ADSORPTION OF BROMOPHENOL BLUE AND BROMOTHYMOL BLUE DYES ONTO RAW MAIZE COB

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ABSTRACT
The adsorption of Bromophenol blue (BPB), and Bromothymol blue (BTB) onto raw maize cob from aqueous solution was studied using batch adsorption technique, in which the influence of contact time, dosage, concentration, temperature, and pH, were investigated as well as characterizing the adsorbent using Fourier Transform Infrared (FTIR) spectroscopy, surface morphology using scanning electron microscopy and pH of point of zero charge (pH\text{PZC}). Results showed that Bromophenol blue and Bromothymol blue removal reaches optimum percentage about 96.53 %, and 94.39 % with equilibrium time within 125 and 110 minutes respectively. For both dyes the removal efficiency was found to increase with increasing initial dye concentration from 10 mg/l to 100 mg/l, and adsorption efficiency were found to be high at lower pH. also, increase in the dosage of the adsorbent leads to increase in the adsorption process for BPB but shows decrease for BTB. The equilibrium adsorption data were analyzed using Langmuir, Temkin, and Dubinin-Radushkevich (D-R). The results revealed that the experimental data fits Temkin isotherm with R\text{2} values of 0.957 and 0.971 for BPB and BTB respectively. Kinetic analyses were conducted using pseudo-first, second-order models, elovich equation and the intra-particle diffusion model. The regression results in addition to q\text{e} experimental and q\text{e} calculated showed that the adsorption kinetics was more accurately represented by pseudo-second-order model. Values of activation parameters such as free energy changes (\Delta G), enthalpy change (\Delta H), and entropy change (\Delta S) were calculated using vant Hoff equation. All \Delta G values were negative indicating that the adsorption was feasible and spontaneous. The result indicated that raw maize cob can be used as adsorbent for the removal of the tested dyes.

Keywords: Adsorbate, Adsorbent, Adsorption, Maize cob, % Removal

INTRODUCTION
Dyes are complex chemical substances that bear stable aromatic rings synthesized to impart strong and persistent colour that does not degrade on exposure to light (Ibrahim and Sani 2014). Dyes are generally applied in an aqueous solution, and may require a mordant to improve their fastness on fibres (Karasavvidis et al., 2013; Saritha et al., 2015). Direct skin contact of dyes has been reported to result in various types of health problems like hypersensitivity, mutagenic and carcinogenic effects, allergy and asthma, skin eczema and immunosuppressive effects (Banerjee and chattopadhyaya, 2013; Omran et al., 2016). This leads to raise concern regarding its use as well as its removal from aqueous solutions. The dye impact toxicity and impedes light penetration and thus setps the biological activity (Alwan et al., 2015; Sayan et al., 2014; Hassan and Mahdi, 2016). Several methods including physical, chemical and biological processes have been used for the removal of dyes from effluents. Chemical and biological methods are effective for decolourisation, however, they require energy and special equipment; in addition, large amounts of by-products are often generated (Ramesh et al., 2013; Kandisa et al., 2016). Physical methods such as adsorption, ion exchange, and membrane filtration were generally effective for decolourisation without producing unwanted by products. Among treatment technologies, sorption process has received a lot of attention due to its simplicity, high efficiency, eco-friendly nature as well as the availability of a wide range of adsorbent with low cost, easy maintenance, no special operational skills and local availability (Suteu et al., 2011; Gayathiri et al., 2013; Zvzdova and Georgieva, 2013). Maize cob is an example of plant residues that are mainly composed of lingocellulose materials. They have relatively large surface areas that can provide intrinsic adsorptive sites to many substrates and inherently adsorb waste chemicals such as dyes and cations in water due to columbic interaction and physical adsorption (Ibrahim and Jimoh 2011).
MATERIALS AND METHODS
Adsorbents Preparation
The maize cob was obtained and washed with tap water followed by distilled water to remove surface impurities and dried in an oven at 105 °C for 2 hours. The dried maize cob (corn cob) was crushed using mortar and pestle and then pulverised using blender and sieved using 425 micrometer, the powder was kept in tightly closed container for application.

Batch Adsorption studies
Adsorption studies of Bromophenol blue, and Bromothymol blue dyes were performed. In each experiment 50 cm\(^3\) of dye solution in a 120 cm\(^3\) sample bottle of known concentration of desired time, temperature, dosage, and pH. The bottle were agitated and the mixture was filtered and the filtrate was then centrifuged for 5 minutes at 4000 rpm and the clear supernatant was used to determined the final concentration of the dyes spectrophotometrically using UV-Visible spectrophotometer (model Hitachi 2800) at a corresponding \(\lambda_{\text{max}}\) of 591.22 nm for Bromophenol blue (BPB) and 430.9 nm for Bromothymol blue (BTB). The percentage of dye adsorbed and the amount adsorbed were calculated as (Abechi \textit{et al.}, 2013).

\[
\%R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)
\]

\[
q_e = \frac{(C_0 - C_e)V}{w} \quad (2)
\]

Where Co is the initial concentration of the adsorbate (mg/L) and Ce is the equilibrium concentration (mg/L).

RESULTS AND DISCUSSION
Characterization of the adsorbent
Fourier Transform- Infrared (FT-IR)
The FT-IR absorption peaks of raw maize cob (RW) before and after adsorption and the functional group assignment are given in Table 1. Values in parenthesis represent the change in the wavenumber (cm\(^{-1}\)) after the respective dye adsorption. The result demonstrates that after the adsorption shifting occurs both to higher and lower wave numbers, indicating that there were binding processes, taking place on the surface of adsorbents as equally observed by Nale \textit{et al.} (2012) on the adsorption of Pb(II) and Ni(II) on activated maize cob.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Raw Maize cob (\bar{\nu}) (cm(^{-1}))</th>
<th>Before Adsorption</th>
<th>After Adsorption with BPB</th>
<th>After Adsorption with BTB</th>
<th>Functional Group Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3287</td>
<td>3273 (-14)</td>
<td>3286 (-1)</td>
<td>N-H stretching</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2922</td>
<td>2921 (-1)</td>
<td>2922 (0)</td>
<td>Bonded-OH</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1023</td>
<td>997 (-26)</td>
<td>1022 (-1)</td>
<td>C-N group</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2129</td>
<td>2114 (-15)</td>
<td>2114 (-15)</td>
<td>C≡C group</td>
<td></td>
</tr>
</tbody>
</table>

Scanning Electron Microscopy (SEM)
The micrograph of Maize cob revealed a smooth surface with irregular pores, which could likely provide favoured adsorption site. After dye adsorption, a significant change is observed in the structure of the adsorbents, which appeared to have a rough surface and pores containing new shiny particles after adsorption (Figure 1a - c)
pH at Point of zero Charge (pH_{PZC})

The value obtained at the intersection of the initial pH (pHo, x-axis) with the pH = 0 line (y-axis) in Figure 2 gives the pH_{PZC} of the raw maize cob at 5.02. This relatively low pH_{PZC} value according to Cardenas-Peña et al. (2012), signals the predominance of positively-charged surface groups on the surface of the adsorbent.

Effect of contact time

The effect of contact time on the adsorption of BPB and BTB was examined by varying the time from 5 to 135 minutes as shown in Figure 3. From the figure it can be seen that maximum percentage removal of BPB, and BTB was 28.22 %, and 43.75 % respectively with 10.0 mg/L initial dye concentration at room temperature (29°C) using 0.5 g adsorbent which occurred within the first 125, and 110 minutes respectively. Similar observation was reported by Adebayo et al. (2015) with raw maize cob for the removal of Mn(II) and Co(II) and observed that maximum adsorption were obtained at 120min.
Effect of adsorbent Dosage
One of the parameters that strongly affect the sorption capacity is the adsorbent dose. In this work the amount of raw maize cob was varied from 0.5 to 4.0 g (fig 4) in order to test the effect of adsorbent dosage on the adsorption of these dyes with other parameters kept constant. BPB dye adsorption increases with increase in the dosage from 0.5 g to 4.0 g from 21.11 % to 64.68 %, which may be attributed to the fact the number of available adsorption sites increases by increasing the adsorbent dose (Charles and Odoemelam 2010; Chamargore et al., 2010; Balasubramani and Sivarajaseka 2014; Patil et al., 2011; Jimoh and Ibrahim 2017; Dim, 2013). While for BTB increase in the dosage from 0.5 g to 4.0 g leads to decrease in the removal efficiency of the dye from 53.69 % to 13.79 %. This may be due to the fact that increase in the dosage leads to the formation of aggregates which reduces the surface area on the adsorption site as similarly observed by Tahir et al. (2016) and Vijyakumar et al. (2012). or may be due to increase in unsaturation of adsorption sites or particle interaction, such as aggregation which results as sorbent concentration increases, thereby leading to decrease in total surface area of the adsorbent (Ibrahim and Jimoh, 2008).

Effects of Initial Dye Concentration
The adsorption of dyes by an adsorbents is strongly dependent on the initial concentration of adsorbate molecules in solution. It can be seen that as initial concentration of these dyes were increased from 10 mg/L to 100 mg/L, corresponding increase in the adsorption capacities also occurred. This can be due to the increasing driving force, to overcome the mass transfer resistance, between the aqueous and solid phase that occurs by increasing the initial concentration of the adsorbates (Taha et al., 2013; Thitame and Shukla 2016; Sartape et al., 2013; Alhaji and Begum, 2015). Moreover, the number of collisions between dye molecules and adsorbent increases, thereby increasing the adsorption (El-Dars et al., 2015).

![Figure 4: Effect of dosage on removal of BPB & BTB with Raw maize cob](image1)

![Figure 5: Effect of concentration on removal of BPB & BTB with raw maize cob](image2)
Effects of Temperature
The effect of temperature was studied by using the temperatures 298K, 303K, 308K, 313K and 318K. The other parameters were all kept constant at their equilibrium time. Figure 6 shows the effect of solution temperature on the dyes uptake at 100 mg/L initial concentration. It shows that for BTB percentage removal was slightly increased with increase in temperature from 63.92 to 68.42 %, which is due to the increased diffusion of dye molecule across the external and internal boundary layer of the adsorbent due to decrease in solution viscosity. In addition, at higher temperature more dye molecules have sufficient energy to undergo an interaction with active sites of the adsorbent and enhance the dye mobility to penetrate inside the adsorbent’s pores (Ahmad et al., 2014). While for BPB the adsorption performance increases with increase in temperature to an optimum value of 89.4 % at 308K after which it decreased.

Effect of pH
In this work the pH of the dyes was varied from 2 to 12 (Figure 7) as the other parameters were kept constant. At lower pH, increased percentage removal was observed which decreased at higher pH. This behavior can theoretically be explained by the point of zero charge of the adsorbent, at pH < isoelectrical point, the surface gets positively charged, which enhances the adsorption of the negatively charged adsorbates through electrostatic forces of attraction. At pH > isoelectrical point, the surface of adsorbent particles gets negatively charged, which favours the adsorption of cationic adsorbates (Santhi et al., 2011; Vijayakumar et al., 2012). This result also is in agreement with the result obtained by Ishaq et al. (2014) and Tchuifon et al. (2014).

Adsorption Kinetics
Values of Kinetics parameters as deduce from various kinetic plots are as presented in table 2. From the table, the qe experimental and the qe calculated values for all the dyes are very close to each other. The calculated correlation coefficients (R²) are also close to unity. Therefore, the adsorption can be approximated more appropriately by pseudo second order kinetic model. Also from the table value of
\[ \alpha > \beta \] from Elovich equation for BTB indicates adsorption to predominates desorption process and vice versa. While from intraparticle diffusion \( \alpha \) values less than 0.50 indicates that intraparticle diffusion is not a rate determining step during the adsorption process (Ramesh et al., 2013).

### Adsorption Isotherms

Adsorption isotherm describes how adsorbates interact with adsorbents and therefore it is critical in optimizing the use of adsorbents (Hadi et al., 2010; Boumchita et al., 2016). Results from Table 3 indicated that the adsorption of the dyes onto the adsorbent surface showed a physical sorption character since the Temkin isotherm constant \( b \) was found to be lower than 8 kJ/mol. In addition, high linear regression value indicates that adsorption process fits closely with Temkin isotherm model. Also from the Table, the \( E \) from D-R isotherm values for the adsorption of the dyes are in the range of 0–2 kJ/mol. Therefore, the adsorption process by the adsorbent indicated physical process (Akalin et al., 2017).

<table>
<thead>
<tr>
<th>Model</th>
<th>Kinetic Parameters</th>
<th>BPB</th>
<th>BTB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_{e,exp.} ) (mg/g)</td>
<td>0.318</td>
<td>0.546</td>
</tr>
<tr>
<td>Pseudo First Order</td>
<td>( q_{e,cal.} ) (mg/g)</td>
<td>0.112</td>
<td>0.004</td>
</tr>
<tr>
<td>( \ln(q_e - q_t) = \ln q_e - k_1 t )</td>
<td>( k_1 ) (min(^{-1}))</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.003</td>
<td>0.000</td>
</tr>
<tr>
<td>Pseudo Second Order</td>
<td>( q_{e,cal.} ) (mg/g)</td>
<td>0.325</td>
<td>0.516</td>
</tr>
<tr>
<td>( \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} )</td>
<td>( k_2 ) (g/mg.min)</td>
<td>0.212</td>
<td>0.694</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.981</td>
<td>0.989</td>
</tr>
<tr>
<td>Elovich</td>
<td>( a ) (mg/g.min)</td>
<td>0.131</td>
<td>430.38</td>
</tr>
<tr>
<td>( q_t = \frac{1}{B} \ln (a \beta) + \frac{1}{B} \ln (t) )</td>
<td>( B ) (g/mg)</td>
<td>20.408</td>
<td>27.78</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.911</td>
<td>0.733</td>
</tr>
<tr>
<td>Intraparticle Diffusion</td>
<td>( K_{diff} ) (min(^{-1}))</td>
<td>5.957</td>
<td>29.309</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.955</td>
<td>0.752</td>
</tr>
</tbody>
</table>

For Adsorption Isotherms:

**Langmuir**

\[
\frac{C_e}{q_e} = \frac{1}{K_l q_m} + \frac{C_e}{q_m} \\
R_l = \frac{1}{1 + K_l C_0}
\]

**Freundlich**

\[
\log q_e = \log K_f + \frac{1}{n_f} \log C_e \\
R^2 = 0.924, 0.953
\]

**Temkin**

\[
q_e = B_T \ln K_T + B_T \ln C_e \\
B_T = \frac{RT}{b_T} \\
K_T (L/mg) = 0.521, 0.185
\]

**D-R**

\[
\log q_e = \log q_{e,0} - \beta e^2 \\
e = RT \ln (1 + 1/C_e) \\
E (kJ/mol) = 0.679, 0.283
\]

### Table 3: Langmuir, Freundlich, Temkin and D−R isotherm parameters for the adsorption of BPB and BTB onto Raw maize cob

<table>
<thead>
<tr>
<th>Adsorption isotherm</th>
<th>Parameters</th>
<th>Raw Maize Cob</th>
<th>BPB</th>
<th>BTB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( Q_m ) (mg/g)</td>
<td>-1.822</td>
<td>-14.706</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( R_l )</td>
<td>-0.397</td>
<td>5.258</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( K_f ) (L/mg)</td>
<td>-0.035</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.228</td>
<td>0.178</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>( n_f )</td>
<td>0.809</td>
<td>0.841</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( K_f ) (mg/g)</td>
<td>0.057</td>
<td>0.086</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.924</td>
<td>0.953</td>
<td></td>
</tr>
<tr>
<td>Temkin</td>
<td>( K_T ) (L/mg)</td>
<td>0.521</td>
<td>0.185</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( b_T ) (kJ/mol)</td>
<td>4.532</td>
<td>0.910</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( B_T ) (J/mol)</td>
<td>0.554</td>
<td>2.759</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.957</td>
<td>0.971</td>
<td></td>
</tr>
<tr>
<td>D−R</td>
<td>( Q_0 ) (mg/g)</td>
<td>1.042</td>
<td>4.656</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( B ) (mol(^2)/kJ(^2))</td>
<td>1.086</td>
<td>6.226</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( E ) (kJ/mol)</td>
<td>0.679</td>
<td>0.283</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.944</td>
<td>0.936</td>
<td></td>
</tr>
</tbody>
</table>
Adsorption thermodynamics
Thermodynamic parameters are essential for the interpretation of the nature and characteristics of adsorption process concerning their physicochemical attributes. Gibbs free energy, adsorption enthalpy, and entropy hold fundamental knowledge about the character of sorption. Gibbs free energy change ($\Delta G$), provides the information of whether the sorption process is spontaneous or not, Adsorption free enthalpy ($\Delta H$) change gives the knowledge of the thermal character of the sorption, providing whether the sorption of metal ions on adsorbent is endothermic or exothermic and finally, adsorption free entropy change ($\Delta S$) is an indicator of magnitude concerning the disorder among the adsorbate molecules and adsorbent. Equilibrium constant ($K_c$) indicate the ability of an adsorbent to hold dye molecule onto its porous structure and amplitude of adsorbate mobility in the adsorption media (Akalin et al., 2017). The general expression of $\Delta G$ is given in Eq.3 and rearranging $\Delta G$ as $-RT\ln K_c$ from Eq.4 gives the Eq. 6 The plot of lnKc versus 1/T gives the slope of $\Delta H/RT$ and the intercept of $\Delta S/R$.

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

(3)

$$\Delta G = -RT\ln K_c$$  

(4)

$$K_c = \frac{Q_e}{C_e}$$  

(5)

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$  

(6)

Result demonstrated that dyes adsorption process onto maize cob occurred spontaneously, since $\Delta G$ values were all negative. The negative $\Delta H$ value for BPB indicated that adsorption process had exothermic character, meaning as the temperature increased, the amount of adsorbed dye gradually decreased, indicating physisorption. While for BTB its percentage removal increases as the temperature increases indicating endothermic character (chemisorptions) as seen in Table 4 and Positive $\Delta S$ value for BPB, BTB indicated spontaneous process.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Temperature</th>
<th>$K_c$</th>
<th>$\Delta G$(kJ/mol)</th>
<th>$\Delta H$(kJ/mol)</th>
<th>$\Delta S$ (kJmol$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPB</td>
<td>298</td>
<td>7.126</td>
<td>-5.039</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>7.313</td>
<td>-5.052</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>8.434</td>
<td>-5.066</td>
<td>-4.226</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>7.319</td>
<td>-5.079</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>6.195</td>
<td>-5.093</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTB</td>
<td>298</td>
<td>1.772</td>
<td>-1.528</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>2.026</td>
<td>-1.669</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>2.103</td>
<td>-1.810</td>
<td>6.871</td>
<td>0.028</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>2.085</td>
<td>-1.951</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>2.167</td>
<td>-2.092</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CONCLUSION
The raw maize cob was found to be efficient for removal of the dyes (BPB, and BTB) from aqueous solution, and the adsorption process was found to fit closely to Pseudo-Second-Order model and the adsorption mechanism can be described by physical means as confirmed from thermodynamic data and isotherm parameters.

REFERENCES


