascertain its influence on the response (percentage of dye adsorbed). pH adjusters (0.1M HCl and 0.1M NaOH stock solutions) were used to alter the pH of the solutions prepared for investigation of effect of pH. The samples were filtered at the elapse of the experimental time. The absorbance of the supernatant solution obtained was analyzed using vis-spectrophotometer set at 590nm wavelength. The concentration of BB dye adsorbed was calculated from the difference in solution concentration before and after adsorption. The percentage of dye adsorbed (%ads) and amount of dye adsorbed (qe) were calculated by equations 1 and 2 respectively:

\[
\%_{\text{ads}} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 
\]

\[
q_e = \frac{(C_0 - C_e)}{W} \cdot \frac{V}{m} 
\]

Where Co and Ce are initial and equilibrium dye concentrations (mg/L) respectively, W is the mass of adsorbent (g) and V, the volume of solution (ml).

E. ADSORPTION KINETICS STUDY

The kinetics of the adsorptive process was studied by mechanically agitating at constant speed of 200rpm a mixture of 1g PAARC and 100ml of the BB dye solution of known concentration at a set temperature and pH of 2. At pre-determined time intervals aliquots were removed from the solution, filtered and analyzed using vis-spectrophotometer to determine the amount of BB dye adsorbed. Pseudo-first order (PFO), pseudo-second order (PSO) and Elovich kinetic models were used to describe the kinetics of the adsorptive process. Pseudo-first order, pseudo-second order and Elovich kinetic models respectively are expressed mathematically as:

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Table 1: Physic-chemical properties of BB dye
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 mg g$^{-1}$. $k_2$ (g mg$^{-1}$ min$^{-1}$) is the pseudo-second order adsorption kinetic parameter, $\alpha$ is the initial adsorption rate (mg g$^{-1}$ min$^{-1}$) and $\beta$ is related to the extent of surface coverage and the activation energy for chemisorptions (g mg$^{-1}$).

The sum of squared errors (SSE,%) and root mean square (RMS) error were employed in selecting the model that best described the kinetic of the process. SSE, % and RMS were calculated using equations 6 and 7 respectively:

$$SSE(\%) = \frac{\sum(q_{exp} - q_{calc})^2}{N}$$

$$RMS = \sqrt{\frac{1}{N} \sum(q_{exp} - q_{calc})^2}$$

F. THERMODYNAMIC STUDY

Thermodynamic parameters, (Gibbs free energy change, $\Delta G^\circ$, enthalpy change, $\Delta H^\circ$ and entropy change, $\Delta S^\circ$) for the adsorption of BB dye on PAARC were evaluated using the following equations (Pankaj and Harleen, 2011):

$$\ln K_d = \frac{\Delta H^\circ}{R} \cdot \frac{1}{T} + \frac{\Delta S^\circ}{R}$$

Equation 9 is an expression of the thermodynamics relationship of $\Delta G^\circ$ to $\Delta S^\circ$ and $\Delta H^\circ$ at constant temperature.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

Where $R$ (universal gas constant) = 8.314 J/molK, $T$ is the solution temperature, $K_d$ is the distribution coefficient and was calculated using equation 10:

$$K_d = \left(\frac{C_0 - C_e}{C_e}\right) \cdot \frac{V}{W}$$

C. SCANNING ELECTRON MICROSCOPY (SEM) ANALYSIS OF CLAY SAMPLES

The morphologies of the clay samples were pictured with SEM micrographs presented in Figures 1 and 2. According to Bajwa, 2002, SEM analyses of some clay indicate 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). In line with this report, clay minerals could be identified by examining the morphological features of the clay. The clay samples under investigation are kaolin dominated considering the observed coarseness and loose packs. It can be seen that PAARC revealed more porous nature than the natural clay.

Table 2: Physic-Chemical Parameters of the clay Sample

<table>
<thead>
<tr>
<th>Property</th>
<th>PAARC</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.75</td>
<td>6.38</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>6</td>
<td>7.5</td>
</tr>
<tr>
<td>Surface area (m$^2$/g)</td>
<td>92.6</td>
<td>29.4</td>
</tr>
</tbody>
</table>

Table 3: AAS elemental analysis for River Niger clay

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>458.4375</td>
</tr>
<tr>
<td>Al</td>
<td>258.4375</td>
</tr>
<tr>
<td>Fe</td>
<td>48.629</td>
</tr>
<tr>
<td>Ca</td>
<td>2.067</td>
</tr>
<tr>
<td>Mg</td>
<td>30.226</td>
</tr>
<tr>
<td>Na</td>
<td>1.003</td>
</tr>
<tr>
<td>K</td>
<td>4.567</td>
</tr>
<tr>
<td>Zn</td>
<td>43.317</td>
</tr>
<tr>
<td>Mn</td>
<td>157.205</td>
</tr>
<tr>
<td>Cu</td>
<td>2.458</td>
</tr>
</tbody>
</table>

Figure 1: SEM micrograph for RC
D. EFFECT OF ADSORPTION SYSTEM PARAMETERS

a. EFFECT OF PH

Solution pH plays an important role in the sorption process. It appears to interrupt the solution chemistry of dyes and functional groups of the adsorbents. Adsorption capacity of dye depends on pH of the solution. Previously reported literatures indicate that optimized pH depends upon nature of dye, type of clay used and modification of the clay. (Kausara et al., 2018). Ramachandran et al, 2011 revealed that 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. BB is an anionic dye (i.e. negatively charged dyes). It was observed in Fig 3 that the solution pH was inversely proportional to the percentage of BB dye adsorbed. At high pH values, the surface charge of the adsorbent becomes negatively charged hence electrostatic repulsion between the dye molecules and adsorbent. This may have resulted to the poor adsorbance observed. At low pH values acidic environment prevails, thereby increasing the positive charges on the adsorbent surfaces. This attracted the negatively charged functional groups located on the dyes. BB dye recorded its best performance at pH 2.

Figure 2: SEM micrograph for PAARC

Figure 3: Effect of pH on percentage of BB dye adsorbed on PAARC

b. EFFECT OF DOSAGE

The effect of PAARC dosages on the percentage of BB dye adsorbed is presented on Fig. 4. The solid/solution ratio was varied between 0.3 – 2g. The graph followed a predicted initial increase in the percentage of BB dye adsorbed as PAARC dosage was increased. El-Sayeed et al, 2011 suggested that plot followed the trend observed probably because of the resistance to mass transfer of dye from bulk liquid to the surface of the solid, which becomes important at high adsorbent loading in which the experiment was conducted. At constant initial dye concentration, 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; Grimm et al., 2008).

Figure 4: Effect of dosage on percentage of BB dye adsorbed on PAARC

c. EFFECT OF TEMPERATURE AND CONTACT TIME

At constant initial concentration of 100mg/l, the effect of temperature on the adsorptive uptake of BB dye on PAARC was studied over temperature range of 30°C - 60°C and contact times (10 - 90 minutes). Fig. 5 clearly shows that for all the temperatures considered, the amount of BB dye adsorbed increased with increase in time. Increase in temperature influenced the amount of dye adsorbed negatively. The observed trend suggests some kind of exothermic control of the adsorptive process. According to Rao & Nair, 2006, the decrease in the adsorption capacity at elevated temperatures may be that at higher temperatures a part of the dye leaves the solid phase and re-enters the liquid phase. Jiwalak et al, 2010, reported a similar result.

Figure 5: Effect of temperature on percentage of BB dye adsorbed on PAARC
The effect of initial dye concentration on adsorption of BB dye onto PAARC 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 temperatures 30°C, 40°C and 50°C studied. This may be as a result that at higher adsorbate concentrations, the fixed adsorptive sites became saturated therefore leaving some unadsorbed dye molecules in the supernatant solution. El-Sayed et al., 2011 reported that the lower uptake at higher concentration resulted from an increased ratio of initial adsorption number of moles of the dye to the available surface area. Similar result was reported by Bharathi and Ramesh (2013).

**KINETIC STUDIES**

PFO, PSO and Elovich kinetic models were used to study the kinetics of BB dye adsorption on PAARC. Figs 7 - 8 show non-linear plots of PFO, PSO and Elovich kinetic models at various temperatures. The precision of the output obtained from fitting the experimental data to the kinetic model equations were adjudged using root mean square (RMS) and sum of squared errors (SSE) techniques. Examining Figs 7 and 8, it is clearly shown that Elovich and PSO better fitted the experimental data compared to PFO model. The summary of the calculated kinetics parameters for the adsorption of BB dye onto PAARC was presented on Table 4. Fig 9 shows the graphical representation of the predictive capability comparison of PFO, PSO and Elovich kinetic models. The coefficient of determination values for PFO was generally lower than that for PSO and Elovich kinetic models. SSE and RMS values for PFO model were higher than the values for PSO and Elovich. SSE and RMS values for PFO, PSO and Elovich kinetics models were ≤ 5.666, 0.928; 0.543, 0.145; 0.552, 0.134 respectively. This finding reveals that PSO and Elovich kinetics models adequately described the adsorptive process. However, Elovich equation is mainly applicable for chemisorptions kinetics (Namasivayam and Kavitha 2002).

**THERMODYNAMICS STUDY**

The values of the thermodynamic parameters were presented on Table 5. Standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated from the slope and intercept of Fig 10. The positive Standard Gibbs free energy values calculated from equation 9 show that the process is non-spontaneous. The negative standard enthalpy value confirms the exothermic nature of the process. According to Oliveira et al, 2008, negative ΔS° value indicates the decreased randomness at the solid-solute interface during the adsorption process. Generally, the change in adsorption
enthalpy for physical adsorption is in the range of -20 to -40kJ/mol, but chemisorption is between -400 and -80kJ/mol (Bayramoglu et al., 2009). Therefore, the calculated enthalpy value of -15.979kJ/mol for the uptake of BB dye on PAARC is physisorption in nature.

![Figure 10: Thermodynamic plot for the adsorption of BB on PAARC](https://example.com/figure10.png)

**Table 5: Calculated thermodynamics parameters for the adsorption of BB dye on PAARC**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Thermodynamic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAARC</td>
<td>$\Delta G$ (kJ/mol) $\Delta H$ (kJ/mol) $\Delta S$ (kJ/mol)</td>
</tr>
<tr>
<td>303</td>
<td>1.929</td>
</tr>
<tr>
<td>313</td>
<td>2.520</td>
</tr>
<tr>
<td>323</td>
<td>3.111</td>
</tr>
<tr>
<td>333</td>
<td>3.702</td>
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**IV. CONCLUSION**

The treatment of Bromophenol blue dye aqueous solution with Phosphoric acid activated River Niger clay has been demonstrated under different experimental conditions. The characterization results of the raw and activated clay samples show improvements on the properties of the activated clay. Adsorptive process variables such as pH, adsorbent dosage, solution temperature, contact time and concentration had significant effect on the percentage of BB dye adsorbed onto PAARC. The kinetics of the process best followed the pseudo-second order kinetic model. The thermodynamics of BB-PAARC system reveals non-spontaneous and exothermic nature of the process. The results obtained suggest the potential of PAARC to serve as an efficient adsorbent.

REFERENCES


