

Removal of Congo Red Dye from Simulated Wastewater Using Activated Carbon Derived from Corn Cobs; Kinetics and Equilibrium Studies

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ABSTRACT: *The released of dyes into hydrological systems in textile manufacturing, printing and other dyeing processes are hazardous and toxic to human and aquatic lives. Activated carbons have been remarkably used to treat dye contaminated waste water due to their large surface area and porosity, however regeneration and high cost have limited their applications. This study investigated the use of activated corn cobs (ACC) on the adsorption of methyl green dye from aqueous solution. The raw cobs were collected, crushed into particle size of about 600 μm and modified in-situ with KOH to prepare ACC which was characterized using some analytical techniques; Energy Dispersive X-ray (EDX) spectroscopy and Scanning Electron Microscopy (SEM). The absorbance of the dye solution was monitored at 500 nm with UV-Visible spectrophotometer. SEM results revealed the ACC has a porous surface with heterogeneous pores which became compact after dye adsorption. EDX confirmed the presence of C, O, H and K in the adsorbent. The suitability of the pseudo-first, pseudo second, Elovich and Intra-particle kinetic models for the removal of congo red dye onto ACC was examined. The equilibrium data were subjected to Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich, Sips and Relich-Peterson isotherm models. The pseudo-second order kinetic model provided the best correlation and was found to be more statistically significant. Langmuir model was found to fit well based on the high values of the coefficient of regression R^2 and low % standard error values. The monolayer adsorption capacity Q_{max} was found to be 37.81 mgg^{-1} . Thermodynamic adsorption processes showed the spontaneous, exothermic and randomness of the systems with free energy change less than zero, enthalpy change (ΔH) of $-62.47 \text{ kJmol}^{-1}$ and entropy change (ΔS) of $145.27 \text{ Jmol}^{-1} \text{ K}^{-1}$.*

KEYWORDS: Thermodynamic, adsorption, congo red, activated corn cobs, isotherm; Kinetics.

INTRODUCTION

Increase anthropogenic activities as a result of rapid urbanization and industrialization have led to increase environmental pollution with grave consequence in the quality of water available for industrial, agricultural and domestic use. Dyes are highly stable compounds to light, chemical, biological and other exposures[1]. Dyes are basically natural or synthetic organic compounds that can connect themselves to surfaces or fabrics to produce bright and lasting colour [2]. Synthetic dyes are one of the major water pollutants mostly released from various industrial processes such as dyestuff manufacturing, dyeing, printing, textile finishing, etc. Annually, 12 % of the synthetic dyes are discharged into aquatic body from anthropogenic activities. The textile industries account for two thirds of the world's annual production estimated to be 7×10^5 tonnes [3]. Pollution from this source are the major concern for the developing countries because of various factors such as visibility of dyes even in low concentrations; adverse effect on the photosynthetic activities of the aquatic life among others. It is necessary to effectively treat effluents containing dyes due to the environmental and toxicology threats posed to human and aquatics animals. Colour removal is one of the daunting tasks faced by industries, while the development of cost effective and environmentally safe method in dyes adsorption is challenging to researchers. Many processes such as liquid-liquid extraction[4], ozonation, adsorption [5] etc, have been adopted to dyes removal in wastewater. However; some of these techniques are inefficient and expensive to treat wastewater containing dyes. Adsorption technique has been found to be a superior separation and purification method because of its easy-nature, low cost, high selectivity and high removal efficiency.

Most countries of the world are agrarians with abundant cellulosic by-products from the production of crops such as groundnuts, millet, soybean rice etc. The natural fiber comes from stalks, leaves and seeds, such as kenaf, sisal, flax, sorghum, wheat and rice [6 - 9] . Natural fiber have been found to be advantageous over the synthetic ones in terms of biodegradability, flammability and non-toxicity [7]. Cellulose, a biopolymer is considered a promising natural source that has been extensively explored by researchers for adsorption. Surface modification of cellulose improves its potential in adsorption process, hence, needs to modify the groundnut pods in this work. Also thermal and mechanical resistance may also increase its pollutant adsorption capacity in aqueous and non-aqueous solutions [8]. Therefore, this work aimed at investigating the adsorption of congo red dye from aqueous solutions using activated corn cobs (ACC) as adsorbent. The kinetic, isotherm and thermodynamic parameters of the adsorption were considered in a batch process.

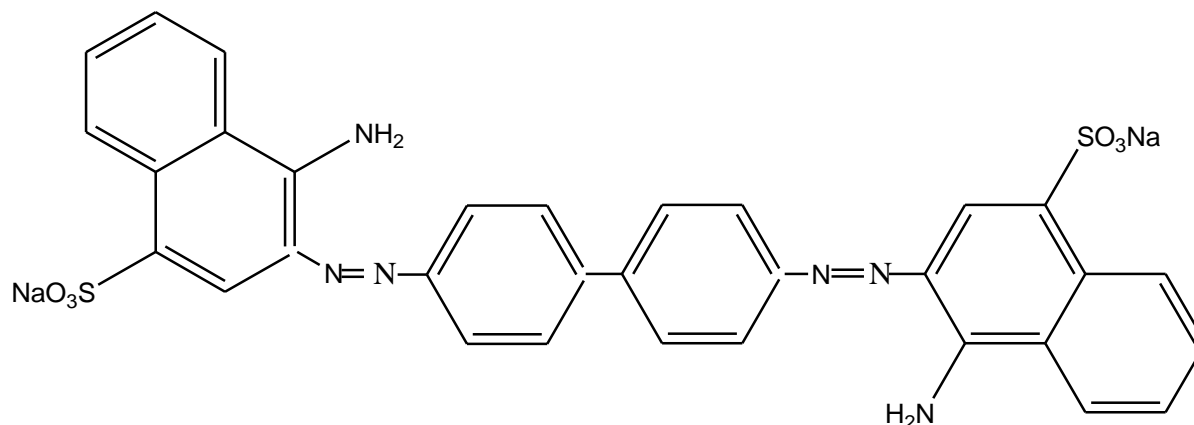


Fig. 1: Structure of congo red dye.

MATERIALS AND METHODS

Materials

Congo red dye was obtained from Merck laboratory, India. Hydrochloric acid (HCl), Urea ($\text{CH}_4\text{N}_2\text{O}$) and Sodium hydroxide (NaOH) were procured from BDH, London. Other reagents used were of analytical standard.

Characterization

Scanning electron microscopy (SEM; Hitachi S4800) equipped with EDAX was used to determine the surface morphology of the adsorbent before and after adsorption, while the EDAX monitored the elemental component of the adsorbent. Organic functionalities were determined by Fourier transform infrared (FTIR) spectroscopy and recorded from 400 to 4000 cm^{-1} in TENSOR 27 Spectrophotometer (Bruker, Germany) using KBr pellet technique.

Synthesis of activated corn cobs (ACC)

Corn cobs were collected, washed with tap water and rinsed with distilled water to remove dust and impurities. The cobs were air-dried then oven dried at 50°C to constant mass. The dried cobs were pulverized, sieved to obtain particle sizes less than 600 μm and preserved in an air-tight polythene bag to prevent from moisture and made ready for the analysis.

The sieved cobs (70 g) were suspended in 100 ml of 0.2M KOH, 20 ml of 2M urea solution was added as a stabilizer and stirred continuously for 1hr on a magnetic stirrer. The suspension was centrifuged, washed thoroughly with distilled water till a neutral pH attained. It was then carbonized at 110°C for 2hrs in a vacuum oven and kept in an air tight container.

Preparation of adsorbate

Congo red dye (1.0 g) was dissolved in 1litre of distilled water to give a concentration of 1000 mgL⁻¹. The working solutions were prepared form the stock solution by serial dilution.

$$C_1V_1 = C_2V_2 \quad (1)$$

Adsorption Studies

The batch equilibrium and kinetics adsorption studies were conducted in process in Erlenmeyer flasks containing 25 mL of dye solutions with concentration range between 10 – 50 mgL⁻¹ and 0.1 g of the adsorbent. The contents were placed in a regulated water bath (30 °C) with shaker at 150 rpm, samples were collected at pre-set time intervals. The dye concentrations in aqueous media were determined after the adsorbent was centrifuged by reading the absorbance at 586 nm. The amount of methyl green dye adsorbed (mg/g) by the adsorbent as a function of time (Q_t) and at equilibrium (Q_e) were estimated according to equations 2 and 3 below:

$$Q_t = \frac{(C_o - C_t)}{m} \times V \quad (2)$$

$$Q_e = \frac{(C_o - C_e)}{m} \times V \quad (3)$$

where C_o , C_t and C_e are the initial, time t and equilibrium concentrations (mg/L) of the dye respectively, V is volume (L) of the solution and m is the mass (g) of the adsorbent.

Adsorption mechanism and isotherms studies

The mechanisms of adsorption of congo red dye onto the adsorbent were investigated by subjecting the data from time dependent adsorption to pseudo-first order, pseudo-second order kinetic and intra-particle diffusion models to describe the kinetics of the adsorption process. The mathematical expressions of these models (equations 4 – 7) are as presented in Table 1. All data were analyzed with nonlinear regression analysis method using a program written on MicroMath Originpro, 2022 software.

Table 1: Kinetic models for the adsorption studies of congo red dye

Name	Model
Pseudo-first order	$Q_t = Q_e(1 - e^{-k_1 t})$ <p style="text-align: right;">4</p> <p>Q_e and Q_t are the amounts (mg g⁻¹) of dye adsorbed per unit mass of adsorbent at equilibrium time and time t, respectively, while k_1 (min⁻¹) is the rate constant for the pseudo-first order kinetics</p>
Pseudo-second order	$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t}$ <p style="text-align: right;">5</p>

Elovich	<p>Q_e and Q_t are the amounts (mg) of dye adsorbed per unit mass of adsorbent at equilibrium time and time t, respectively, while k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant for the pseudo-second order kinetics</p> $Q_t = \frac{1}{\beta} \ln(\alpha\beta * t) \quad 6$ <p>where α (mg g^{-1}) is the initial adsorption rate constant and the parameter β ($\text{g mg}^{-1} \text{min}^{-1}$) is related to the extent of surface coverage and activation energy for chemisorptions</p>
Intraparticle diffusion	$Q_t = K_{id}t^{0.5} + C_i \quad 7$ <p>where K_{id} is the intraparticle diffusion rate constant ($\text{mg mg}^{-1} \text{min}^{-0.5}$), and C is a constant (mg mg^{-1}) which gives information about the thickness of boundary layer</p>

Adsorption equilibrium data were also subjected to the Langmuir, Freundlich, Tempkin Pyzhev, Dubinin - Radushkevich, Sips and Relich-peterson isotherms models (represented by equations 8 – 11). The isotherm parameters were obtained by the least square fit method as earlier mentioned. The mathematical expressions of these isotherm models (equations 10 – 13) are as presented in Table 2.

Table 2: Isotherm models applied in adsorption studies

Name	Model
Langmuir	$Q_{eq} = \frac{Q_{\max} b C_e}{1 + b C_e} \quad 8$ <p>Q_{eq} and Q_{\max} are the amounts (mg/g) of dye adsorbed per unit mass of adsorbent and maximum adsorption capacity at equilibrium, respectively, C_e is the equilibrium concentration of adsorbate, while b (L mg^{-1}) Langmuir constant.</p>
Freundlich	$Q_{eq} = K_F C_e^{1/n} \quad 9$ <p>K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$ is a rough estimation of adsorption capacity of the adsorbent, $1/n$ is the adsorption intensity.</p>
Tempkin	$Q_e = \frac{RT}{b_T} \ln a_T C_e \quad 10$

Dubinin–Radushkevich

R (J molK⁻¹) is the gas constant, T (K) is absolute temperature, a_T (mg L⁻¹) is the binding constant and b_T (L g⁻¹) is related to the heat of adsorption

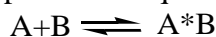
$$Q_e = Q_s e^{-\beta \varepsilon^2} \quad 11$$

Q_s (mg g⁻¹) is the saturation capacity, β (mol J)² is a constant relation to adsorption energy while ε is related to the mean free energy of adsorption and

$$\text{given } \varepsilon = RT * \ln \left(1 + \frac{1}{C_e} \right)$$

Thermodynamic parameters

The thermodynamic parameters, ΔG^o, ΔH^o and ΔS^o explain the feasibility, spontaneity and the nature of adsorbate-adsorbent interactions during the adsorption process (Adeogun et al., 2016). Their values were obtained from the temperature dependent equilibrium study by viewing the process at equilibrium using the notation below:



The equilibrium constant in term of the adsorbate (C_e), adsorbent dosage (m) and adsorbed quantity (Q_e) could be written as:

$$K = \frac{Q_e}{C_e * m} \quad (12)$$

$$\Delta G^o = -RT \ln K \quad (13)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (14)$$

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

The van't Hoff plot, (lnK_D versus 1/T) for the adsorption process gives the slope and intercept from which thermodynamic parameters were obtained.

RESULTS**SEM and EDAX analysis**

The SEM images of raw corn cobs and activated corn cobs (ACC) are shown in Fig 2. It was deduced that the ACC became compacted after adsorbed with congo red dye. Several large pores in a rod shape were shown on the surface as compared with raw cobs. The open pores on ACC indicated an effective activation process of the adsorbent which enhances adsorption of dye [25]. The EDX analysis (Fig.3) shown a high percentage of carbon in the ACC adsorbent which make it suitable and effective adsorbent.

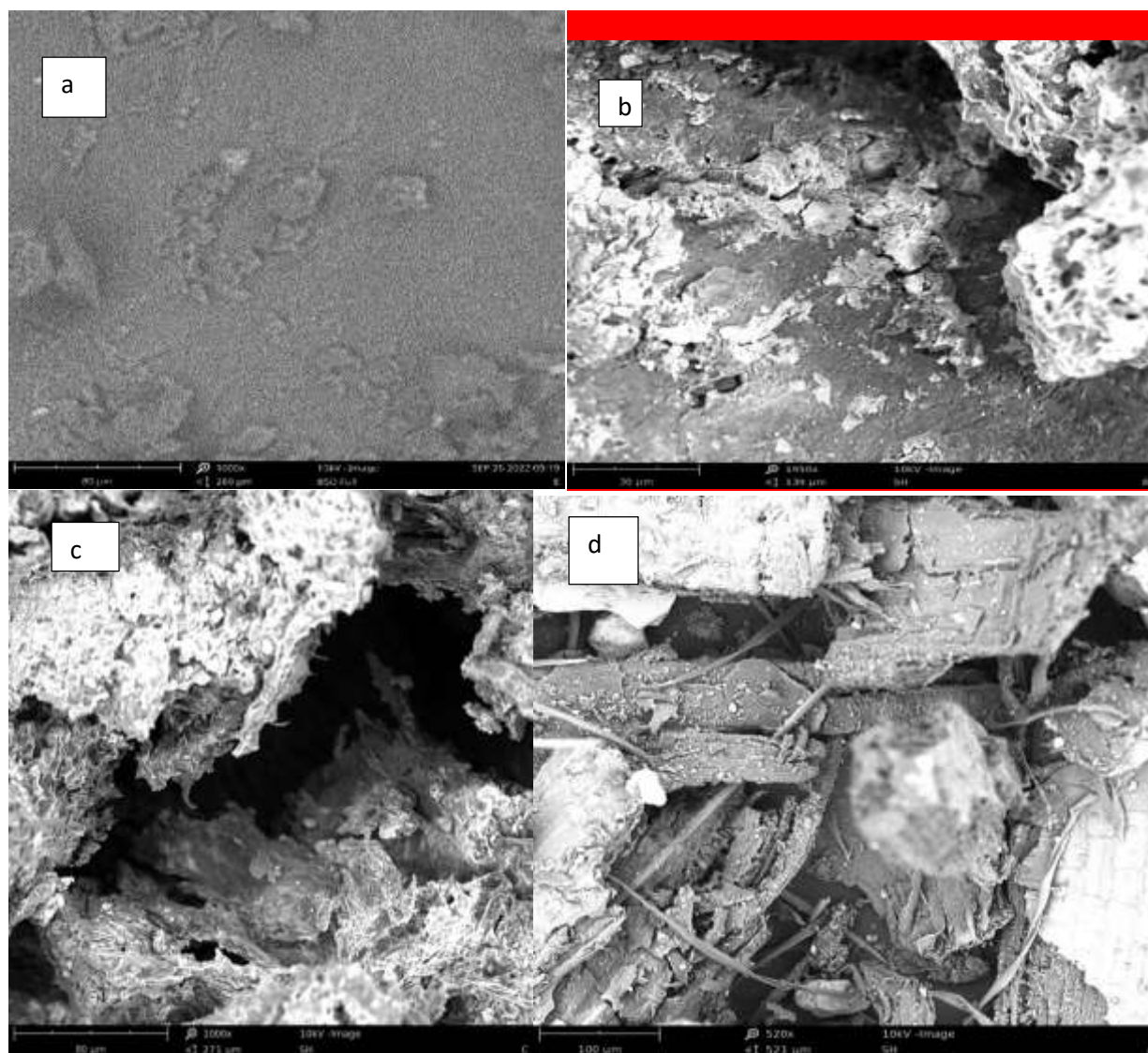


Figure 2: SEM analysis of activated corn cobs before and after the adsorption of Congo red dye (a) modified cobs (b) adsorbed with dye (c) adsorbed with dye at 50°C (d) raw corn cobs

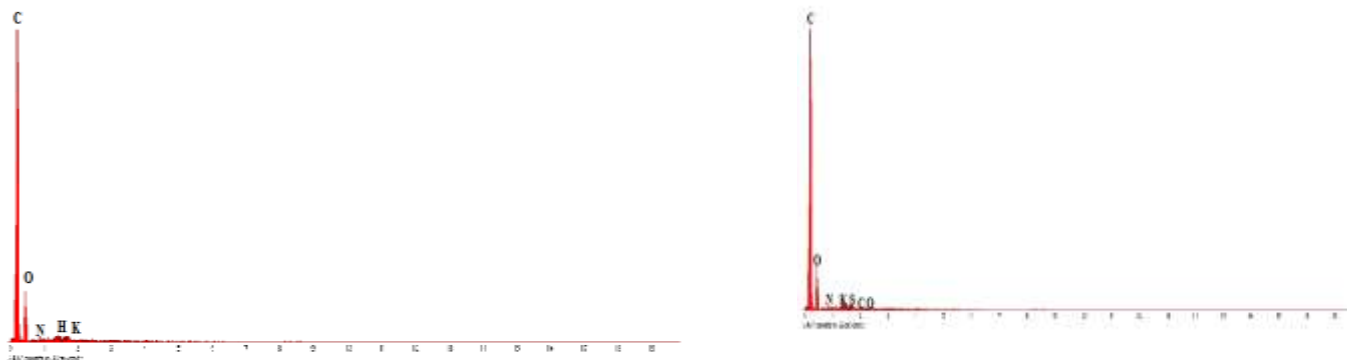


Figure 3: EDAX of ACC: (a) Modified corn cobs (b) adsorbed with CR dye.

Adsorbent dosage study

The adsorbent dosage increase at 0.05 – 1.0g proportionally increases its removal efficiency from 92.5 - 98.6 % as presented in Figure 4, which could be attributed to the increase in adsorption sites of the ACC adsorbent. [26]. The reduction of the removal efficiency noted on further increase in the adsorbent dosage resulted from particle interactions that collapsed the active sites of the adsorbent [27].

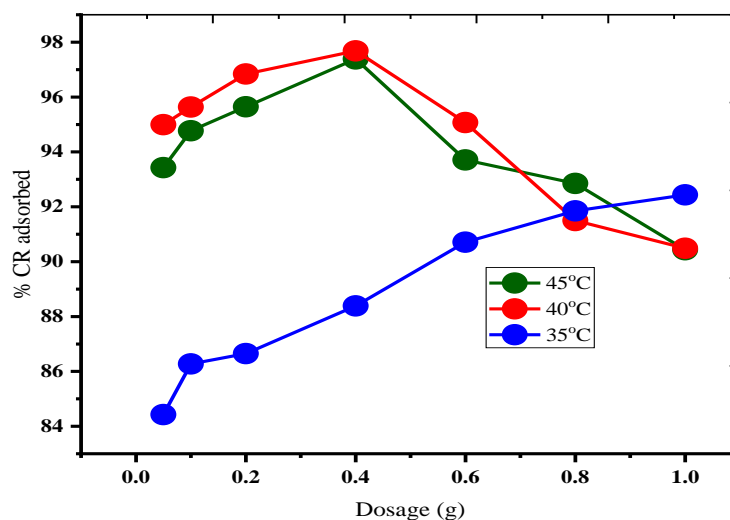


Figure 4: Adsorbent dosage against % removal of CR dye

Solution pH study of the adsorption of congo red dye

The removal efficiency of dye decreases as pH increases (Figure 6). pH affects the chemical properties of the dye solution, the adsorbent surface charge, as well as interactions in the media [28]. The maximum 92.45% removal efficiency was obtained at pH 4.8. The acidic pH values favoured the adsorption of congo red dye due to non-competition with the hydrogen ion on the available adsorption sites of the adsorbent.

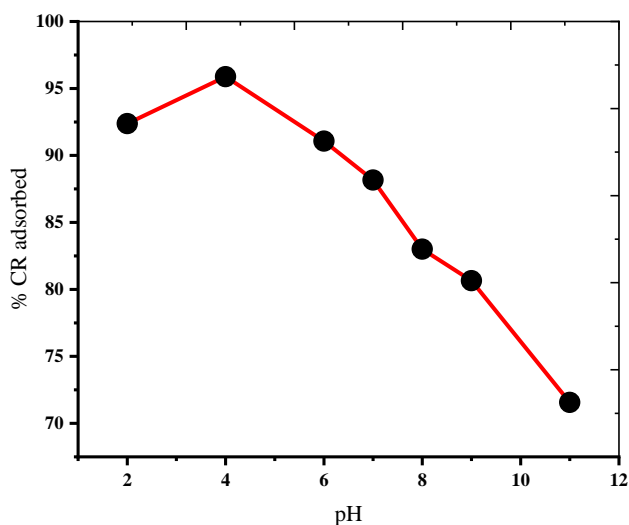


Fig. 5: The Plot of solution pH against CR % adsorbed

Adsorption Kinetics

Adsorption kinetics was characterized by mechanisms; chemical interactions between the adsorbent (ACC) and adsorbate (congo red dye), mass transfer of the adsorbate into and within the adsorbent or combination of these mechanisms, hence combination of models were required to elucidate the mechanism of adsorption [32, 39]. The pseudo first-order, pseudo second-order as well as Elovich and intra-particle kinetic models were used to examine the kinetics of adsorption data which are depicted Fig 6, 7, 8 and 9 while the parameters for these fits are presented in Tab.3.

By considering the values of the regression coefficients R^2 for the models, error function analyses and the closeness of the Q_e determined experimentally with the theoretical values showed that pseudo-second order kinetic model was much favoured, suggesting physical interactions between the adsorbent and adsorbate [30]. The Elovich kinetic model fit (Figure 9) agreed with the experimental data (Table 7) and showed that $R^2 > 0.90$, the values β_{el} indicate the available site for adsorption decreases with increase dye concentrations [34-36]. The positive values of these constants confirmed the model, hence Elovich model properly explained the initial kinetics of adsorption of the dye onto the adsorbent as previously reported in literature [31]. The high value

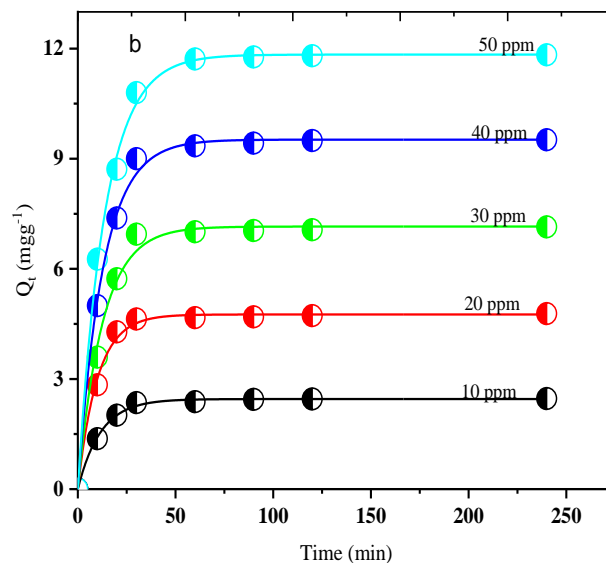
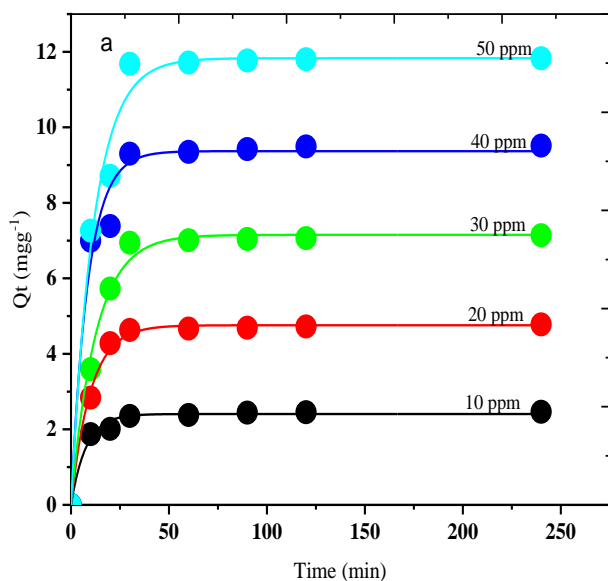
of C_2 observed showed that the boundary layer is thick and the rate of diffusion of the adsorbate across the cell wall of the adsorbent was very low, the larger the intercept, the greater the surface adsorption that contributes to the rate controlling step. The K_{id} values increase as the initial concentration of the dye increases. This could be attributed to the resistance of the surface boundary to the increased driving force with the concentration gradient as the dye molecules access the available sites in the composite. The values of the intercepts C_1 and C_2 obtained showed that the initial stage of adsorption was characterized by the intra-particle diffusion model.

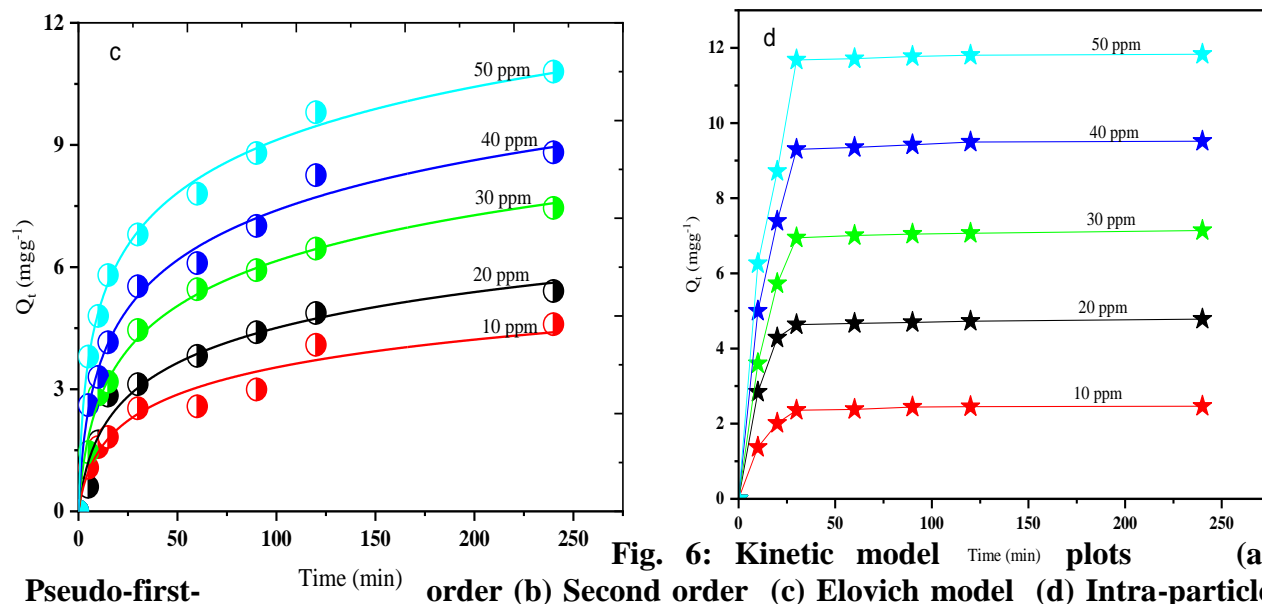
Table 3: Analysis of kinetic parameters

	C_0 (mg/L)	10	20	30	40	50
First order	Q_e (exp) (mg/g)	10.365	20.206	25.372	28.794	29.967
	Q_e (cal) (mg/g)	8.421	16.148	22.104	24.151	24.226
	k_1 (mins ⁻¹)	0.025	0.019	0.025	0.032	0.047
	R^2	0.998	0.998	0.999	0.998	0.999
	Adj. R^2	0.989	0.976	0.993	0.967	0.989
	% SSE	0.002	0.001	0.004	0.011	0.001
Second order	Q_e (cal) (mg/g)	10.224	20.163	26.783	28.512	28.411
	k_2	0.002	0.001	0.001	0.001	0.002
	R^2	0.991	0.997	0.998	0.998	0.999
	Adj. R^2	0.989	0.992	0.991	0.969	0.991
	%SSE	0.078	0.093	0.07	0.051	0.049
Elovich	α (mg/gmin ⁻¹)	0.541	0.899	1.523	2.111	3.403
	β_{el} (g/mg)	0.445	0.233	0.177	0.166	0.177
	R^2	0.993	0.997	0.996	0.996	0.996
	Adj. R^2	0.989	0.918	0.992	0.987	0.986
	% SSE	0.065	0.0875	0.092	0.061	0.054
Intra particle		1.182	1.893	3.108	4.425	5.919

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K_{id} ($\text{mg/g/g/min}^{1/2}$)	¹					
K_{id} ($\text{mg/g/g/min}^{1/2}$)	²	0.364	0.873	1.014	0.959	0.845
C_1 (mg/g)		0.3135	-0.4197	-0.486	-0.7075	0.6835
C_2 (mg/g)		3.256	3.68	7.847	11.163	14.02
R^2		0.953	0.966	0.978	0.985	0.981
Adj. R^2		0.887	0.899	0.911	0.897	0.958
% SSE		0.037	0.087	0.085	0.091	0.056





Pseudo-first-
diffusion

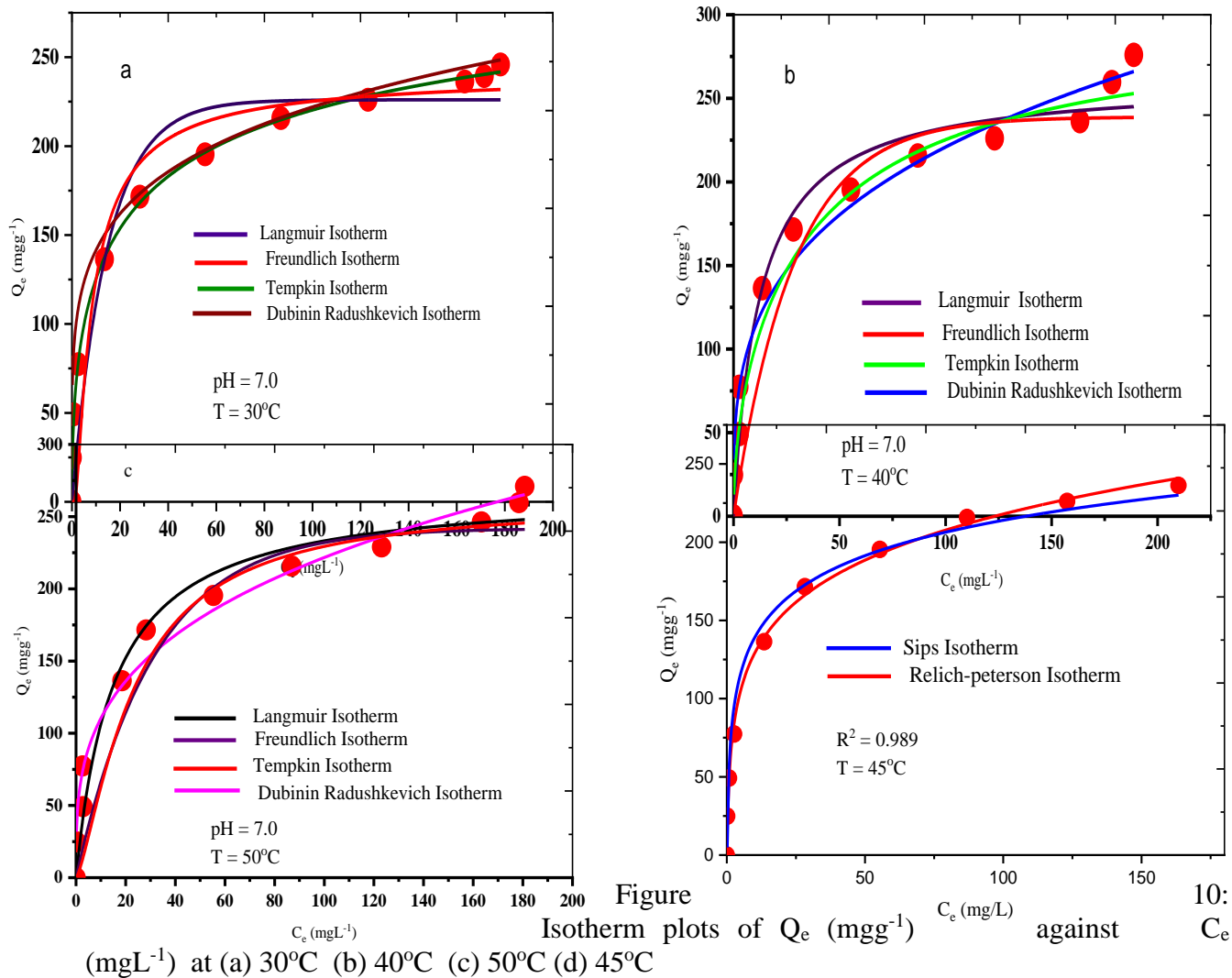
order (b) Second order (c) Elovich model (d) Intra-particle

Adsorption isotherm

Adsorption isotherms described the phenomenon governing the release or mobility of a substance from the aqueous media to a solid-phase at a constant temperature and pH, the interpretations of these information are critical to the overall improvement of adsorption mechanism pathways and effective design of adsorption system [32]. The adsorption isotherm models predicted to confirm the adsorption of congo red dye onto ACC are shown in Figure 10 - 12 and parameters (Table 8). The isotherm parameters revealed that the entire isotherms model investigated fit very well with the data at temperature 40°C and correlation coefficient R^2 values in the order of Langmuir > Freundlich > Tempkin > Sips > Relich-peterson > Dubinin-Radushkevich with maximum adsorption capacities (Q_{max}) of 84.81 mg g^{-1} . At temperature 30°C , Langmuir > Freundlich = Tempkin > Sips > Dubinin-Radushkevich > Relich-peterson and 65.75 mg g^{-1} . The R_L values is less than one, indicated a favourable adsorption. Freundlich parameters confirmed the heterogeneity nature of the surface of adsorbent, $1/n$ value of < 1 indicates a normal Langmuir isotherm, otherwise cooperative adsorption [33]. The Tempkin isotherm parameters and the R^2 values showed favourable fits for the dye, to imply that adsorption process is characterized by uniform distribution of binding energies. The mean free energies obtained for the adsorption of the dye is 1.65 kJ/mol , confirming the physisorption adsorption as suggested by the kinetic fit [34].

Table 8: Adsorption isotherms parameters at 30 and 40°C

Isotherms	Parameters	30°C	40°C
Langmuir	Q_{\max} (mg/g)	65.08	84.457
	R_L	0.168	0.099
	b (mg/L)	0.166	0.063
	R^2	0.997	0.996
	Adj. R^2	0.993	0.991
Freundlich	$KF(mg/g)(mg/L)^{-1/2}$	9.888	20.663
	$1/n$	0.456	0.351
	R^2	0.999	0.997
	Adj. R^2	0.998	0.996
Tempkin	α_T (L/g)	1.27	7.085
	b_T (J/mol)	231.9	231.2
	R^2	0.993	0.994
	Adj. R^2	0.991	0.989
Dubinin Radushkevich	Q (mg/g)	33.869	43.115
	$E(kJmol^{-1})$	0.539	1.596
	$(mol/J)^2$	113.2	194.8
	R^2	0.988	0.991
	Adj. R^2	0.986	0.987
Redlich- peterson	Q_0 (mg/g)	9.324	22.38
	K_R (mg/g)	1.651	0.289
	G	0.387	0.109
	R^2	0.983	0.989
	Adj. R^2	0.981	0.983
Sips	Q_s (mg/g)	42.359	84.87
	$K_s(mg/L)^{1/\beta_s}$	0.056	0.147
	B	0.867	0.615
	R^2	0.99	0.991
	Adj. R^2	0.988	0.982



Thermodynamic Analysis

The thermodynamic parameters, ΔG° , ΔH° and ΔS° explain the feasibility, spontaneity and the nature of adsorbate-adsorbent interactions during the adsorption process[38].The equilibrium constant in term of the adsorbate (C_e), adsorbent dosage (m) and adsorbed quantity (Q_e) could be written as:

$$K = \frac{Q_e}{C_e * m} \quad (25)$$

Where k is the equilibrium adsorption constant[39]

$$\Delta G = \Delta H - T\Delta S \quad (26)$$

T is the temperature in Kelvin, other parameters had already been discussed.

$$\Delta G = -RT \ln K \quad (27)$$

R is the gas constant and equal to 8.314 kJmol^{-1}

$$\ln k = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (28)$$

The van't Hoff plot, ($\ln K_D$ versus $1/T$) for the adsorption process gives the slope and intercept from which thermodynamic parameters were obtained.

$$C = \frac{\Delta S}{R} \quad (29)$$

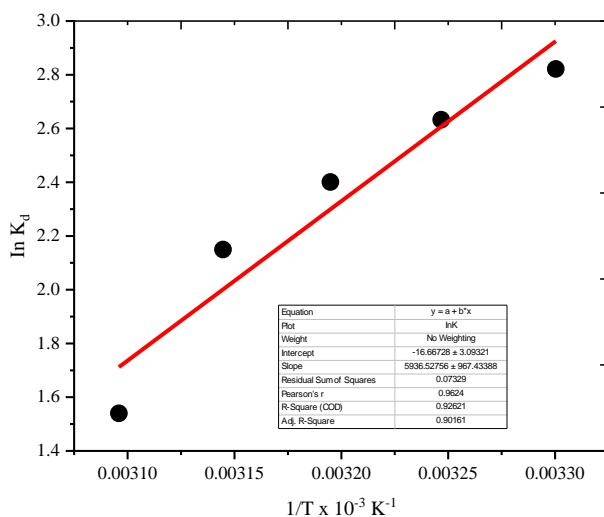
$$m = \frac{\Delta H}{R} \quad (30)$$

The van't Hoff plot (Fig.7) for the adsorption of CR dye were obtained using equations above as previously described [2] and the thermodynamic parameters (Table 6) depicts negative enthalpy (ΔH) and positive entropy change (ΔS) of $-62.48 \text{ kJmol}^{-1}$ and $145.27 \text{ Jmol}^{-1}\text{K}$ respectively. This illustrate exothermic adsorption process and revealed that heat absorbed when dye ions transported to the active sites of the adsorbent. The positive value of ΔS indicates an increase in the degree of randomness of the system with changes in the hydration of the adsorbed dye ions [2].The negative values of Gibb's energy indicated the spontaneity of the adsorption process and the decrease of the values with increasing temperature indicated more efficient adsorption at higher temperatures.

Table 12: Thermodynamic Parameters for the adsorption of dye.

Temp (K)	$\ln K_d$	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	R^2
308.15	1.282	-3.431	-62.48	145.27	0.985
313.15	1.705	-4.317			
318.15	1.785	-5.204			
323.15	2.404	-6.091			

$\ln k$ = equilibrium constant, ΔG = Change in Gibb's free energy, ΔH = Enthalpy change, ΔS = Entropy change, R^2 = Correlation coefficient.

**Figure 12: Van't Hoff plot of $\ln K$ against $1/T$.**

CONCLUSION

Activated carbon derived from corn cobs biomass was prepared and applied to adsorb congo red dye from aqueous solution. The treatment adopted batch adsorption method to consider some parameters; contact time, initial dye concentration, solution pH, adsorbent dosage and temperature. The kinetics of adsorption of the dye was best explained with pseudo second-order kinetic while Langmuir isotherm model fitted the equilibrium data with monolayer adsorption capacity of 84.53 mg/g. The models showed that the predicted models are suitable for the prediction of the adsorption process with $R^2 = 0.998$. The thermodynamic parameters proved that the adsorption process was feasible, spontaneous, exothermic and random in nature.

REFERENCE

- [1] El Qada E.N., S. J. Allen, and G. M. Walker, "Adsorption of basic dyes from aqueous solution onto activated carbons," *Chem. Eng. J.*, vol. 135, no. 3, pp. 174–184, 2008.
- [2] Giraldo L. and J. C. Moreno-Pirajan, "Synthesis of activated carbon mesoporous from coffee waste and its application in adsorption zinc and mercury ions from aqueous solution," *E-Journal Chem.*, vol. 9, no. 2, pp. 938–948, 2012.
- [3] Park H. and W. Choi, "Visible light and Fe (III) -mediated degradation of Acid Orange 7 in the absence of H₂O₂," *J. Photochem. Photobiol. A Chem.*, vol. 159, pp. 241–247, 2003.
- [4] Muthuraman G., T. T. Teng, C. P. Leh, and I. Norli, "Extraction and recovery of methylene blue from industrial wastewater using benzoic acid as an extractant," *J. Hazard. Mater.*, vol. 163, pp. 363–369, 2009.
- [5] Vadivelan V. and K. Vasanth Kumar, "Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk," *J. Colloid Interface Sci.*, vol. 286, no. 1, pp. 90–100, 2005.
- [6] Garcia M., I. Garmendia, and J. Garcia, "Influence of Natural Fiber Type in Eco-Composites," *J. Appl. Polym. Sci.*, vol. 107, pp. 2994–3004, 2008.
- [7] Wang W., M. Sain, and P. A. Cooper, "Study of moisture absorption in natural fiber plastic composites," *Compos. Sci. Technol.*, vol. 66, pp. 379–386, 2006.
- [8] Fungaro D.A., M. Bruno, and L. C. Grosche, "Adsorption and kinetic studies of methylene blue on zeolite synthesized from fly ash," *Desalin. Water Treat.*, vol. 2, no. 1–3, pp. 231–239, 2009.
- [9] Adeogun A.I., J. A. Akande, M. A. Idowu, and S. O. Kareem, "Magnetic tuned sorghum husk biosorbent for effective removal of cationic dyes from aqueous solution: isotherm, kinetics, thermodynamics and optimization studies," *Appl. Water Sci.*, vol. 9, no. 7, pp. 1–17, 2019.
- [10] Porter J.F., G. McKay, and K. H. Choy, "The prediction of sorption from a binary mixture of acidic dyes using single- and mixed-isotherm variants of the ideal adsorbed solute theory," *Chem. Eng. Sci.*, vol. 54, no. 24, pp. 5863–5885, 1999.
- [11] Kapoor A. and R. T. Yang, "Correlation of equilibrium adsorption data of condensable vapours on porous adsorbents," *Gas Sep. Purif.*, vol. 3, no. 4, pp. 187–192, 1989.
- [12] Aksu S.T.Z., U. Acikel, E. Kabasakal, "Equilibrium modelling of individual and simultaneous biosorption of chromium (VI) and nickel (II) onto dried activated sludge," *Water Res.*, vol. 36, pp. 3063–3073, 2002.
- [13] Ho R., *General Linear Model: Repeated Measures Analysis: In: Ho R. Handbook of Univariate and Multivariate Data Analysis and Interpretation with SPSS*. 2006.
- [14] Kumar A., B. Prasad, and I. M. Mishra, "Adsorptive removal of acrylonitrile by commercial grade activated carbon: Kinetics, equilibrium and thermodynamics," *J. Hazard. Mater.*, vol. 152, no. 2, pp. 589–600, 2008.

- [15] Akinhanmi F.T., A. I. Adeogun, and A. Adegbuyi, "Removal of Cu²⁺ from aqueous solution by adsorption onto quail eggshell: Kinetic and isothermal studies," *J. Environ. Biotechnol. Res.*, vol. 5, no. 1, pp. 1–9, 2016.
- [16] Wang S., L. Li, H. Wu, and Z. H. Zhu, "Unburned carbon as a low-cost adsorbent for treatment of methylene blue-containing wastewater," *J. Colloid Interface Sci.*, vol. 292, pp. 336–343, 2005.
- [17] Dakhil I.H., "A comparative Study for Removal of Dyes from Textile Effluents by Low Cost Adsorbents To cite this article :," *Mesopotamia Environ. J.*, vol. 9, pp. 1–9, 2016.
- [18] Shahwan T., "Lagergren equation: Can maximum loading of sorption replace equilibrium loading?," *Chem. Eng. Res. Des.*, vol. 95, pp. 172–176, 2015.
- [19] Ho Y.S., J. C. Y. Ng, and G. McKay, "Kinetics of pollutant sorption by biosorbents: Review," *Sep. Purif. Methods*, vol. 29, no. 2, pp. 189–232, 2000.
- [20] Elovich S. and OG Larionov, "Theory of adsorption from nonelectrolyte solutions on solid adsorbents," *Bull. Acad. Sci. USSR Chem. Sci.*, vol. 11, pp. 198–203, 1962.
- [21] Halsey G.D., "On Multilayer Adsorption," *J. Am. Soc.*, vol. 74, no. 4, pp. 1082–1083, 1952.
- [22] Zhao M., Z. Tang, and P. Liu, "Removal of methylene blue from aqueous solution with silica nano-sheets derived from vermiculite," *J. Hazard. Mater.*, vol. 158, no. 1, pp. 43–51, 2008.
- [23] Ebrahimi A., E. Pajootan, M. Arami, and H. Bahrami, "Optimization, kinetics, equilibrium, and thermodynamic investigation of cationic dye adsorption on the fish bone," *Desalin. Water Treat.*, vol. 53, no. 8, pp. 2249–2259, 2015.
- [24] Khandanlou R., M. Bin Ahmad, K. Shameli, and K. Kalantari, "Synthesis and Characterization of Rice Straw/Fe₃O₄ Nanocomposites by a Quick Precipitation Method," *Molecules*, vol. 18, pp. 6597–6607, 2013.
- [25] Asif Tahir M., H. N. Bhatti, and M. Iqbal, "Solar Red and Brittle Blue direct dyes adsorption onto Eucalyptus angophoroides bark: Equilibrium, kinetics and thermodynamic studies," *J. Environ. Chem. Eng.*, vol. 4, no. 2, pp. 2431–2439, 2016.
- [26] Hoseinzadeh E., M. R. Samarghandi, G. McKay, N. Rahimi, and J. Jafari, "Removal of acid dyes from aqueous solution using potato peel waste biomass: A kinetic and equilibrium study," *Desalin. Water Treat.*, vol. 52, no. 25–27, pp. 4999–5006, 2014.
- [27] Kakavandi B., A. Takdastan, N. Jaafarzadeh, M. Azizi, A. Mirzaei, and A. Azari, "Application of Fe₃O₄@C catalyzing heterogeneous UV-Fenton system for tetracycline removal with a focus on optimization by a response surface method," *J. Photochem. Photobiol. A Chem.*, vol. 314, pp. 178–188, 2016.
- [28] Ahsaine H.A., M. Zbair, Z. Anfar, Y. Naciri, El haouti R, N. El Alem, M. Ezahri, "Cationic dyes adsorption onto high surface area ' almond shell ' activated carbon : Kinetics , equilibrium isotherms and surface statistical modeling," *Mater. Today Chem.*, vol. 8, pp. 121–132, 2018.
- [29] Bestani B., N. Benderdouche, B. Benstaali, M. Belhakem, and A. Addou, "Bioresource Technology Methylene blue and iodine adsorption onto an activated desert plant," *Bioresour. Technol.*, vol. 99, pp. 8441–8444, 2008.

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- [30] Akpomie K.G., O. M. Fayomi, C. C. Ezeofor, R. Sha’Ato, and W. E. Van Zyl, “Insights into the use of metal complexes of thiourea derivatives as highly efficient adsorbents for ciprofloxacin from contaminated water,” *Trans. R. Soc. South Africa*, vol. 74, no. 2, pp. 180–188, 2019.
- [31] Vassileva P., A. Detcheva, I. Uzunov, and S. Uzunova, “Removal of Metal Ions from Aqueous Solutions Using Pyrolyzed Rice Husks: Adsorption Kinetics and Equilibria,” *Chem. Eng. Commun.*, vol. 200, no. 12, pp. 1578–1599, 2013.
- [32] Ayawei N., A. N. Ebelegi, and D. Wankasi, “Modelling and Interpretation of Adsorption Isotherms,” *J. Chem.*, vol. 2017, 2017.
- [33] Pathania D., S. Sharma, and P. Singh, “Removal of methylene blue by adsorption onto activated carbon developed from Ficus carica bast,” *Arab. J. Chem.*, vol. 10, pp. S1445–S1451, 2017.
- [34] Ozdes D., C. Duran, H. B. Senturk, H. Avan, and B. Bicer, “Kinetics, thermodynamics, and equilibrium evaluation of adsorptive removal of methylene blue onto natural illitic clay mineral,” *Desalin. Water Treat.*, vol. 52, no. 1–3, pp. 208–218, 2014.
- [35] Dhawane S.H., T. Kumar, and G. Halder, “Biodiesel synthesis from Hevea brasiliensis oil employing carbon supported heterogeneous catalyst: Optimization by Taguchi method,” *Renew. Energy*, vol. 89, pp. 506–514, 2016.
- [36] Inam E.I., U. J. Etim, E. G. Akpabio, and S. A. Umoren, “Simultaneous adsorption of lead (II) and 3,7-Bis(dimethylamino)-phenothiazin-5-ium chloride from aqueous solution by activated carbon prepared from plantain peels,” *Desalin. Water Treat.*, vol. 57, no. 14, pp. 6540–6553, 2016.
- [37] Mall I.D., V. C. Srivastava, N. K. Agarwal, and I. M. Mishra, “Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 264, no. 1–3, pp. 17–28, 2005.
- [38] Mohammadi N., H. Khani, V. K. Gupta, E. Amereh, and S. Agarwal, “Adsorption process of methyl orange dye onto mesoporous carbon material-kinetic and thermodynamic studies,” *J. Colloid Interface Sci.*, vol. 362, no. 2, pp. 457–462, 2011.
- [39] Greluk M. and Z. Hubicki, “Kinetics, isotherm and thermodynamic studies of Reactive Black 5 removal by acid acrylic resins,” *Chem. Eng. J.*, vol. 162, no. 3, pp. 919–926, 2010.