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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 bach 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_{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, Freundlich, Temkin, and Dubinnin-Ruduskevich (D-R). The results revealed that the experimental data fits Temkin isotherm with R^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_e experimental and q_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 (ΔG), enthalpy change (ΔH), and entropy change (ΔS) were calculated using vant Hoff equation. All ΔG 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 upsets 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 decolourization, 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 decolourization 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 ℃ 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 filterate 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 Hitach 2800) at a corresponding λ_{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 *et al.*, 2013).

$$\%R = \frac{C_O - Ce}{C_O} X\ 100 \qquad (1)$$

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

$$q_e = \frac{(C_O - C_e)\ V}{W} \qquad (2)$$

Where w (g) is the weight of adsorbent and V (cm^3) is the volume of the adsorbate. The effects of various parameters on dye adsorption by raw maize cob were investigated such as adsorbent dosage (0.5-4.0 g), contact time (5 - 135 min), initial dye concentration (10 - 100 mg/L), temperature (25 - 45 °C) and pH (2 - 12) (Bentahar et al., 2016).

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 *et al.* (2012) on the adsorption of Pb(II) and Ni(II) on activated maize cob.

Table 1: FT-IR results of raw maize cob before and after adsorption of dyes.

Peaks	Raw Maize cob ῡ (cm^{-1}) Before Adsorption	After Adsorption with BPB		After Adsorption with BTB		Functional Group Assignment
1	3287	3273	(-14)	3286	(-1)	N-H stretching
2	2922	2921	(-1)	2922	(0)	Bonded−OH
3	1023	997	(-26)	1022	(-1)	C-N group
4	2129	2114	(-15)	2114	(-15)	C≡C group

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 (Figure1 a – c)

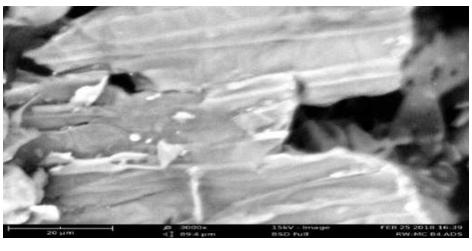

Fig 1a: SEM image of raw maize cob before adsorption

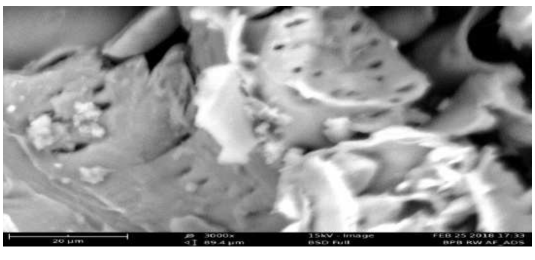

Fig 1b: SEM image of raw maize cob after adsorption of BPB

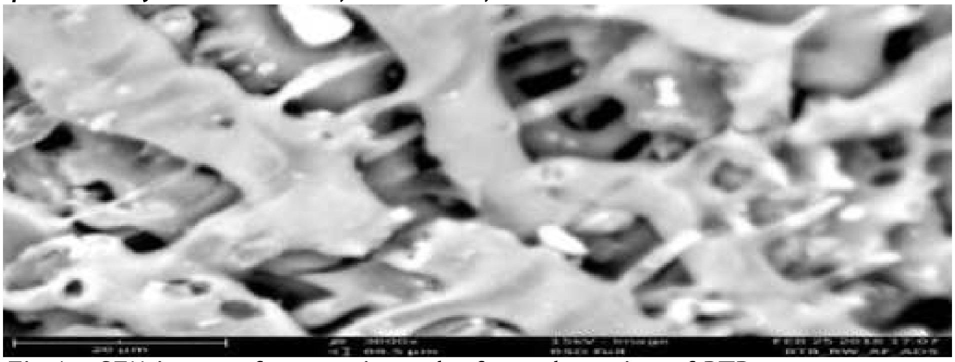

Fig 1c: SEM image of raw maize cob after adsorption of BTB

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.

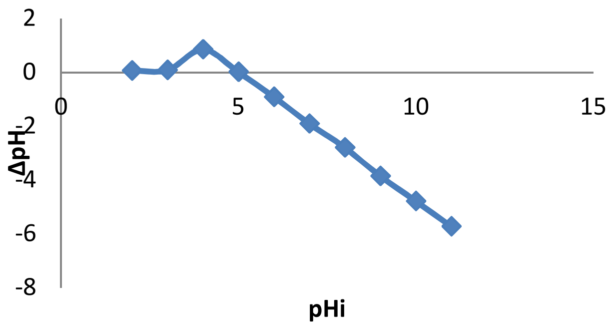

Figure 2: Point of Zero charge of raw maize cob

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 ℃) 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.

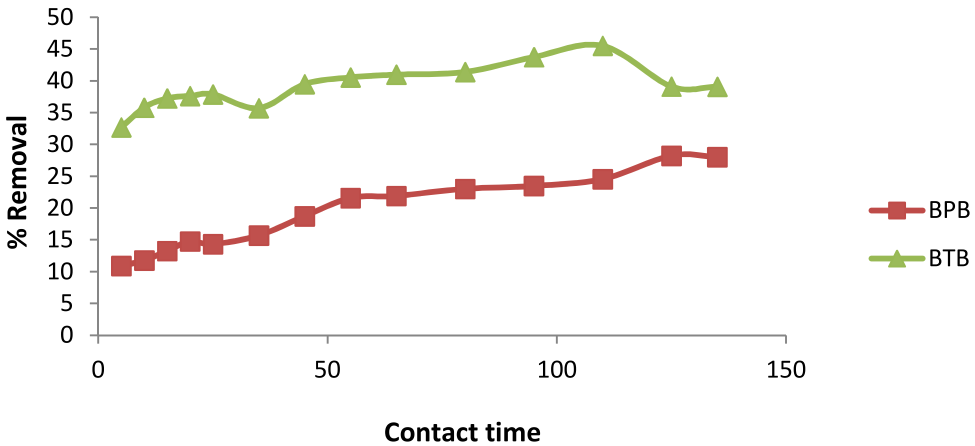

Figure 3: Effect of contact time on the removal of BPB &BTB with raw maize cob

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).

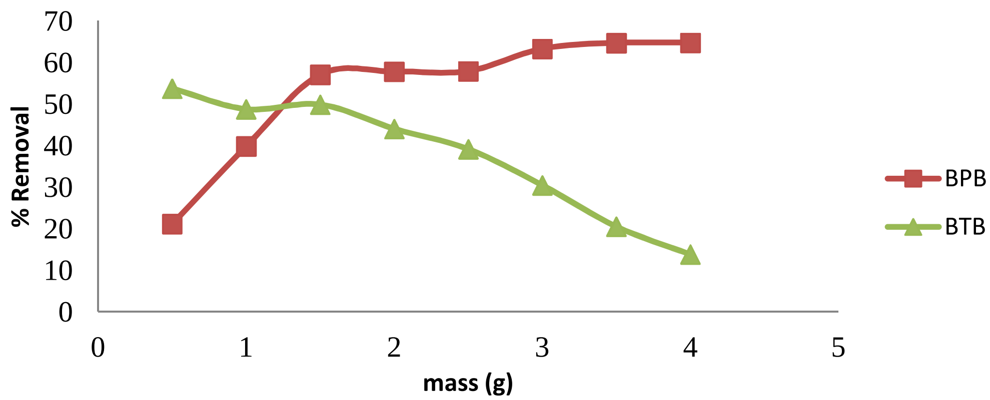

Figure 4: Effect of dosage on removal of BPB & BTB with Raw maize cob

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).

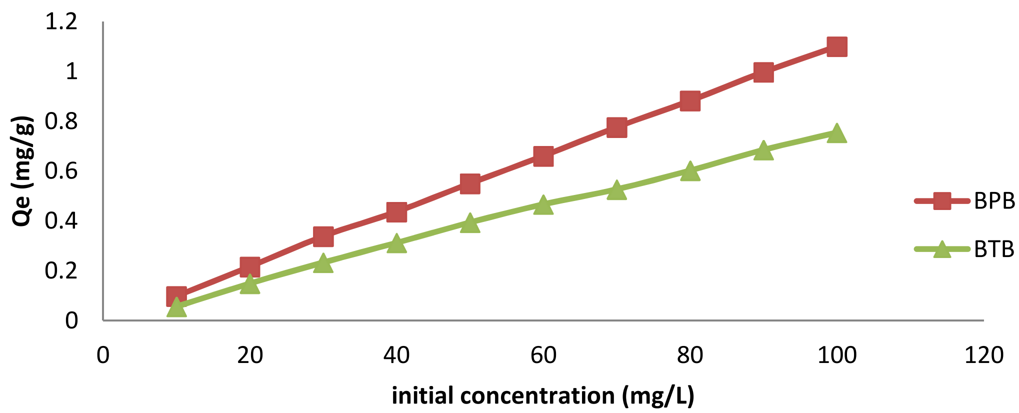

Figure 5: Effect of concentration on removal of BPB & BTB with raw maize cob

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.

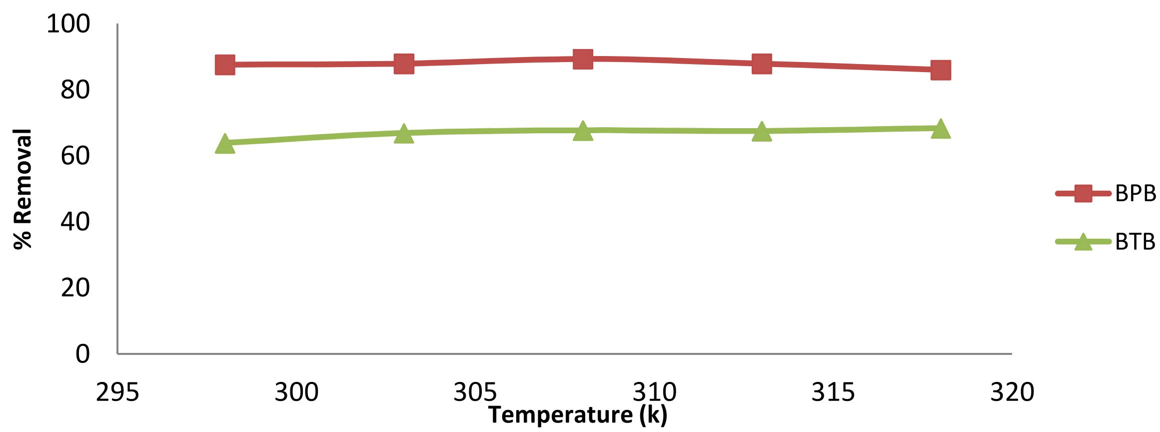

Figure 6: Effect of temperature on removal of BPB & BTB with raw maize cob

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).

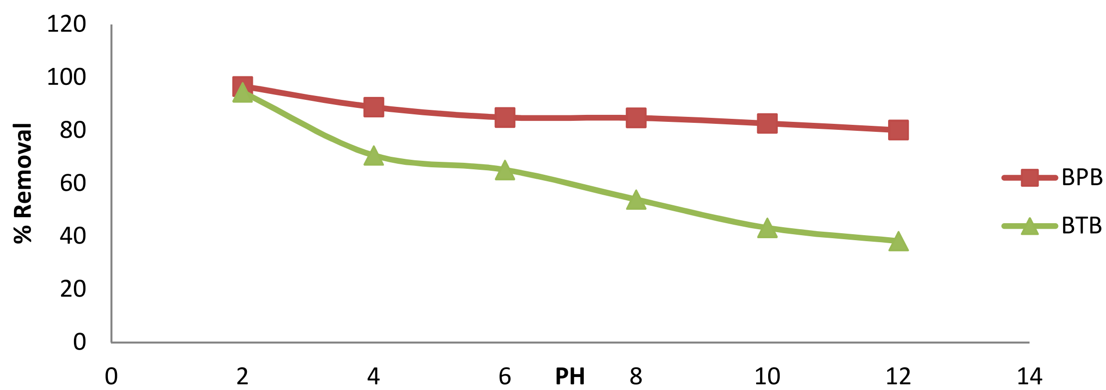

Figure 7: Effect of pH on removal of BPB & BTB with raw maize cob

Adsorption Kinetics
Values of Kinetics parameters as deduce from various kinetic plots are as presented in table 2. From the table, the q_e experimental and the q_e calculated values for all the dyes are very close to each other. The calculated correlation coefficients (R^2) 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 α —values less than 0.50 indicates that intraparticle diffusion is not a rate determining step during the adsorption process (Ramesh *et al.*, 2013).

Table 2: Adsorption Kinetic Parameters for adsorption of BPB and BTB onto Raw maize cob

Model	Kinetic Parameters	Raw Maize Cob BPB	Raw Maize Cob BTB
	$q_{e,exp.}$(mg/g)	0.318	0.546
Pseudo First Order	$q_{e,cal.}$(mg/g)	0.112	0.004
$\ln(q_e - q_t) = \ln q_e - k_1 t$	k_1(min^{-1})	0.001	0.000
	R^2	0.003	0.000
Pseudo Second Order	$q_{e,cal.}$(mg/g)	0.325	0.516
$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	k_2(g/mg.min)	0.212	0.694
	R^2	0.981	0.989
Elovich	α(mg/g.min)	0.131	430.38
$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$	β(g/mg)	20.408	27.78
	R^2	0.911	0.733
Intraparticle Diffusion	α (mg/g)	0.304	0.078
$\log R = \log K_{id} + \alpha \log(t)$	k_{diff}(min^{-1})	5.957	29.309
	R^2	0.955	0.752

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

Adsorption isotherm	Parameters	Raw Maize Cob BPB	Raw Maize Cob BTB
Langmuir	Q_M(mg/g)	-1.822	-14.706
$\frac{Ce}{qe} = \frac{1}{Kl\,Qm} + \frac{Ce}{Qm}$	R_L	-0.397	5.258
$R_L = \frac{1}{1+Kl\,Co}$	K_L(L/mg)	-0.035	0.008
	R^2	0.228	0.178
Freundlich	n_F	0.809	0.841
$\log q_e = \log K_f + \frac{1}{n_f}\log C_e$	K_F(mg/g)	0.057	0.086
	R^2	0.924	0.953
Temkin	K_T(L/mg)	0.521	0.185
$q_e = B_T \ln K_T + B_T \ln C_e$	b_T (kJ/mol)	4.532	0.910
$B_T = \frac{RT}{b_T}$	B_T(J/mol)	0.554	2.759
	R^2	0.957	0.971
D–R	Q_M(mg/g)	1.042	4.656
$\log q_e = \log q_m - \beta\varepsilon^2$	B(mol^2/kJ^2)	1.086	6.226
$\varepsilon = RT \ln(1 + 1/Ce)$	E(kJ/mol)	0.679	0.283
$E = \frac{1}{\sqrt{2\beta}}$	R^2	0.944	0.936

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 (ΔG), provides the information of whether the sorption process is spontaneous or not, Adsorption free enthalpy (ΔH) 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 (ΔS) is an indicator of magnitude concerning the disorder among the adsorbate molecules and adsorbent. Equilibrium constant (Kc) 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 ΔG is given in Eq.3 and rearranging ΔG as –RTlnKc from Eq.4 gives the Eq. 6 The plot of lnKc versus 1/T gives the slope of ΔH/RT and the intercept of ΔS/R.

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

$$\Delta G = -RTlnKc \quad (4)$$

$$K_C = \frac{Qe}{Ce} \quad (5)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

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

Table 4: Thermodynamic parameters for adsorption of BPB and BTB on Raw maize cob

			Raw Maize Cob		
Dyes	**Temperature**	**K_C**	**ΔG(kJ/mol)**	**ΔH(kJ/mol)**	**ΔS (kJmol^{1}K^1)**
BPB	298	7.126	-5.039		
	303	7.313	-5.052		
	308	8.434	-5.066	-4.226	0.003
	313	7.319	-5.079		
	318	6.195	-5.093		
BTB	298	1.772	-1.528		
	303	2.026	-1.669		
	308	2.103	-1.810	6.871	0.028
	313	2.085	-1.951		
	318	2.167	-2.092		

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.

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