Kinetic and Equilibrium Studies of Congo Red Adsorption on Adsorbent from Bambara Groundnut Hulls

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Abstract

Kinetics and equilibrium isotherms of Congo red adsorption on adsorbent derived from Bambara groundnut (Vigna subterranea (L) Verdc.) hulls were investigated in a series of batch experiments. Using a one-factor-at-a-time (OFAT) approach, optimum removal efficiency of Congo red by the adsorbent occurred at pH of 6.0 at lower adsorbent dosage, attaining a peak value of 72.79% after 4 hours of agitating time. Findings also revealed that, among the kinetic and isotherm models tested, the experimental data fitted best to pseudo-second order model (R^2 = 0.957) and Freundlich adsorption isotherm (R^2 = 0.981). This suggests that Congo red adsorption on Bambara groundnut hulls involves chemisorption and the process is indicative of cooperative adsorption. The study demonstrates that Bambara groundnut hulls can serve as an alternative low-cost adsorbent for removing Congo red from industrial wastewater.

Keywords: Adsorption, Congo red, Isotherm, Kinetics, *Vigna subterranea*

Abbreviations and Symbols

A_T = Tempkin isotherm equilibrium binding constant (L/g)
b = Langmuir isotherm constant (dm^3/mg)
b_T = Tempkin isotherm constant
C_i = adsorbate initial concentration (mg/L)
C_e = equilibrium concentration of adsorbate (mg/L)
C_t = residual concentration of adsorbate at time t (mg/L)
k_{int} = intraparticle diffusion rate constant ($mg\ g^{-1} min^{-0.5}$)
k_1 = pseudo-first order rate constant (min^{-1})
k_2 = pseudo-second order rate constant ($g\ mg^{-1}\ min^{-1}$)
K_F = Freundlich isotherm constant (mg/g).(dm^3/g)^n
m = mass of the adsorbent (g)
q_t = amount of adsorbate sorbed on the adsorbent at any time t (mg/g)
q_e = amount of adsorbate sorbed on the adsorbent at equilibrium (mg/g)
q_{max} = maximum monolayer coverage capacities (mg/g)
R = universal gas constant (J/mol.K)
t = time of adsorption (hours)
T = temperature (K)
V = volume of the adsorbate (L)

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1.0 Introduction

In recent time, the magnitude of contamination of aquatic environment by synthetic dyes has captured the attention of many scientists and the general public. This is partly due to the realization that contamination of aquatic environment by dyes causes reduction in the growth of algae due to obstruction of light required for photosynthesis, which subsequently leads to ecological imbalance in the aquatic ecosystem [1]. Moreover, exposure of human being to synthetic dyes and their metabolic products can induce cytotoxic, genotoxic, mutagenic and carcinogenic effects [2]. Congo red (Fig. 1) is a secondary diazo dye that is used in textile, paper, and leather industries. It is a water-soluble dye and can be used as a pH indicator due to its color change from blue to red at pH 3.0 – 5.2. Besides serving as an indicator, Congo red has also been shown to have certain histological uses, especially as a cytoplasm and erythrocyte stain [3]. It is currently being used to stain a variety of other biological tissue constituents, including cellulose, amyloid and elastic fibers [4]. As a result of enormous utilization of Congo red, substantial amount of this dye is released into the environment during production, usage and disposal.

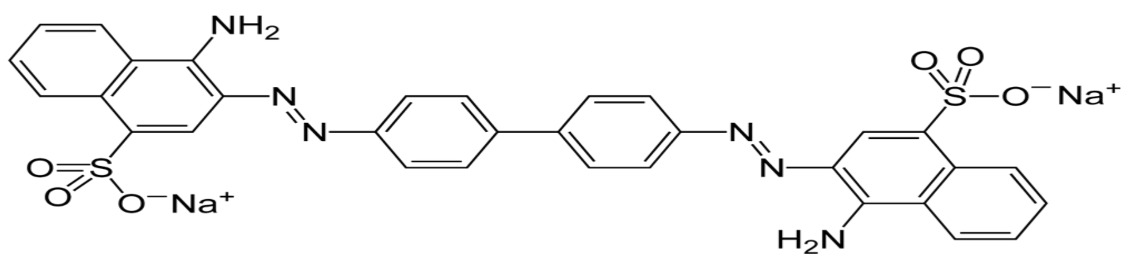

Fig. 1: Structural formula of Congo red

Due to the deleterious effects of dyes on human being and aquatic ecosystem, approaches such as biodegradation [5-8], phytoremediation [9], photocatalytic degradation [10, 11], adsorption [12-17] and advanced oxidation process [18] have been employed for the removal or degradation of Congo red in aqueous solutions. Among the environmental remediation techniques, adsorption is the most widely used because it does not leave toxic residue behind in the treated water. Although adsorption by activated carbon is very effective in removing dyes from contaminated water, the cost of activated carbon and the difficulty associated with its regeneration impose a serious restriction on its use as adsorbent [19, 20]. In view of this restriction, efforts are being made globally to invent alternative low-cost adsorbents from agricultural wastes [21, 22]. The use of agricultural solid wastes from cheap and readily available sources as precursors for adsorbents provides a two-fold advantage to solving environmental pollution problem. Firstly, the amount of waste materials could be partly reduced and secondly, the low-cost adsorbent would reduce the treatment of wastewaters to a reasonable cost [23].

Bambara groundnut, a plant known scientifically as *Vigna subterranea*, is a member of the *Fabaceae* family and it originated from West Africa [24]. In Nigeria, the plant is known locally as *Gurjiya* in Hausa, *Ngangala* in Kanuri, *Okpa* in Igbo and *Epa-Roro* in Yoruba. In Africa, Bambara groundnut is regarded as the third most important crop after peanuts (*Arachis hypogeal*) and cowpeas (*Vigna unguiculata*). It is cultivated mainly because of its high nutritional value, drought tolerance and its ability to grow in soils considered insufficiently fertile for cultivation of peanuts and cowpeas [24]. Although low cost adsorbents derived from various agricultural waste materials have been investigated for their potential use in removing Congo red from aqueous solutions, review of available literature reveals that no investigation has been conducted on Congo red removal by adsorption onto Bambara groundnut hulls. In spite of its large scale production and the huge abundance of its hulls in Nigeria and other West African countries, efficacy of low-cost adsorbent derived from Bambara groundnut hulls has only been demonstrated for the removal of atrazine [25] and copper (II) ions [26]. It is against this background that the present study set out to investigate the kinetics and equilibrium isotherms of Congo red removal from aqueous solution by adsorption onto adsorbent derived from Bambara groundnut hulls.

2.0 Materials and Methods

2.1 Collection and Preparation of Adsorbent

Fresh Bambara groundnuts (*Vigna subterranea*) were harvested from farms in Darazo, Bauchi State, Nigeria. The hulls obtained, after removing the seeds from the pods, were thoroughly washed with water to remove dust and other impurities. These hulls were then air-dried and oven-dried at 80 ^{0}C to constant mass in the laboratory as described elsewhere [27]. The dried hulls were then pulverized and sieved into fine particles as previously described [28]. The final product was stored in a clean, air-tight container for further use as adsorbent in subsequent batch experiments.

2.2 Preparation of Reagents

Analytical grade reagents were used to prepare stock solutions containing 1000 mg/L Congo red, 0.1 mol/L HCl and 0.1 mol/L NaOH by dissolving appropriate amount of each reagent in doubly distilled water and the resulting solutions diluted to volume in 1000 cm^3 volumetric flasks using standard procedure [29]. These standard solutions were later used in subsequent batch experiments.

2.3 Effects of Operating Variables on Removal Efficiency

The effects of initial solution pH (in the range of 2.0 to 12.0), adsorbent dose (in the range of 0.5 to 3.0g) and contact time (in the range of 0.5 to 8.0 hours) on the removal efficiency of Congo red from aqueous solutions were investigated using a one-factor-at-a-time (OFAT) approach [30]. This approach consists of selecting a baseline set of levels for each factor (pH = 2.0; adsorbent dose = 1.0 g; contact time = 3 hours were selected as baseline set in this study), and then successively varying each factor over its range with the other factors held constant at the baseline level. For each treatment combination, selected amount of adsorbent was added to 50 cm^3 of dye solution containing 50 mg/L Congo red in 250 cm^3 Erlenmeyer flask. The flasks were then agitated at 250 rpm for selected periods of time using WSZ series Orbital Shaker. The content of each flask was filtered and the residual concentrations of Congo red in the flasks were determined at 495 nm using UNICO UV-2100 Spectrophotometer (UNICO Instrument Co., Ltd, Shanghai, China). The removal efficiency of Congo red (expressed as % removal) was then calculated using equation (1). Optimum condition was selected for each operating factor by constructing a graph that indicates how the removal efficiencies are affected by varying the factor with all other factors held constant.

$$\% \text{ Removal} = \frac{C_i - C_e}{C_i} \text{ x } 100\% \quad (1)$$

2.4 Batch Experiment for Kinetic Study

Sorption kinetic study was carried out by adding 1.0 g of adsorbent to eight 250 cm^3 Erlenmeyer flasks containing 50 cm^3 of dye solutions. The concentration of Congo red in each flask was maintained at a value of 50 mg/L while the pH of each solution was adjusted to an optimum value of 6.0. The flasks were then agitated at ambient temperature (28 ^{0}C) for specific periods of time (0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0 and 6.0 hours) using WSZ series Orbital Shaker at 250 rpm. The content of each flask was filtered and the residual concentrations of Congo red in these filtrates were determined at 495 nm using UNICO UV-2100 Spectrophotometer (UNICO Instrument Co., Ltd, Shanghai, China). The amount of Congo red adsorbed onto the adsorbent at various time intervals was calculated using equation (2). This experiment was replicated and the fitness of the average data obtained was tested using intraparticle diffusion model (equation 3), pseudo-first order model (equation 4) and pseudo-second order model (equation 5).

$$q_t = \frac{V}{m}(C_i - C_t) \quad (2)$$

$$q_t = k_{int} t^{1/2} \quad (3)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (4)$$

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

2.5 Batch Experiment for Equilibrium Study

Sorption isotherm study was carried out by adding 1.0 g of adsorbent to eight 250 cm^3 Erlenmeyer flasks containing 50 cm^3 of dye solutions of various concentrations of Congo red (25, 50, 75, 100, 125, 150, 175 and 200 mg/L). The content of each flask was agitated at ambient temperature (28 ^{0}C) for 6 hours using WSZ series Orbital Shaker at 250 rpm. The pH values of all solutions were maintained at the optimum value of 6.0. The content of each flask was filtered and the equilibrium concentrations of residual Congo red in these filtrates determined at 495 nm using UNICO UV-2100 Spectrophotometer (UNICO Instrument Co., Ltd, Shanghai, China). The amount of Congo red adsorbed onto the adsorbent at equilibrium was calculated using equation (6). This experiment was replicated and the fitness of the average data obtained was tested using Langmuir adsorption isotherm (equation 7), Freundlich adsorption isotherm (equation 8) and Tempkin adsorption isotherm (equation 9).

$$q_e = \frac{V}{m}(C_i - C_e) \quad (6)$$

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \quad (7)$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad (8)$$

$$q_e = \frac{RT}{b_T}\ln A_T + \frac{RT}{b_T}\ln C_e \quad (9)$$

3.0 Results and Discussion

3.1 Optimum Operating Variables

The effects of initial solution pH, adsorbent dosage and contact time on the removal efficiency of Congo red by adsorbent derived from Bambara groundnut hulls are presented in Figs. 2, 3 and 4 respectively. Maximum removal efficiency of 61.39% was observed for Congo red adsorption at a pH value of 6.0 and at lower adsorbent dosage; and this value decreases gradually as the mass of added adsorbent increases. The removal efficiency of Congo red increases gradually from 47.28% at 0.5 hour to 72.79% at 4 hours. Beyond 4 hours, the removal efficiency remained more or less constant. In view of these findings, a pH of 6.0, 1g of adsorbent per 50 cm^3 of solution, and 4 hours of agitating time were selected as the optimal operating conditions for subsequent experiments. Findings reported in literature for adsorbents derived from Bambara groundnut hulls, using similar optimization approach, indicate that optimal conditions occurred for adsorption of atrazine at pH of 7.0, equilibrium period of 2 hours and adsorbent dosage of 0.9 g [25] while optimal conditions for adsorption of copper occurred at pH of 6.0, contact time of 1 hour and adsorbent dosage of 6g/L [26].

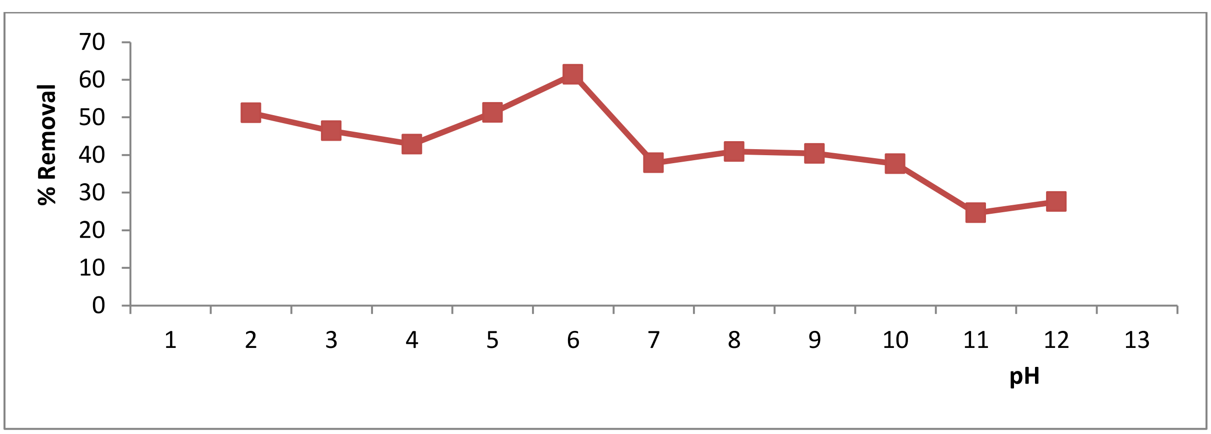

Fig. 2: A Plot of removal efficiency against initial solution pH

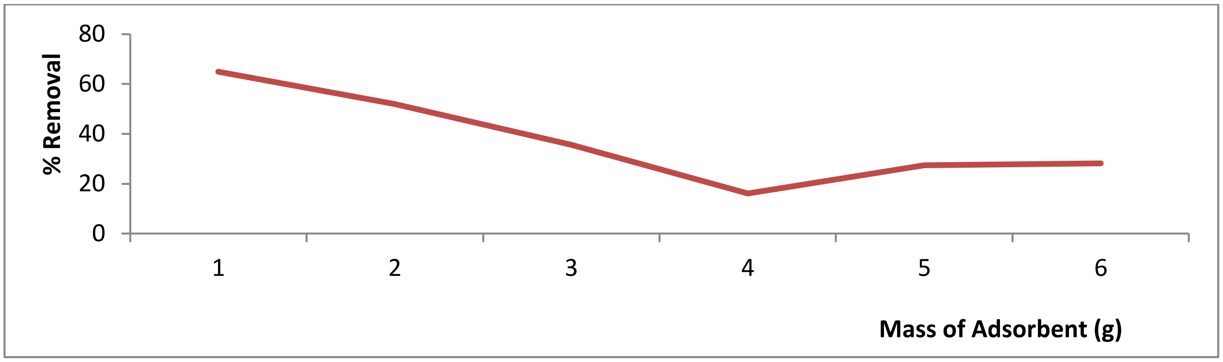

Fig. 3: A plot of removal efficiency against mass of adsorbent

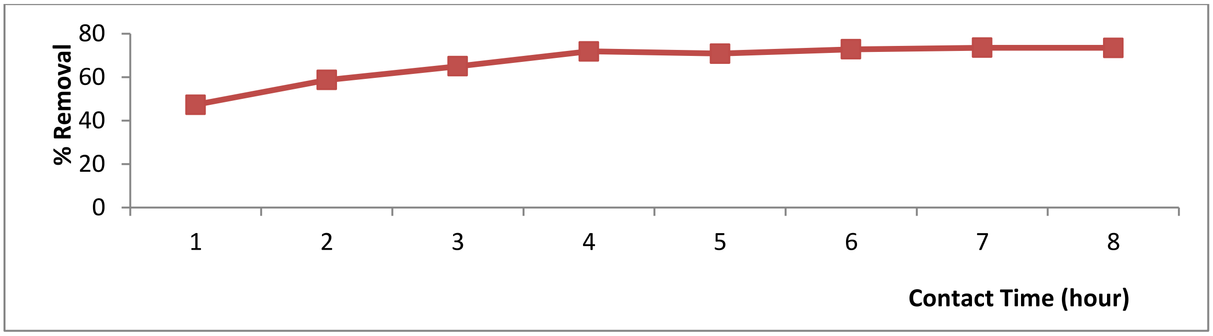

Fig. 4: A Plot of removal efficiency against contact time

3.2 Sorption Kinetics

Figs. 5, 6 and 7 present the plots of intraparticle diffusion model, pseudo-first order model and pseudo-second order model for testing the kinetic data obtained for the adsorption of Congo red on *V. subterranean* hulls. The rate constants and the coefficients of determination obtained from these plots are presented in Table 1. The pseudo-second order model gives the best fit for the sorption kinetic data as indicated by the values of the coefficient of determination (R^2 = 0.957) and rate constant (k_2) (1.445 $g\ mg^{-1}\ min^{-1}$). The model is based on the assumption that adsorption process involves chemisorptions, which requires valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate [31]. Pseudo-second order model has been successfully applied to explain the kinetics of Congo red adsorption on a variety of other adsorbents [14, 17, 32-34].

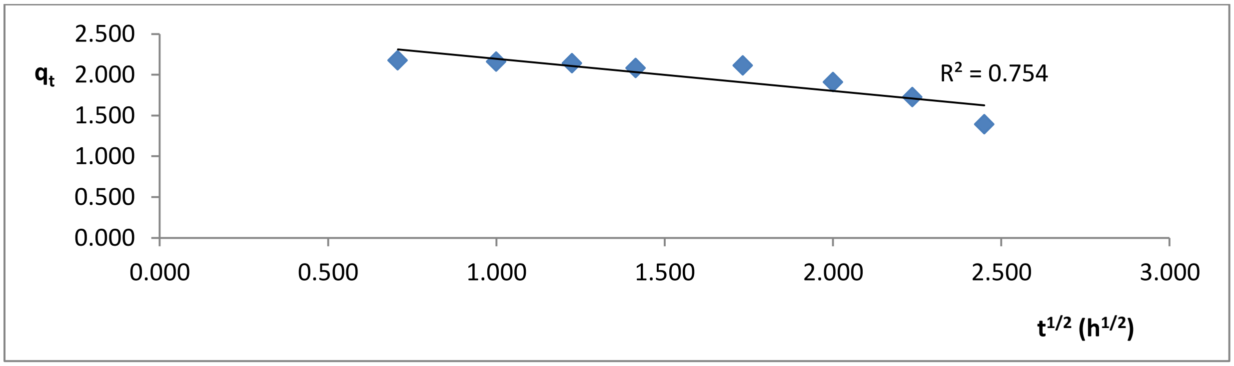

Fig. 5: Intraparticle diffusion plot for Congo red adsorption on Bambara groundnut hull

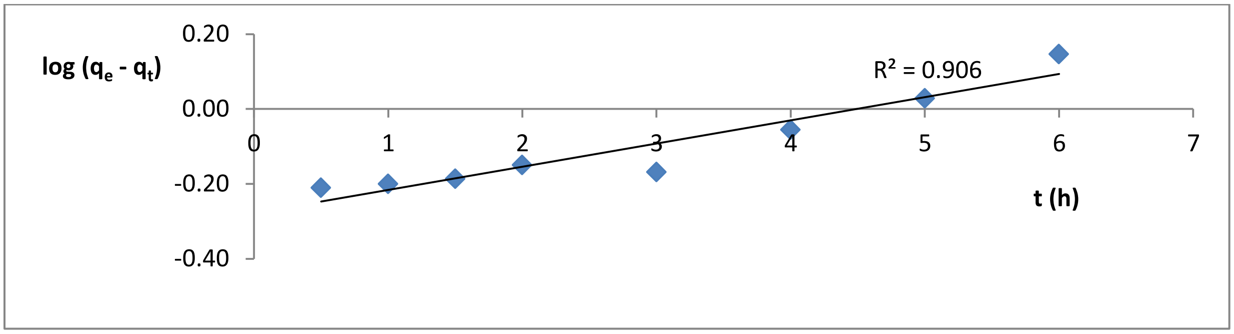

Fig. 6: Pseudo-first order plot for Congo red adsorption on Bambara groundnut hull

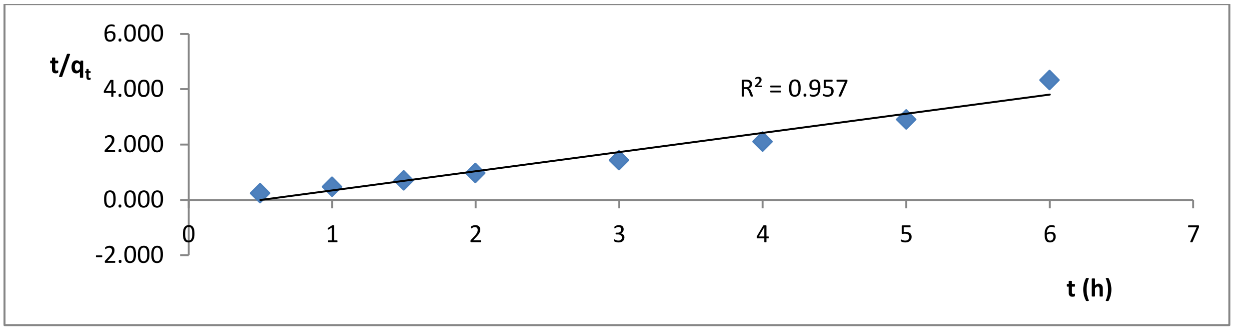

Fig. 7: Pseudo-second order plot for Congo red adsorption on Bambara groundnut hull

Table 1: Rate constants for Congo red adsorption on Bambara groundnut hull

Kinetic model	Parameters	
Intraparticle diffusion model	k_{int} R^2	0.392 0.754
Pseudo-first order model	k_1 R^2	0.143 0.906
Pseudo-second order model	k_2 R^2	1.445 0.957

3.3 Sorption Isotherms

The plots displayed in Figs. 8, 9 and 10 are Langmuir, Freundlich and Tempkin isotherms for the adsorption of Congo red on *V. subterranean* hulls, and the adsorption parameters obtained from these plots are summarized in Table 2. The adsorption data fitted well to Freundlich adsorption isotherm as indicated by the value of the coefficient of determination obtained for this model (R^2 = 0.981). Freundlich adsorption isotherm is an empirical model that describes non-ideal and reversible adsorption, and it is not restricted to the formation monolayer [35]. In other words, Freundlich adsorption isotherm can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over heterogeneous surface of the adsorbent. For Freundlich adsorption isotherm, the value of $^1/_n$ above unity, as obtained in this study ($^1/_n$ = 1.285 in Table 2), is indicative of cooperative adsorption [35]. Freundlich adsorption isotherm has been successfully used to explain the adsorption of Congo red on *Eichhornia crassipes* [36].

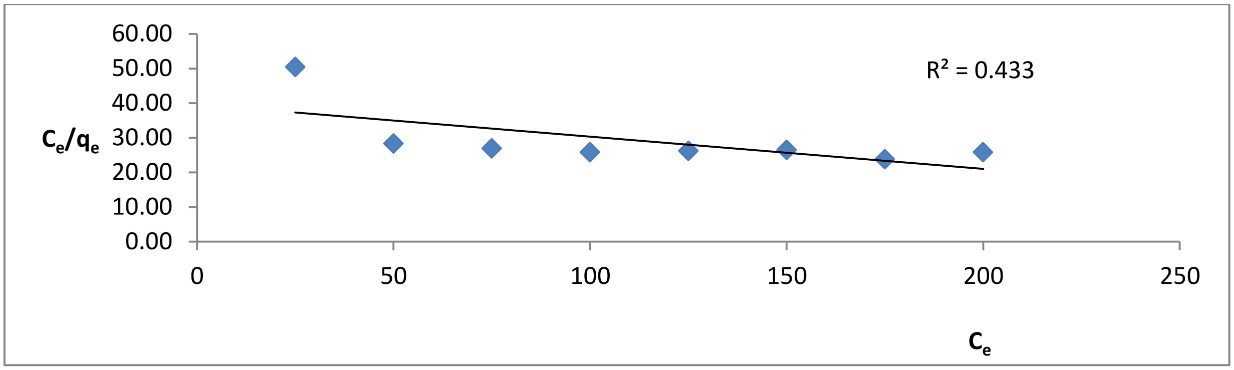

Fig. 8: Langmuir isotherm for Congo red adsorption on Bambara groundnut hull

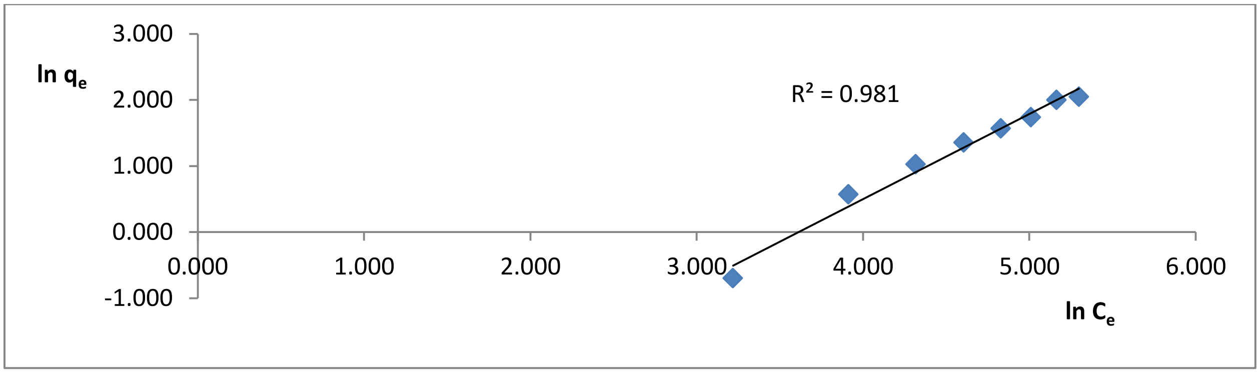

Fig. 9: Freundlich isotherm for Congo red adsorption on Bambara groundnut hull

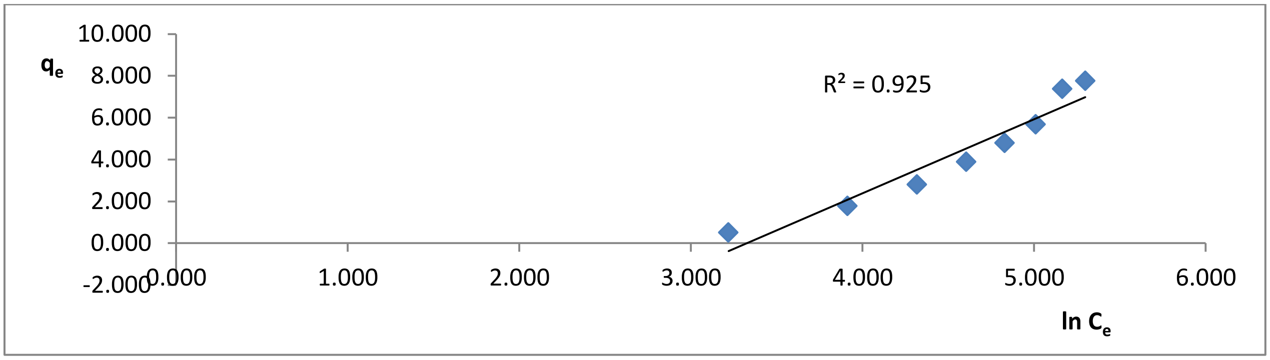

Fig. 10: Tempkin isotherm for Congo red adsorption on Bambara groundnut hull

Table 2: Equilibrium Isotherm Constants for Congo Red Adsorption on Bambara Groundnut Hull

Isotherm model	Parameters	
Langmuir adsorption isotherm	q_{max}	10.75
	B	2.34 x 10^{-3}
	R^2	0.433
Freundlich adsorption isotherm	K_F	9.62 x 10^{-3}
	$1/n$	1.285
	R^2	0.981
Tempkin adsorption isotherm	A_T	3.60 x 10^{-2}
	b_T	708.88
	R^2	0.925

4.0 Conclusion

The search for an alternative low-cost and environmentally friendly adsorbent, suitable for the removal of toxic dyes from contaminated wastewater provided the impetus for this research work. Performance characteristics of Congo red removal from aqueous solution by adsorption onto adsorbent obtained from Bambara groundnut hulls were evaluated by investigating the kinetics and equilibrium isotherms of the adsorption system. It was observed that the adsorption process involves a non-ideal, reversible adsorption; reflecting a multilayer and cooperative adsorption. The process also involves sharing or exchange of electrons between the surface of the adsorbent and Congo red molecule. The study demonstrates that adsorbent derived from Bambara groundnut hulls may be suitable for removing Congo red from contaminated wastewater.

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