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Batch Adsorption Of Methyl Green Dye using Activated Carbon Derived from Corn Cobs

James Akande Asamu[1*], Adeogun AI[2], Ogunniran KO[3]

[1]Department of Chemistry and Biochemistry , Caleb University, Imota Lagos, Nigeria

[2]Department of Chemistry, Federal University of Agriculture, Makurdi, Nigeria

Research Article

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***For Correspondence:**
James Akande Asamu, Department of Chemistry and Biochemistry, Caleb University, Imota Lagos, Nigeria

E-mail:
james.akande@calebuniversity.edu.ng

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ABSTRACT

Dyes released 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 such as Fourier Transform Infrared (FTIR), Energy Dispersive X-ray (EDX) spectroscopy and Scanning Electron Microscopy (SEM). The absorbance of the dye solution was monitored at 620 nm with UV-Visible spectrophotometer. FTIR analysis showed the vibration frequency for C-H, O-H, C=O and C-O stretches at 2950, 3400, 1710, and 1150 cm^{-1} respectively. 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 and Elovich kinetic models for the sorption of methyl green onto ACC was examined. The equilibrium data were subjected to Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich 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 85.83 mgg^{-1}. Thermodynamic adsorption processes showed the spontaneous, endothermic and randomness of the

systems with free energy change less than zero, enthalpy change (ΔH) of 62.47 kJmol^{-1}and entropy change (Δ S) of 125.37 Jmol^{-1}K^{-1}.

Keywords: Thermodynamic; Adsorption; 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 × 105 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, ozonation, adsorption etc, have been adopted to dyes removal in wastewater [4,5]. 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 fibre comes from stalks, leaves and seeds, such as kenaf, sisal, flax, sorghum, wheat and rice. Natural fibre have been found to be advantageous over the synthetic ones in terms of biodegradability, flammability and non-toxicity. 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 [6-9].Therefore, this work aimed at investigating the adsorption of methyl green dye from the aqueous solutions using Activated Corn Cobs (ACC) as adsorbent. The kinetic, isotherm and thermodynamic parameters of the adsorption were considered in a batch process.

MATERIALS AND METHODS

Materials

Methyl green dye were obtained from Merck laboratory, India. Hydrochloric Acid (HCl), Urea (CH_4N_2O) 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 groundnut pods

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 600µm and preserved in an air-tight polythene bag to prevent from moisture and made ready for the analysis. The sieved cobs (50 g) were suspended in 100 ml of 0.1M KOH, 20 ml of 2M urea solution was added as a stabilizer and stirred continuously for 1 hr 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 at and kept in an air tight container.

Preparation of adsorbate

Methyl green 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.

$C_1V_1=C_2V_2$ ..... (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:

..... (2)

..... (3)

Where Co, Ct and Ce 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 methyl green 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 analysed with nonlinear regression analysis method using a program written on MicroMath Originpro, 2022 software (Table 1).

Table 1. Kinetic models for the adsorption studies of methyl green dye.

Name	Model
Pseudo-first order	$Q_t \quad Q_e(1 \quad e^{k_1 t})$ .....4 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
Pseudo-second order	.....5 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(g mg^{-1} min^{-1}) is the rate constant for the pseudo-second order kinetics
Elovich	.....6 where α (mg g^{-1}) is the initial adsorption rate constant and the parameter β (g mg^{-1} min^{-1}) is related to the extent of surface coverage and activation energy for chemisorptions
Intraparticle diffusion	.....7 where K_{id} is the intraparticle diffusion rate constant (mg mg^{-1} $min^{-0.5}$), and C is a constant (mg mg^{-1}) which gives information about the thickness of boundary layer

Adsorption equilibrium data were also subjected to the Langmuir (1916), Freundlich (1906), Tempkin and Pyzhev (1940), and Dubinin and Radushkevich, (1947) 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 for the adsorption of studies of Crystal Violet (CV) and Methylene Blue (MB).

Name	Model
Langmuir	.....8 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.
Freundlich	.....9 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.
Tempkin	.....10 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
Dubinin–Radushkevich	.....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 given

Thermodynamic parameters

The thermodynamic parameters, Δ G°, Δ H° and Δ S° explain the feasibility, spontaneity and the nature of adsorbate-adsorbent interactions during the adsorption process [10]. Their values were obtained from the temperature dependent equilibrium study by viewing the process at equilibrium using the notation below:

..... (12)

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

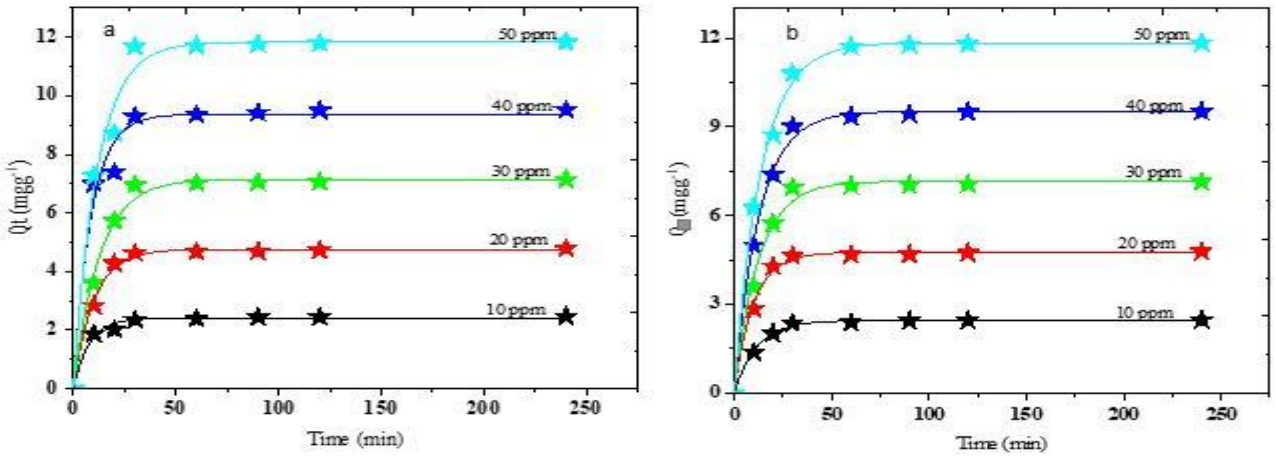
..... (13)

$'G^{o}$ RT ln K ..... (14)

..... (15) .....

..... (16)

Figure 8. Kinetic model plots. (A) Pseudo-first-order; (B) Second order; (C) Elovich model; (D) Intra-particle diffusion. Note:



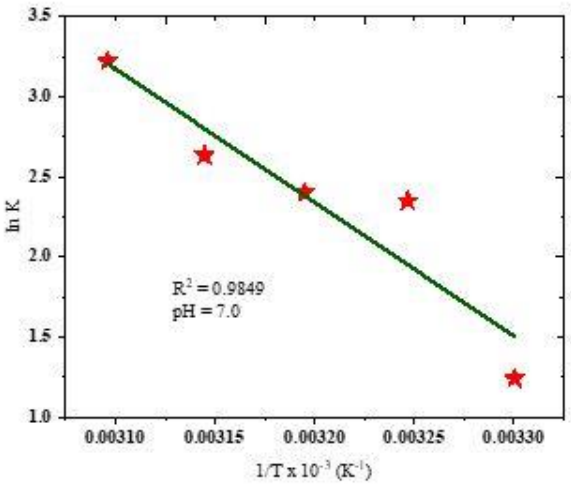
Adsorption isotherm

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 [19]. The adsorption isotherm models predicted to confirm the adsorption of methyl green dye onto ACC are shown in Figure 9 and parameters (Table 4). 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>Dubinin-Radushkevich, with maximum adsorption capacities (Q_{max}) of 85.83 mgg^{-1}. At temperature 30 °C, Langmuir>Freudlich=Tempkin>Dubinin-Radushkevich and 56.75 mgg^{-1}.The RL 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 [25]. The Tempkin isotherm parameters and the R^2 values showed favourable fits for the dyes, 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 1.45 kJ/mol, confirming the physisorption adsorption as suggested by the kinetic fit (Table 4) (Figure 9) [13].

Adsorption thermodynamic study

The Van't Hoff plot for the adsorption of methyl green dye using ACC and the thermodynamic parameters showing enthalpy change (Δ H) and entropy change (Δ S) had positive values of 62.48 KJmol^{-1} and 135.27Jmol^{-1}K respectively, hence, endothermic adsorption process and this indicate that some amount of heat was consumed to transfer dye ions from aqueous solution to the active site of ACC adsorbent. The positive value of Δ S illustrate an increase in the degree of randomness of the system with changes in the hydration of the adsorbed dye ions [26].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 (Figure 10).

Figure 10. Van't Hoff plot of lnK against 1/T.



Thermodynamic analysis

The thermodynamic parameters, ΔGo, ΔHo and ΔSo explain the feasibility, spontaneity and the nature of adsorbate-adsorbent interactions during the adsorption process [11,27-33].The equilibrium constant in term of the adsorbate (C_e), adsorbent dosage (m) and adsorbed quantity (Q_e) could be written as:

..... (17)

Where k is the equilibrium adsorption constant [20].

$$'G \quad 'H \quad T'S$$ ..... (18)

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

$$'G \quad RT\ln K$$ ..... (19)

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

$$\ln k \quad \frac{'S}{R} \quad \frac{'H}{RT}$$ ..... (20)

$$C \quad \frac{'S}{R}$$ ..... 21)

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