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Adsorptive removal of bromocresol green dye using activated corn cob

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Abstract
The adsorption of Bromocresol green (BCG) dye was investigated using activated carbon prepared from corn cob with sulphuric acid. Batch adsorption was carried out and the physical properties of the corn cob activated carbon (CCAC) was determined. The effects of pH, temperature, adsorbent dosage, contact time and concentration on the adsorption process and the Kinetics, Isotherms and Thermodynamics studies were all carried out. The adsorption kinetic study indicated that the First-order and Natarajan & Khalaf models best described the rate of adsorption of BCG with the highest correlation coefficient of 0.985 compared to the pseudo first-order and pseudo second-order model. The Isotherm models investigated confirmed that Freundlich and Halsay models gave the best fit for the equilibrium data and best representation of the BCG removal on to CCAC (R^2=0.977). The thermodynamics study through the calculated enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy (ΔG) indicated that the process was exothermic, with a decreased randomness at the solid-solution interface and a non-spontaneous process respectively. The separation factor R_L value for BCG removal by activated corn cob was calculated as 0.02 meaning that the adsorption process was favorable. The maximum adsorption capacity (q_e) of 14.153 mg/g was obtained using CCAC as adsorbent in the adsorption process of BCG. The results showed that the adsorption of BCG yielded a good efficiency with CCAC.

Keywords: Bromocresol Green, Corn cob, Kinetics, Isotherm, Thermodynamics

1. Introduction

The economic impact of the textile industry is partly dependent on the management of the wastes which can create extreme water pollution in both industrial and environmental habitats. These wastes are approximately generated from 70% of the chemical process in these industries through discharge of large volumes of wastewater. There is the need sustain and decentralize water reuse due to the water-intensive nature of the textile industry in sizing, de-sizing, scouring, bleaching and finishing. The type of pollutants from the effluent is dependent on many variables like the processes, type of facility and chemical used. Dyes are one of the most damaging pollutants found in textile wastewater among others like phenols, pesticides, phosphates, surfactants, high biological oxygen demand (BOD), high chemical oxygen demand (COD) and high levels of total dissolved solids (TDS). The presence of these dyes can decrease rate of photosynthesis, destroy the aesthetic nature, creates imbalance in the ecosystem etc. (Onu & Nwabanne, 2014; Nnenna et al. 2020; Nwabanne et al. 2016; Onu et al. 2020). There are generally biological, chemical and physical methods of textile wastewater treatment (Fluence News Team, 2020).

Organic dyes are extensively used domestically and industrially depending on the type with some used as dying agents in textile, plastic, rubber, paper and food industries (Murmu *et al*., 2018; Moussavi &Khosravi, 2011; Feng *et*

al., 2011). The dyes generated from industrial effluent contaminates the soil and water environments which end up causing threats to aquatic and human lives due to their toxic nature (Bello *et al*., 2008; Duran-Jimenez *et al*., 2014). According to Duran-Jimenez *et al* (2014) and Guzel *et al*. (2015), the cost effect of dye manufacturing industry is reduced by approximately 15-20 % which is an estimation estimated by World Bank. The chemical nature and solubility determine the various types of dyes which are basically classified into acidic dyes, basic dyes and disperse dyes(Bello *et al*., 2008).Bromocresol green (BCG) is typical brand of dye that decompose to produce various categories of carcinogenic aromatic amines(Mandal &Natarajan, 2015; Malina & Radenovic, 2014)and usually used as pH indicator, as a DNA tracer and as dying agent in the textile industry(Ghaedi *et al*., 2012). BCG is from the dye group called triphenylmethane (triarylmethane dyes) which is anionic and belongs to the classification of dye termed sulfonephthaleins (Teng *et al*., 2011). BCG is a solid in dark green form when in alkaline pH but in acidic form, it is a solid made of light brown (Ghaedi *et al*., 2012).

Several researches have been carried out investigations on how to remove dye from wastewater with various processes adopted which include biological, chemical and physical (Teng *et al*., 2011; Bello *et al*., 2012; Elass*et al*., 2011). Filtration through membrane, oxidation by photocatalysts, and adsorption process are popular methods adopted by researchers in achieving dye removal (Duran-Jimenez *et al*., 2014; Guzel *et al*., 2015; Karagozoglu et al., 2007). Adsorption is a surface phenomenon which involves the deposition of large concentration of species made up of molecules on a surface called adsorbent while the species that gets absorbed is known as adsorbate (Nwabanne et al. 2018; EmedicalPrep, 2020; Ositadinma et al. 2019). In adsorption, the quantity of adsorbate on the adsorbent is a function of the concentration or pressure at constant temperature. The advantages of adsorption are that it does not result in the formation of toxic substances, is relatively less expensive, simple to design and operate and highly efficient (Onu et al. 2014b; Nwabanne et al. 2022; Iheancho et al. 2021, Asadu et al. 2021a; Asadu et al. 2021b). Adsorption process is often studied with use of graphs called adsorption isotherm. It is very important to use a suitable adsorbent during the adsorption process to give a good efficiency. There are bio-adsorbents like apricot stones (Djilani *et al*., 2015), rice husks (Chen *et al*., 2013), orange peels (Fernandez *et al*., 2014), bamboo charcoal (Liao *et al*., 2012) that can be used but for effective use, there are taken through the process of modification or activation by chemical and physical means to enhance the efficiency of the adsorption.

Corn cob (CC) is a residue from agricultural product which is gotten from maize and it is the part of the ear on which the kernels grow. CC is also a biomass feedstock which has a good potential of being a source of energy in different applications. Its dense form, high energy content, low sulfur and nitrogen content gives it an advantage over other biomass feedstocks used for different purposes (Anukam *et al*., 2017). Activated carbon is a highly porous material used in separating organic compounds from liquids and gases and can be made from any carbon-containing input material (calgoncarbon.com, 2020). There are several commercial activated carbons used as adsorbent but because of the high cost of preparation, there are alternative means which are cost effective during preparation that can be adopted. Saw dust, fruit stones, coconut husks, rice husks and more which are agricultural byproducts that are very cheap and with ease of access, can produce activated carbon (Ghaedi *et al*., 2012). This investigation is aimed at producing a cheap, effective and eco-friendly activated carbons from corn cob for the effective removal of Bromocresol green. The corn cob was activated and used for the adsorptive removal of BCG with data extracted for adsorption isotherm (which describes the equilibrium relationships between adsorbent and adsorbate).

2.0 Material and methods

2.1 Materials

The raw materials used for this work are Bromocresol which has a molecular formula of $C_{12}H_{14}Br_4O_5S$, corn cob (CC). Hydrochloric acid and sodium hydroxide used were of high grade with distilled water used for dilution. The CC was gotten from the farm in Awka, Anambra State of Nigeria.

2.1.1 Preparation of activated corn cob

The adsorbent materials used were extracted from agricultural wastes with tests carried out to determine some physical properties after being washed with distilled water to get rid of impurities and were dried at high temperature to remove the moisture content. The corn cob was prepared for activation after being reduced into small pieces by crushing in a mill and sieved. The sample was mixed and treated with about 25% of sulphuric acid and kept in an oven at 90^{o}C for 24 hours. The sample was subsequently washed several times with deionized water and leached with warm water to remove any trace of metal that might be present in the sample. The sample was made to undergo carbonization after being placed in a furnace at 500^{o}C for 5 hours and further dried, crushed (using mortar

and pistil), sieved to particle size of 75µm. This process was repeated different percentage concentration of sulphuric acid, carbonization temperature and duration according to the experimental design. All produced activated samples were stored in airtight containers, sealed in a desiccator for experimental purpose.

2.2 Experimental procedure

The removal of BCG through adsorption using activated corn cob was carried out in a batch experimental process. The simulated wastewater was prepared by dissolving 0.1g of the dyes in 1000ml of distilled water each to get a solution of 100mg/l. The effects of varies parameters were determined during the experiment for corn cob activated carbon (CCAC). The effects of initial pH and initial concentration were determined by agitating 1.5g of the produced CCAC added into 250ml volume of Erlenmeyer flask containing varies concentration of dye solution in a magnetic stirrer each for 30 minutes contact time. The pH was adjusted by adding few drops of diluted 0.1 mol/L NOH per HCl at a constant agitation of 200 rpm under constant temperature of 40^{o}C. The effects of contact time, adsorbent dosage and temperature were also determined by agitating 0.5g of CCAC with 100ml of dye solution in a magnetic stirrer while varying the contact time, masses of CCAC and temperature. The agitation speed was maintained at 200 rpm for CCAC and the amount of BCG dye that was adsorbed at equilibrium by the activated carbon was determined using

$$qe = \frac{(Ci - Ce)V}{\mathrm{m}} \quad (1)$$

Where Ci and Ce (mg/L) are the liquid phase concentrations of BCG at initial and equilibrium respectively, V (L) is the volume of the solution and m (g) is the mass of adsorbent (CCAC) used.

The percentage of BCG dye adsorbed from liquid (aqueous) solution with CCAC was calculated using equation 2:

$$Percent\ Adsorbed = \frac{(Ci - Ce)100}{Ci} \quad (2)$$

3.0 Results and Discussions

3.1 Physical Properties of the Adsorbents

Table 1 shows the physical properties of the adsorbent used. The moisture content was less than 7.0% which is due to carbonization. Onu&Nwabanne(2014) had similar range with moisture content between 13 -16% for Nteje clay. The chemical nature of the carbon surfaces was inferred from the pH of the carbon and these generated weak acidic surface properties for CCAC.

Table 1: Physical Properties of the activated adsorbents

Property	CCAC
pH	6.3 $\pm$ 0.2
Ash content (%)	5.82
Moisture content (%)	5.5

3.2 Effect of Process parameters on the Adsorption of BCG by corn cob

3.2.1 Effect of temperature

One of the most important parameters used to determine nature of the adsorption process is the effect of temperature on adsorption. Figure 1 shows the effect of temperature on adsorption of BCG which was investigated at a temperature range of 303-333K, with an absorbent mass of 1.5g, initial dye concentration of 100mg/l and constant pH of 6 for 30 minutes. As the percentage of BCG adsorbed increases, the temperature of the solution increases and this is due to increase in the rate of diffusion of adsorbate molecules across the external boundary surface and internal pores of the adsorbent particles (Onu & Nwabanne, 2014). For corn cob, the rapid adsorption of bromocresol green dye was from 303-313K with slow adsorption from 313-333K butrice husk yielded a more rapid adsorption rate from 303-323K and slow adsorption from 323-333K.

3.2.2 Effect of adsorbent dosage

The quantity of adsorbent CCAC dosages used varied from 0.5g to 2.5g with dye concentration of 100mg/l. The results as shown in Figure 2 indicates that as the adsorbent dosage increases, the percentage of bromocresol adsorbed also increases with the highest adsorption of BCG gotten in RHAC between dosage of 0.5-1.0g. The enhanced percentage of bromocresol green dye adsorbed is attributed to the increased mass of CCAC per unit volume solution which generates more active functional groups and eventually increase adsorption sites (Murmu*et al*., 2018; Onu & Nwabanne, 2014).

3.2.3 Effect of contact time

The effect of contact time on the adsorption of BCG was studied with contact time range of 10 to 60 min, with 100mg/l of dye solution, pH of 6, at temperature of 313K and adsorbent dosage of 1.5g. There was rapid increase of percentage of BCG adsorbed in CCAC from time 10-30 minutes compared to other contact time as shown in Figure 3. This high rate of adsorption at initial contact time is attributed to the presence of more adsorption sites and high solution concentration which resulted to quick force of interaction of the anions in BCG with the individual activated carbon of corn cob (Murmu*et al*., 2018).

3.2.4 Effect of initial amount of concentration

The initial concentration of dye is significant in determining the adsorption potentials of the adsorbents and this is illustrated in Figure 4. This investigation was done while the BCG concentrations from 50-300 mg/L while adsorbent dose, time interval, pH and temperature were kept constant at 1.5g, 30 min, 6, and 313K respectively. As the concentration of BCG increases, the percentage of BCG adsorbed decreased which is due to the lack of surface sites needed for the concentration of the dye. It can also be attributed to the fact that the available solutes are absorbed faster at smaller concentration of the BCG (Murmu *et al*., 2018; Onu & Nwabanne, 2014).

3.2.5 Effect of pH value

The percentage of BCG adsorbed was investigated over the pH range of 4 to 10, with 100mg/L of dye solution, 1.5g of adsorbent 30 min time interval and constant temperature of 313K as shown in figure 5 below. From the results, the percentage of BCG removed initially increased as the pH increases (pH 4 to 6) but steadily decrease from pH 6 to 10. This maximum removal of BCG at pH 6 shows that under alkaline, the change of initial pH had no significant impact on the removal of BCG using CCAC and this can be attributed to the anionic form of BCG leading to increase in electrostatic interaction with adsorbent site (Murmu *et al*., 2018; Onu & Nwabanne, 2014). The reduction in adsorption efficiency at higher pH could be as a result of an increase in pH, leading to an increase in number of negatively charged binding sites and subsequently the anionic BCG will not be adsorbed (Murmu *et al*., 2018; Djilani *et al*., 2015; Zheng *et al*., 2015).

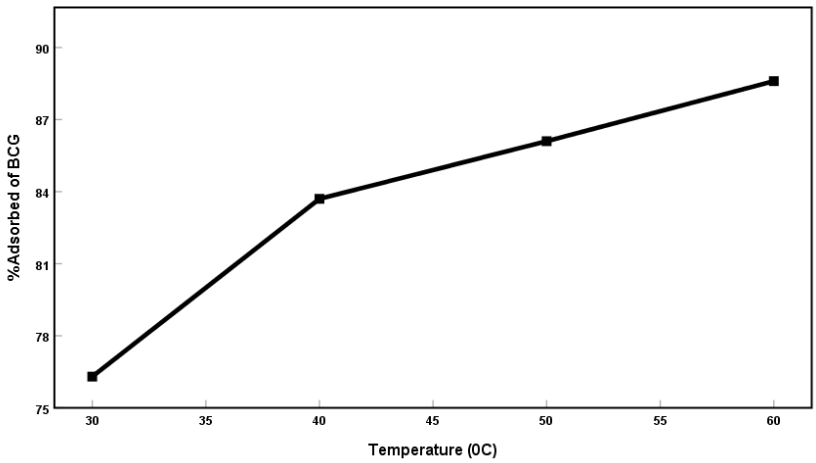

Figure 1: Effect of Temperature on Adsorption of BCG by Corn cob

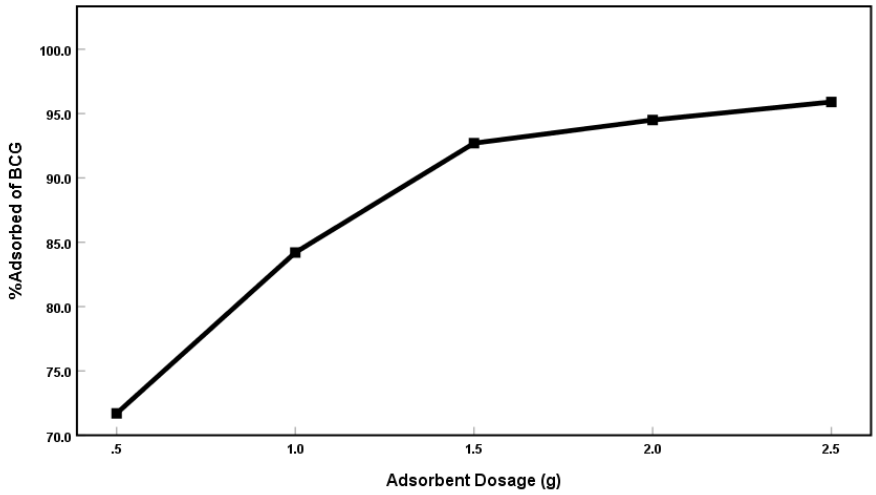

Figure 2: Effect of Adsorbent dosage on Adsorption of BCG by Corn cob

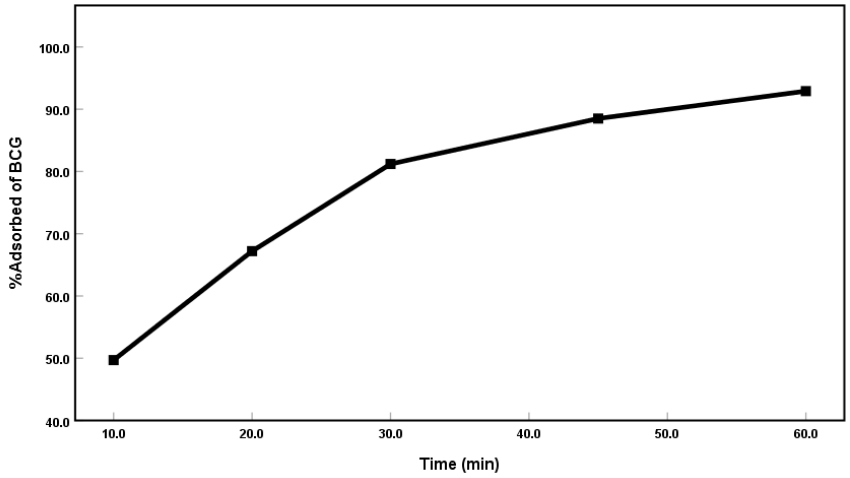

Figure 3: Effect of Time on Adsorption by Corn cob of BCG

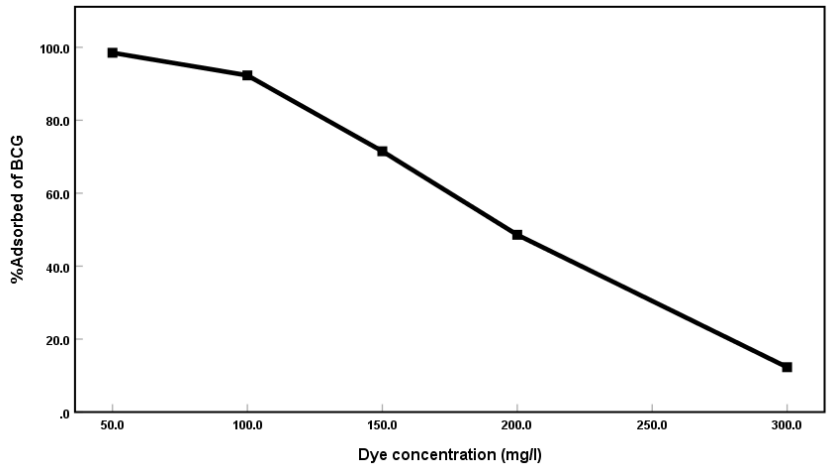

Figure 4: Effect of Dye concentration on Adsorption of BCG by Corn cob

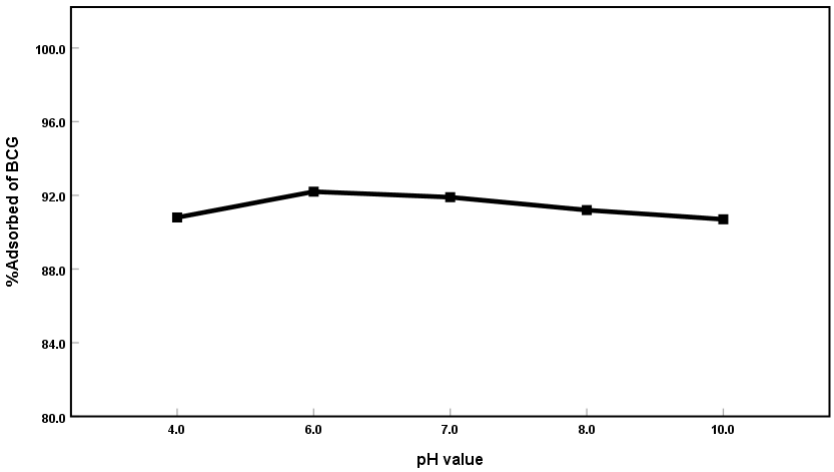

Figure 5: Effect of pH on Adsorption of BCG by Corn cob

3.3 Kinetic model

The kinetic study can be used to investigate the mechanism of the adsorption process and the potential rate controlling steps involving mass transport, pore diffusion and chemical reaction processes (Onu & Nwabanne, 2014; Ekpete & and Jnr, 2011). To analyze this adsorptive kinetics of BCG, first-order, Pseudo first-order and pseudo second-order kinetics were adopted to fit the data gotten from the experiments.

3.3.1 First-order kinetics

The first-order kinetics is given by;

$$-In\left(\frac{C_t}{C_0}\right) = K_1 t \qquad (3)$$

Where C_t= the concentration at time t, C_0=the initial concentration, K_1=first-order rate constant (Zheng *et al*., 2015). A plot of $-In\left(\frac{C_t}{C_0}\right)\ against\ t$ yielded the value for the rate constant as 0.075 and the adsorption data as R^2=0.985

which reflected a good fit to the experimental equilibrium data as compared to other kinetic models. This is shown in Figure 6 below.

3.3.2 Pseudo first-order Kinetics

The Pseudo first-order can be described below according to Lagergren;

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right)t \qquad (4)$$

Where q_e=the amount of adsorbate at equilibrium (mg/g), qt=the amount of adsorbate at time t (mg/g), K_1= the first-order rate constant and *t* is time (min). The plot of log (qe-qt) against the time t produced a linear relationship and the values of K_1 and qe were determined from the slope and intercept respectively as shown below in Figure 7. The adsorption data (R^2=0.873) indicates a poor fit to the experimental data and was not a perfect model for the adsorption of BCG using CCAC.

3.3.3 Pseudo second-order Kinetics

The pseudo second-order model is represented by;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

Where k_2= rate constant of the pseudo second-order adsorption (g/mg.min).

A plot of $\frac{t}{q_t}$against t(min) gives a linear relationship as shown in figure 8 with slope of q_e, intercept k_2, and correlation coefficient R^2 with the help of the straight-line graph. The adsorption data shows that this model is not a good representation of the equilibrium data (R^2=0.704)compared to other kinetic models.

3.3.4 Natarajan and Khalaf kinetic model

The Natarajan and Khalaf model created a relationship between concentration at any time t and the initial concentration as explained in equation 6 according to Srihari & Das (2008),

$$\log\left(\frac{C_o}{C_t}\right) = \left(\frac{K_N}{2.303}\right) t \qquad (6)$$

where Co = initial concentration (mg/L); Ct = concentration (mg/L) at time t. The value of K_N was calculated from the slope of the plot of log (Co/Ct) against time (minutes) and the corresponding values are presented in Table 2. This model gave a good fit to the experimental equilibrium data and good representation of the adsorption process which is synonymous to that obtained in first order model (R^2=0.985)

3.3.5 Intra-particle diffusion

The intra-particle diffusion model helps to examine the chances of the adsorption process diffusing into the interior pores of the adsorbent after the external surface adsorption (Murmu *et al*., 2018; Zheng *et al*., 2015). This kinetic model is explained using Weber-Morris equation;

$$q_t = K_i t^{1/2} + \mathcal{B} \qquad (7)$$

Where K_i = the intra-particle diffusion constant and $\mathcal{B}$ = the intercept of the line and equivalent to the boundary layer thickness.

The plot of $q_t$against$t^{1/2}$was shown in Figure 10 and used to calculate the intra-particle diffusion constant K_i and shown in Table 2.

Table 2: Kinetics results for BCG adsorption by CCAC

Kinetic model	Parameter	Value
First order	K_1 (min^{-1})	0.075
	R^2	0.985
Pseudo first order	K_1 (min^{-1})	-0.069
	q_e(mg/g)	0.251
	R^2	0.873
Pseudo second order	K_2 (g/mg.min)	0.00033
	q_e (mg/g)	33.33
	R^2	0.704
Natarajan & Khalaf	K_N (min^{-1})	0.081
	R^2	0.985
Intra-particle diffusion	K_i(mg/g$min^{1/2}$)	5.00
	R^2	0.975

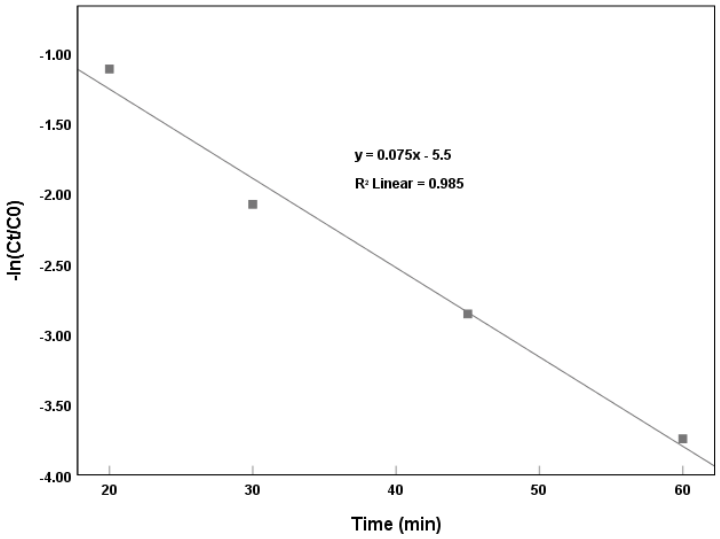

Figure 6: First-order kinetics for Adsorption of BCG by Corn Cob

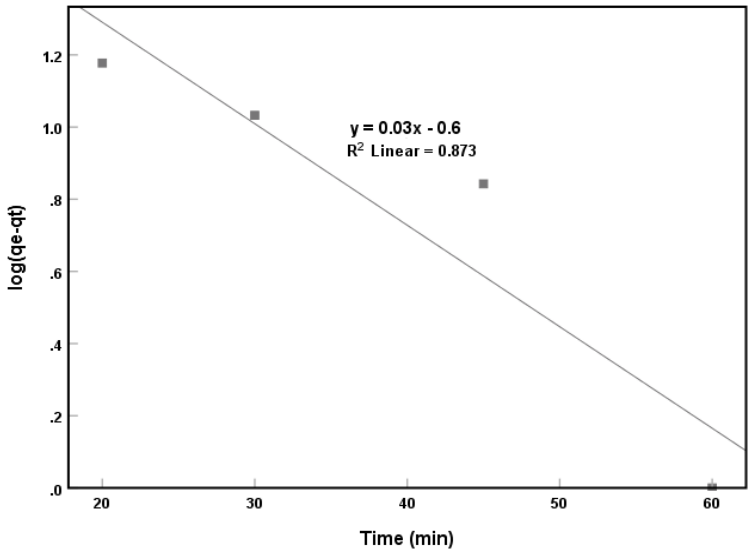

Figure 7: Pseudo first-order kinetics for Adsorption of BCG by Corn Cob

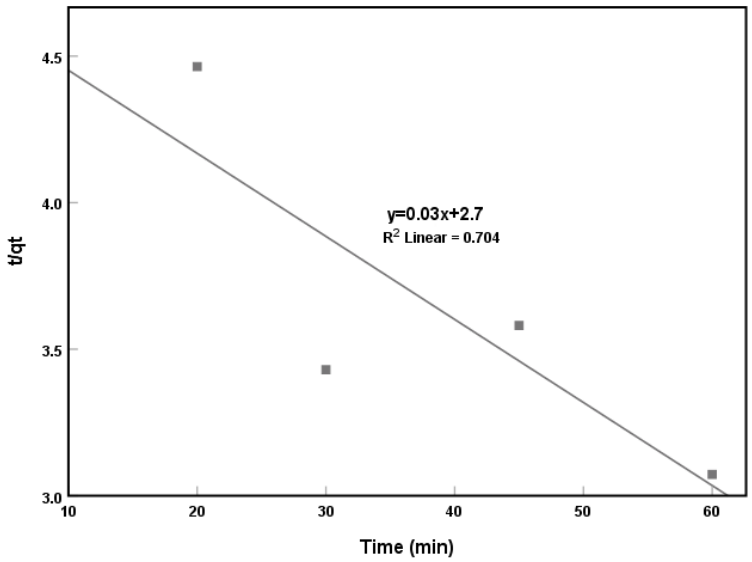

Figure 8: Pseudo second-order kinetics for Adsorption of BCG by Corn Cob

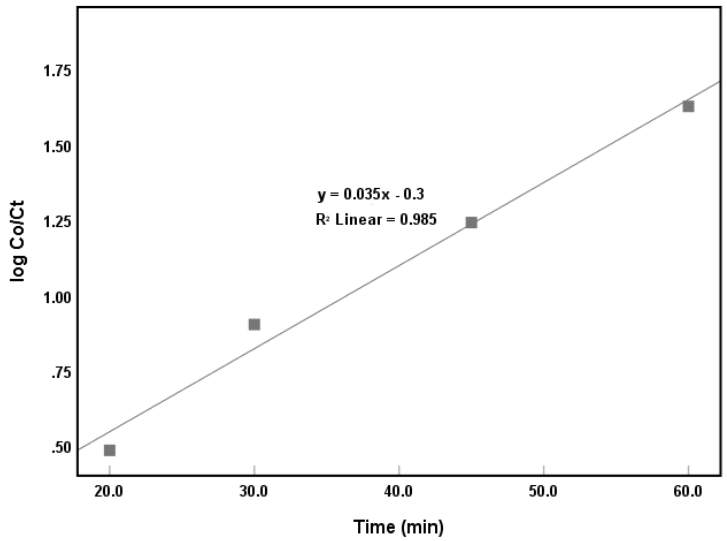

Figure 9:Natarajan & Khalaf kinetics for Adsorption of BCG by Corn Cob

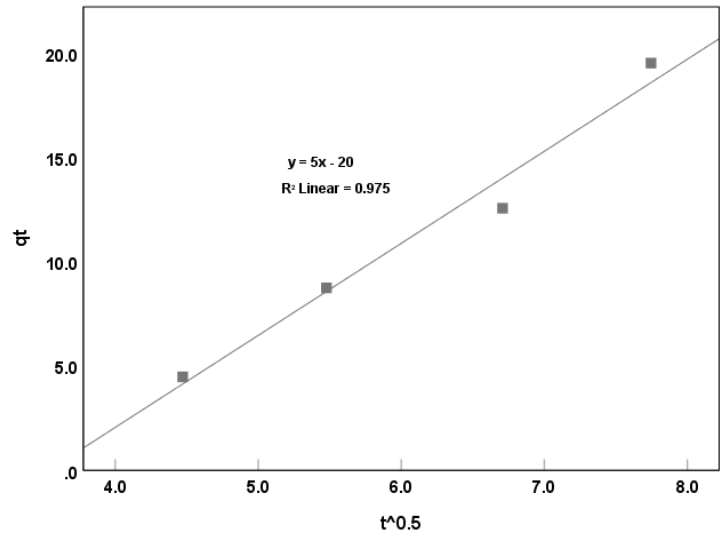

Figure 10: Intra-particle diffusion model for Adsorption of BCG by Corn Cob

3.4 Adsorption Isotherms

Adsorption is often described using isotherms because of the importance of temperature in the adsorption process. The three adsorption isotherms used to analyze the equilibrium adsorption data are; Langmuir isotherm, Freundlich model and Temkin isotherm (Murmu *et al*., 2018; Djilani *et al*., 2015).

3.4.1 Langmuir Isotherm

The Langmuir model is on the assumption that the adsorption process takes place on a homogeneous surface by monolayer adsorption (Zheng *et al*., 2015).

$$\frac{C_e}{q_e} = \frac{1}{b_{qm}} + (\frac{1}{q_m})C_e \qquad (8)$$

Where q_e = equilibrium amount of solute adsorbed per unit weight of adsorbent (mg/g); C_e =equilibrium concentration in aqueous phase (mg/l), q_m = the maximum amount adsorbed per unit mass of adsorbent for a

complete monolayer (mg/g), $b =$ a constant related to the affinity of the binding sites and energy of adsorption (l/mg). The Langmuir isotherm model was plotted as $\frac{C_e}{q_e}$against C_e and the constants qm and b were determined from the intercept and slope as shown in Figure 11 below. The correlation coefficient indicated that this isotherm didn't fit the equilibrium data. The dimensionless constant for Langmuir isotherm can be expressed as a separation factor, R_L and expressed in equation 8;

$$R_L = \frac{1}{1 + bC_0} \quad (9)$$

Where $C_0 =$ the highest initial solute concentration (mg/L), b = Langmuir constant. The value of the calculated R_L gives an indication on the success of the adsorption process. R_L=0, R_L=1, R_L>1 and 0<R_L<1 means the adsorption isotherm was irreversible, linear, unfavorable and favorable respectively. From this study, the R_L values for BCG removal by activated corn cob was calculated and shown in Table 3. The R_L value for the activated corn cob was 0.0187 indicating that the adsorption process was favorable.

3.4.2 Freundlich Model

Freundlich model is suitable for adsorption of heterogeneous surfaces giving an exponential distribution of active sites and energies. The equation below shows the logarithm linear form of the Freundlich isotherm model (Zheng *et al*., 2015):

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) log C_e \quad (10)$$

Where $q_e =$amount of adsorbate (mg/g), $C_e =$the equilibrium concentration of the adsorbate (mg/l),$K_f =$Freundlich adsorption capacity factor, $\frac{1}{n} =$ Freundlich adsorption intensity. The model was shown in Figure 12 with a plot of loqq_e against logC_e and Freundlich factors$K_f$and n were gotten from the intercept and slope respectively. The correlation coefficient R^2which yielded a high value (0.977), confirms that this model well fits the equilibrium data and gave a good description of the adsorption of bromocresol green dye on to activated corn cob.

3.4.3 Temkin Isotherm

The Temkin isotherm involves an assumption stating that the fall in the heat of adsorption is linear rather than being logarithmic as earlier stipulated by Freundlich (Murmu *et al*., 2018; Zheng *et al*., 2015). The linear form of Temkin isotherm is illustrated in equation 11.

$$q_e = \left(\frac{RT}{b}\right) InA + \left(\frac{RT}{b}\right) InC_e \quad (11)$$

Where $\frac{RT}{b} =$ B which is the heat of adsorption, A = the equilibrium binding constant (L/mg). A plot of q_e against InC_e as shown in Figure 13 below with the values of the constants b, A and correlation coefficient determined as shown in Table 3. The value of correlation coefficient (R^2=0.889) signifies that the Temkin isotherm did not give a good representation of the equilibrium data.

3.4.4 Halsey Isotherm

The Halsey isotherm is assumed to be suitable for multilayer adsorption and is generally expressed in linear form illustrated in equation 12(Amin, Alazba & Shafiq, 2015).

$$\ln q_e = \frac{\ln K_{Ha}}{n_{Ha}} - \frac{\ln C_e}{n_{Ha}} \quad (12)$$

Where K_{Ha} (mg/L) and n_{Ha} are the Halsay isotherm constants. A graph of $\ln q_e$ against $\ln C_e$ is plotted as shown in figure 14. From the correlation coefficient (R^2=0.977), this isotherm fits the equilibrium data compared to other

isotherms and the adsorbent is termed to be heterogenous in nature. The equilibrium data is well represented with Halsey isotherm.

3.4.5 Harkins-Jura Isotherm

Harkin-Jura isotherm model also assumes the possibility of multilayer adsorption on the surface of absorbents having heterogeneous pore distribution (Amin, Alazba & Shafiq, 2015) and the linear form of this model is stated in equation 13

$$\frac{1}{q_e^2} = \frac{B_H}{A_H} - \frac{1}{A_H}\log C_e \qquad (13)$$

Where A_H (g^2/L) and B_H (mg^2/L) are two parameters characterizing the adsorption equilibrium. A plot of $\frac{1}{q_e^2}$ against $\log C_e$ was done as shown in figure 15 with the corresponding values of A_H and B_H stated in Table 3. The correlation coefficient (R^2=0.870) from Harkin-Jura isotherm signifies that the fit to the equilibrium data was very poor compared to other isotherms.

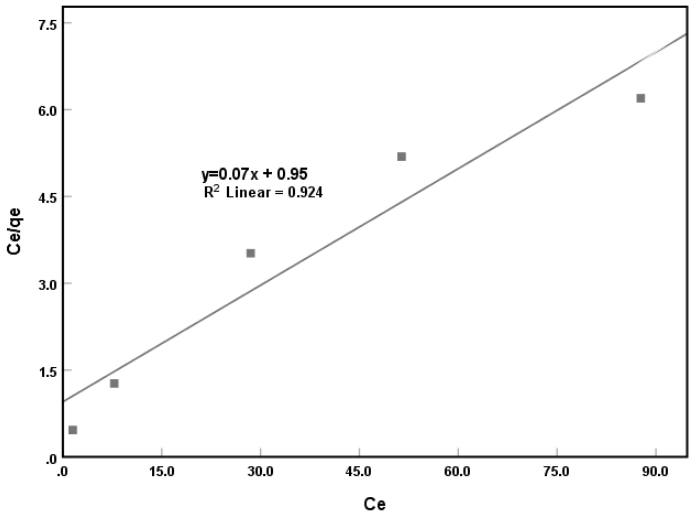

Figure 11: Plot of Langmuir Isotherm for Adsorption of BCG by Corn Cob

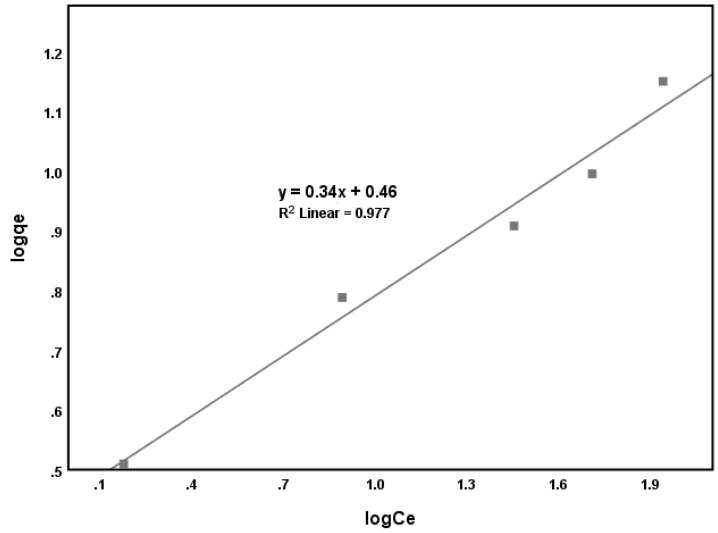

Figure 12: Plot of Freundlich Isotherm for Adsorption of BCG by Corn Cob

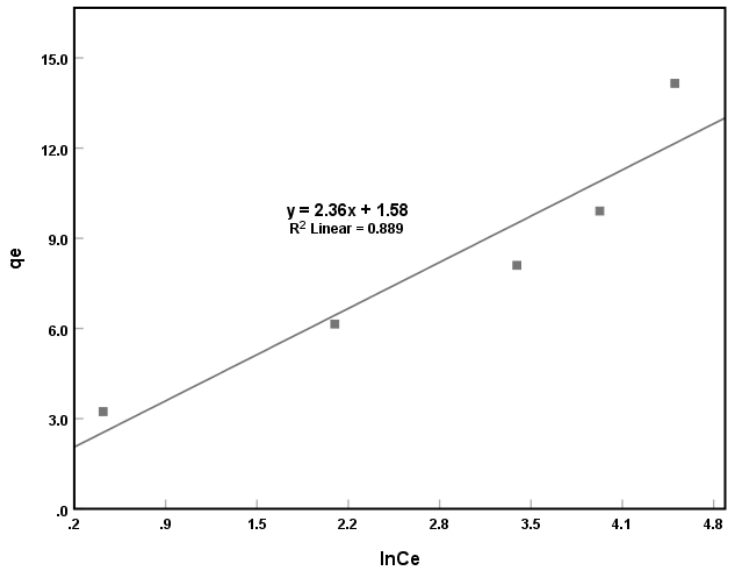

Figure 13: Plot of Temkin Isotherm for Adsorption of BCG by Corn Cob

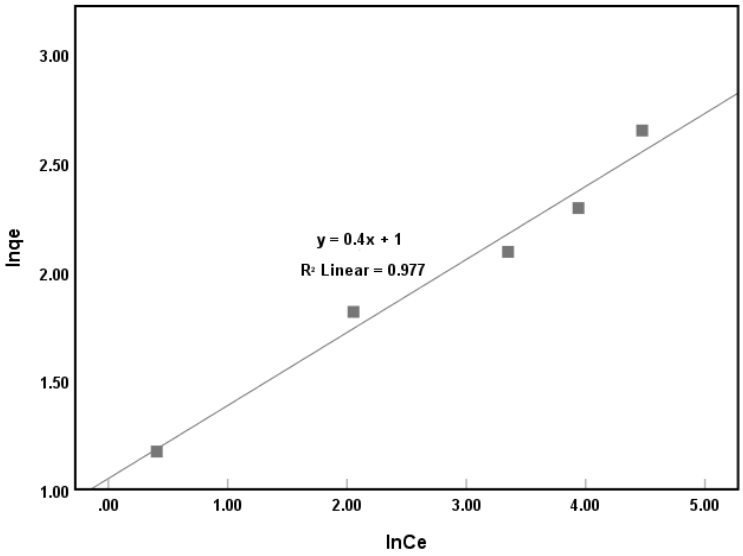

Figure 14: Plot of Halsey Isotherm for Adsorption of BCG by Corn cob

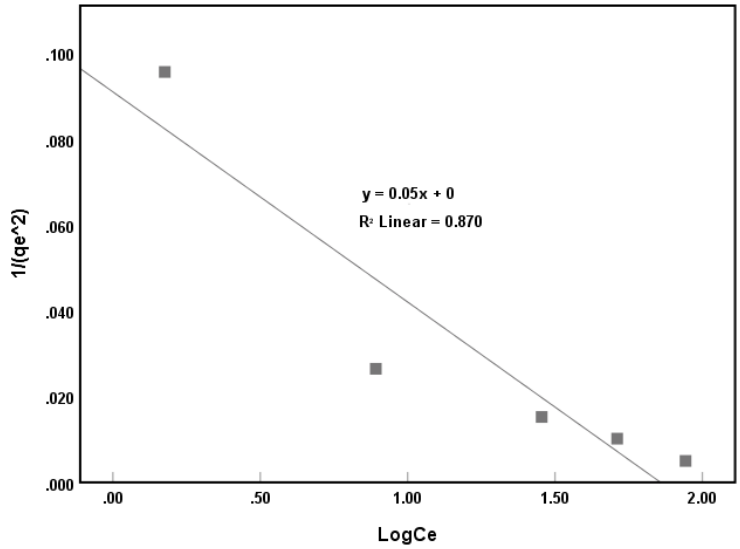

Figure 15: Plot of Harkins-Jura Isotherm for Adsorption of BCG by Corn cob

Table 3: Calculated Isotherm Properties of BCG Adsorption by Activated Corn cob

Isotherm model	Parameter	Value
Langmuir	q_m(mg/g)	14.3
	b (L/mg)	1.052
	R_L	0.0187
	R^2	0.924
Freunlich	n	2.941
	K_f(L/g)	2.884
	R^2	0.977
Temkin	b (J/mg)	1067.43
	A (L/g)	1.953
	R^2	0.889
Halsay	K_{Ha} (mg/L)	0.082
	n_{Ha}	-2.5
	R^2	0.977
Harkins-Jura	A_H (g^2/L)	-20
	B_H (mg^2/L)	0.000
	R^2	0.870

3.5 Thermodynamic Study

The vital thermodynamic properties such as enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy (ΔG)were calculated using the following Van't Hoff equations(Srihari& Das, 2008;Amin, Alazba& Shafiq, 2015; Ohale et al. 2020).

$$\Delta G^o = -RT \ln K_L \quad (14)$$

$$\ln K_L = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (15)$$

$$\Delta s^o = \Delta H - \frac{\Delta G^o}{T} \quad (16)$$

where R= universal gas constant = 8.314 J/Mole/K, K_L = equilibrium constant (amount on adsorbent/amount in solution), T = Temperature in ^{0}K.

The values of ΔS, ΔH and ΔG were calculated from the slope and intercept of equation 15 ($\ln K_L$v 1/T) and shown in Table 4. The negative values of ΔH is an indication that the process is exothermic and stipulates that the molecules were freely diffused (Srihari & Das, 2008). The negative values of ΔS reflected the decreased randomness at the solid-solution interface during the adsorption process and since it is less than 1, it shows that the process is very reversible. The positive values of ΔG confirmed that the adsorption of BCG onto CCAC was a non-spontaneous process.

Table 4: Thermodynamic properties for the adsorption of BCG onto CCAC

Adsorbent	T (K)	ΔG (KJ/mol)	ΔS (kJ/mol K)	ΔH (KJ/mol)
CCAC	303	1.255		
	313	2.669		
	323	4.082	-0.141	-41.57
	333	5.496		

4. Conclusion

The study of the adsorption of bromocresol green dye from activated carbon prepared from corn cob illustrates that this can be done at a cost-effective rate. The effect of process parameters showed that as the removal of BCG increases the temperature, adsorbent dosage and contact time increases. On the other hand, as the removal of BCG decreases, the dye concentration and pH increases. From the investigation, the activated carbon prepared from corn

cob gave good values of the correlation coefficient across the kinetic and isotherm models. The separation factor from the Langmuir model indicates that the adsorption process of BCG by CCAC was favorable. The first-order and Nataran & Khalaf kinetics gave the best description of the adsorption kinetics for CCAC used (R^2=0.985) while the Freundlich and Halsay isotherm illustrates the best fit for the equilibrium data (R^2= 0.977). The correlation coefficient R^2 was higher in the first-order model compared to the pseudo first-order and pseudo second-order models. From these analytical stats, it was assumed that the first-order model gave a more reliable adsorption of bromocresol green dye from aqueous solution using activated carbon from corn cob.

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References

Activated Carbon: Calgon Carbon Corporation https://www.calgoncarbon.com/activated-carbon/(Accessed 01/05/2020).

EmedicalPrep. Adsorption. Available at https://www.emedicalprep.com/study-material/chemistry/surface-chemistry/adsorption/ (Accessed 01/04/2020).

Amin, M.T, Alazba, A.A, and Shafiq, M. 2015. Adsorptive removal of reactive black 5 from wastewater using Bentonite clay: Isotherms, Kinetics and Thermodynamics. Sustainability, 7,15302-15318.

Anukam, A.I., Goso, B.P., Okoh, O.O., and Mamphweli, S.N. 2017. Studies on characterization of corn cob for application in a gasification process for energy production. Hindawi: Journal of chemistry, 2017, 1.

Asadu, C. O., OnU, C. E., Nick O. O., Ezema C. A., Chime T. O., Maxwell I.O., Ike, S. I., Onoghwarite, O. E., Chukwuebuka , A. S. 2021. Treatment of crude oil polluted water using stearic acid grafted mango seed shell (Mangifera indica) composite. Current Research in Green and Sustainable Chemistry 4; 1-15. https://doi.org/10.1016/j.crgsc.2021.100169

Asadu, C. O., Ezema C. A., Onu C. E., Ike, S. I., Onoghwarite, O. E., Umeagukwu, E. O. 2021. Development of an adsorbent for the remediation of crude oil polluted water using stearic acid grafted coconut husk (Cocos nucifera) composite. Applied Surface Science Advances. 6, 1 – 11. https://doi.org/10.1016/j.apsadv.2021.100179

Bello, O. S., Adeogun, I. A., Ajaelu, J. C.& Fehintola, E. O. 2008. Adsorption of methylene blue onto activated carbon derived from periwinkle shells: Kinetics and equilibrium studies.Journal of Chemistry and Ecology, 24(2008), 285.

Bello, O. S., Fatona, T. A., Falaye, F. S., Osuolale, O. M.& Njoku, V. O. 2012. Adsorption of eosin dye from aqueous solution using groundnut hull-based activated carbon: kinetic, equilibrium and thermodynamic studies. Environmental Engineering Science, 29(2012), 186.

Chan, L.S., Cheung, W.H., Allen, S.J.& McKay, G. 2009. Separation of acid-dyes mixture by bamboo derived carbon. Separation and Purification Technology, 67(2009), 166.

Chen, Y., Zhai, S., Liu, N., Song, Y., An, Q.& Song, X. 2013. Dye removal of activated carbons prepared from NaOH-pretreated rice husks by low-temperature solution-processed carbonization and H_3PO_4 activation. Bioresource Technology, 144(2013), 401.

Djilani, C., Zaghdoudi, R., Djazi, F., Bouchekima, B., Lallam, A., Modarressi, A.& Rogalski, M. 2015. Adsorption of dyes on activated carbon prepared from apricot stones and commercial activated carbon. Journal of the Taiwan Institute of Chemical Engineers, 53(2015), 112.

Duran-Jimenez, G., Hernandez-Montoy, V., Montes-Moran, M., Bonilla-Petriciolet & Rangel-Vazquez, N. A. 2014. Adsorption of dyes with different molecular properties on activated carbons prepared from lignocellulosic wastes by Taguchi method. Microporous Mesoporous Mater, 199(2014), 99.

Ekpete, O. and Jnr, M.H. 2011. Kinetic sorption study of phenol onto activated carbon derived from fluted pumpkin stem waste. ARPN Journal of Engineering and Applied science, 6(6), 43–49.

Elass, K., Laachach, A., Alaoui, A. & Azzi, M. 2011. Removal of methyl violet from aqueous solution using a stevensite-rich clay from Morocco. Applied Clay Science, 54(2011), 90.

Feng, Y., Yang, F., Wang, Y., Maa, L., Wua, Y., Kerr, P. G.& Yang, L. 2011. Basic dye adsorption onto an agro-based waste material-Sesame hull (Sesamum indicum L.). Bioresource Technology, 102(22), 10280.

Fernandez, M.E., Nunell, G.V., Bonelli, P.R.& Cukierman, A.L. 2014. Activated carbon developed from orange peels: Batch and dynamic competitive adsorption of basic dyes. Industrial Crops and Products, 62(2014), 437.

Fluence News Team. Fluence Corporation. Textile Industry water use and treatment. Available at https://www.fluencecorp.com/textile-industry-water-use/ (Accessed: 01/04/2020).

Ghaedi, M., Khajesharifi, H., Yadkuri, A. H., Roosta, M., Sahraei, R.& Daneshfar, A. 2012. Cadmium hydroxide nanowire loaded on activated carbon as efficient adsorbent for removal of Bromocresol Green. *Spectrochim Acta A*, 86(2012), 62.

Guzel, F., Saygılı, H., Saygılı, G. A. & Koyuncu, F. 2015. New low-cost nanoporous carbonaceous adsorbent developed from carob (Ceratonia siliqua) processing industry waste for the adsorption of anionic textile dye: characterization, equilibrium and kinetic modeling. Journal of Molecular Liquids, 206(2015), 244.

Iheanacho, C. O., Nwabanne, J. T., & Onu, C. E. 2019. Optimum Process Parameters for Activated Carbon Production from Rice Husk for Phenol Adsorption. Current Journal of Applied Science and Technology, 36(6): 1-11. DOI: 10.9734/CJAST/2019/v36i630264

Karagozoglu, B., Tasdemir, M., Demirbas, E. & Kobya, M. 2007. The adsorption of basic dye (Astrazon Blue FGRL) from aqueous solutions onto sepiolite, fly ash and apricot shell activated carbon: Kinetic and equilibrium studies. J Hazard Mater, 147(2007), 297.

Liao, P., Ismael, Z.M., Zhang, W., Yuan, S., Tong, M., Wang, K.& Bao, J. 2012. Adsorption of dyes from aqueous solutions by microwave modified bamboo charcoal. Chemical Engineering Journal, 195-196(2012), 339.

Malina, J.& Radenovic, A. 2014. Kinetic Aspects of Methylene Blue Adsorption on Blast Furnace Sludge. Chemical and Biochemical Engineering Quarterly, 28(2014), 491.

Mandal, S.& Natarajan, S. 2015. Adsorption and catalytic degradation of organic dyes in water using ZnO/ZnxFe3-x O4, mixed oxides. Journal of Environmental Chemical Engineering, 03(2), 1185.

Moussavi, G. & Khosravi, R. 2011. The removal of cationic dyes from aqueous solutions by adsorption onto pistachio hull waste. Chemical Engineering Research and Design, 89(10), 2182.

Murmu, B.M., Behera, S.S., Das, S., Mohapatra, R.K., Bindhani B.K. and Parhi, P.K.2018. Extensive investigation on the study for the adsorption of Bromocresol Green (BCG) dye using activated Phragmites karka. Indian Journal of Chemical Technology, 25, 409-420.

Nnenna, N. V., Igbokwe, P. K., & Onu, C. E. 2020. Removal of Methylene Blue Dye from Aqueous Solution Using Modified Ngbo Clay. Journal of Materials Science Research and Reviews, 5(2): 33-46. May 2020

Nwabanne, J. T., Okpe, E. C., Igbokwe, P. K., Asadu, C. C. & Onu, C. E. 2016. Isotherm and kinetic modelling of adsorption of dyestuffs onto kola nut (cola acuminate) shell activated carbon. Journal of Chemical Technology and Metallurgy. 51 (2) 188 – 201.

Nwabanne, J. T., Onu, C. E. & Nwankwoukwu, O. C. 2018. Equilibrium, Kinetics and Thermodynamics of the Bleaching of Palm Oil Using Activated Nando Clay. Journal of Engineering Research and Reports 1(3): 1-13. DOI: 10.9734/JERR/2018/42699

Nwabanne, J. T., Iheanacho, O. C., Obi, C. C., Onu, C. E. 2022. Linear and nonlinear kinetics analysis and adsorption characteristics of packed bed column for phenol removal using rice husk-activated carbon. Applied Water Science (2022) 12:91; 1 – 16. https://doi.org/10.1007/s13201-022-01635-1

Ohale, P. E., Onu, C. E., Ohale, N. J., Oba, S. N. 2020. Adsorptive kinetics, isotherm and thermodynamic analysis of fishpond effluent coagulation using chitin derived coagulant from waste Brachyura shell. Chemical Engineering Journal Advances 4 (Oct 2020) 100036, 1 – 13. https://doi.org/10.1016/j.ceja.2020.100036.

Onu, C.E, & Nwabanne, J.T. 2014. Adsorption kinetics for Malachite Green removal from aqueous solution using Nteje clay. Journal of Environmental and Human, 1(2014), 133-150.

Onu, C. E., Oguanobi, N. C., Okonkwo, C. O., & Nnamdi-Bejie, J. 2020. Application of Modified Agricultural Waste in the Adsorption of Bromocresol Green Dye. Asian Journal of Chemical Sciences. 7(1): 15-24. https://doi.org/10.9734/AJOCS/2020/v7i119011

Onu, C. E. & Nwabanne, J. T. 2014. Adsorption studies on the removal of Eriochrome Black-T from aqueous solution using Nteje clay. SOP Transactions on Applied Chemistry. 1 (2) 14 – 25. : https://doi.org/10.15764/STAC.2014.02003

Onu, C. E. & Nwabanne, J. T. 2014. Adsorption kinetics for Malachite green removal from aqueous solution using Nteje clay. Journal of Environment and Human. 1 (2) 133 – 150. : https://doi.org/10.15764/EH.2014.02015

Ositadinma, C. I., Nwabanne, J. T., Obi, C. C., Onu, C. E. 2021. Packed bed column adsorption of phenol onto corn cob activated carbon: linear and nonlinear kinetics modeling. South African Journal of Chemical Engineering 36 (Feb 2021) 80–93. https://doi.org/10.1016/j.sajce.2021.02.003.

Srihari, V. & Das, A. 2008. The kinetic and thermodynamic studies of phenol-sorption ontothree agro-based carbons. Desalination, 225(2008), 220-234.

Teng, M., Li, F., Zhang, B.& Taha, A.A. 2011. Electrospun cyclodextrin-functionalized mesoporous polyvinyl alcohol/SiO2 nanofiber membranes as a highly efficient adsorbent for indigo carmine dye. Colloids Surface A: Physicochemical and Engineering Aspects, 385(1-3), 229.

Zheng, H., Qi, J., Jiang, R., Gao, Y.& Li, X. 2015. Adsorption of malachite green by magnetic litchi pericarps: A response surface methodology investigation. Journal of Environmental Management, 162(2015), 232.