Adsorption Kinetics and Intraparticulate Diffusivities of Congo Red onto Kola Nut Pod Carbon

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Abstract

In this present study, the adsorption kinetics and intraparticulate diffusivities of congo red onto unmodified and modified kola nut pod carbons were studied. Two kinetic models, the pseudo first- and second-order equations, were selected to follow the adsorption process. Kinetic parameters, rate constants, equilibrium adsorption capacities, and correlation coefficients for each kinetic equations were calculated and discussed. Experimental results showed that the amount of congo red adsorbed by all the adsorbents increased with increasing contact time with NH_4Cl modified kola nut pod carbon having the highest adsorption capacity as compared to the unmodified, heat- and HNO_3-modified kola nut pod carbon. Results obtained also indicated that the adsorption of congo red onto kola nut pod carbons is pseudo first-order and the mechanism is particle-diffusion controlled.

Keywords: congo red, kola nut pod, carbon, adsorption kinetics, intraparticulate diffusivities

Introduction

Congo red (CR) is the sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid (Fig. 1). It is a secondary diazo dye, is water soluble, and mainly occurs in effluents discharged from textile, paper, printing, and leather industries. CR is a toxic mutagenic and carcinogenic dye released into wastewaters during dyeing operations, making it harmful to aquatic life in rivers and lakes. The presence of dye in natural water systems inhibits sunlight diffusion into the water, consequently reducing the photosynthetic process of aquatic plants. Hence, the remediation of CR from wastewaters before discharge into the water environment is very important in environmental management. CR can be removed from effluents by physical methods such as adsorption [1, 2], and chemical methods such as ozonation [3], photodegradation [4], and biodegradation [5].

Adsorption has been recognized as the most popular treatment process for the removal of dye from an aqueous solution due to its simplicity, high efficiency, easy recovery and the reusability of the adsorbent [6, 7]. The removal of CR through adsorption onto activated carbon shows high efficiency but it is an expensive process. Hence, low cost adsorbents (activated carbon) prepared from waste materials such as agricultural waste are desirable. Some reported works in this area of research are: Chou et al. [8], who studied the adsorption of CR on rice hull ash. Sharma and
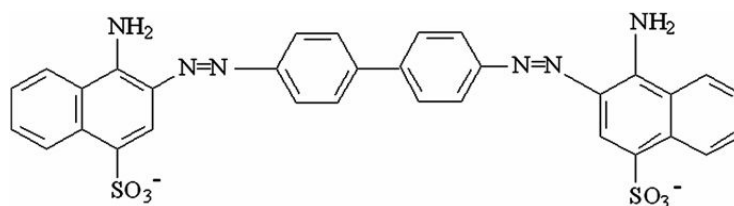
Fig. 1. Congo red.

Janveja [9] also investigated the removal of CR dye from the effluents of textile industry using rice husk carbon activated by steam; Namasivayam and Kavitha [10] reported the adsorption of CR by coir pith carbon, noting that the adsorption of CR followed second-order rate kinetics and that the adsorption capacity was found to be 6.7 mg dye per g of the adsorbent; while Reddy [11] investigated the removal of CR using tamarind fruit shells as an adsorbent, including that the adsorption process of CR by tamarind fruit shell followed the first-order rate expression.

The aim of this research work is therefore to prepare carbon from kola nut pod (agricultural waste), to investigate the effect of surface modification processes on the adsorption of CR dye and to carry out the adsorption kinetics and equilibrium studies of CR dye on the unmodified and modified kola nut pod carbon samples.

Material and Methods

Kola nut pods were collected from Ejigbo, Osun State, Nigeria. The pods were dried after sand and debris were removed. Carbonization of the sample was done by subjecting 500 g of the sample to a low temperature conversion process in an inert atmosphere of nitrogen gas. The carbonization was carried out at two different temperatures of 360ºC and 420ºC in the presence of nitrogen to disallow oxidation of carbon. The conditions of the experiment were 1L/mins of Nitrogen flow and 9.7 J/min of heating rate. The obtained carbon was ground into a particle size ≤ 0.5 mm, washed using de-ionised water to pH 7.10 using 0.1 M NaOH and 0.1 M HCl and labeled KPC.

Surface Modification

± 20 g of the carbon was soaked in 0.1 M nitric acid and 0.1 M ammonium chloride solution for the nitric acid and ammonium chloride carbon modification and were labeled KPNA and KPAC, respectively. The solutions were soaked for three days, filtered, the residue dried and stored appropriately. 20 g of carbon was heated in the oven at 150ºC for 1 hour for the heat-modified kola nut pod carbon and was also labeled KPHT accordingly.

Adsorption of Congo Red

An initial CR concentration of 1000 mg/L was prepared. To determine the effect of contact time, 1.0 g of the unmodified and modified KPC samples were put into a 100 mL solution of CR of initial concentration of 1000 mg/L.

The samples were shaken by means of an orbital shaker at room temperature for between 60-900 min. At the end of each time, the samples were filtered and concentration of CR in filtrates determined by UV spectrophotometer. The amount of CR adsorbed (mg/g) was calculated based on a mass balance equation as given in Equation (1) below:

$$q = \frac{(Co - C) \cdot V}{W} \qquad (1)$$

...where q is the equilibrium adsorption capacity per gram dry weight of the adsorbent, mg/g; Co is the initial concentration of CR in the solution, mg/L; C is the final or equilibrium concentration of CR in the solution, mg/L; V is the volume of the solution, L; and W is the dry weight of the adsorbent, g.

Adsorption Kinetics

To analyze the adsorption rates of CR onto the unmodified and modified KPCs, two simple kinetic models were tested. The adsorption data was analyzed in terms of pseudo first-order and pseudo second-order mechanisms. The slope of the two graphs either pseudo first-order mechanism or pseudo second-order mechanism that gave a linear relationship or having the highest correlation coefficient indicates which kinetics are applicable to the adsorption of CR on relative adsorbents. The linear driving force concept was also used to develop the relationship for particle-diffusion controlled adsorption.

Result and Discussion

Adsorption Studies

Fig. 2 shows the amount of CR adsorbed (mg/g) against time (min) for KPC, KPHT, KPNA, and KPAC. It was observed that the amount of CR adsorbed by all the adsorbents increase with increasing contact time. The results also showed that the modification of KPC by any of the three methods described increases the efficiency of the produced modified KPCs for the removal of CR from aqueous solution. About 40%, 46%, 55.0%, and 61.0% of CR were removed from the initial concentration of 100 mg/g CR dye by KPC, KPHT, KPNA, and KPAC, respectively, at a stirring speed of 200 rpm and 900 min contact time. The order of increasing adsorption capacity was: KPC < KPHT < KPNA < KPAC.
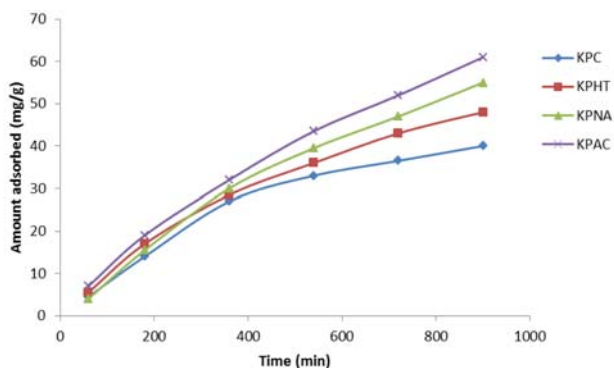
Fig. 2. Amount adsorbed (mg/g) against time (min). (Experimental conditions: mass of KPC samples = 1.0 g, volume of CR solution = 100 ml, stirring speed = 200 rpm, temperature = 25ºC, particle size ≤ 0.5 mm)

Pseudo First-Order Model

The pseudo first-order equation is generally expressed as follows:

$$d_q/d_t = k_1(q_e - q_t) \qquad (2)$$

...where q_e is the amount of CR adsorbed at equilibrium per unit weight of the adsorbent (mg/g), q_t is the amount of CR adsorbed at any time (mg/g), and k_1 is the pseudo first-order rate constant/min.

After integration and applying boundary conditions t=0 to t=t and q_t=0 to q_t=q_t, the integrated form of Equation (2) becomes:

$$\log (q_e - q_t) = \log q_e - k_1 t/2.303 \qquad (3)$$

The values of log (q_e-q_t) were linearly correlated with t. The plot of log (q_e-q_t) versus t should give a linear relationship from which k_1 and qe can be determined from the slope and intercept of the plot, respectively.

Pseudo Second-Order Model

The pseudo second-order adsorption kinetic rate equation is expressed as [12]:

$$d_q/d_t = k_2(q_e - q_t)^2 \qquad (4)$$

...where k_2 is the rate constant of pseudo second-order adsorption (g/mg min). For the boundary conditions t=0 to t=t and q_t= 0 to q_t=q_t, the integrated form of Equation (4) becomes:

$$t/q = 1/h_o + 1/q_e \text{ (t)} \qquad (5)$$

...where h_o is the initial adsorption rate. If the second-order kinetics is applicable, the plot t/q against t in Equation (5) should give a linear relationship from which the constants q_e and h_o can be determined.

When *t* tends to 0, h_o is defined as [13]:

$$h = k_2 q_e^2 \qquad (6)$$

k_2 was calculated for the adsorption of CR onto the modified and unmodified KPCs.

Table 1 thus presents the pseudo first-order and pseudo second-order rate equation constants for CR adsorption on the unmodified and modified kola nut pod carbon.

Comparing the correlation coefficients (R^2) of pseudo first-order and pseudo second-order equation plots (Table 1), the adsorption of CR onto KPC, KPHT, KPNA, and KPAC all follows the same kinetic model.

The pseudo first-order kinetics of KPC, KPHT, KPNA and KPAC gave a good fit to the experimental data, i.e. high correlation coefficient (R^2), as compared to their corresponding pseudo second-order kinetics, hence the adsorption of CR onto the modified and unmodified KPCs are pseudo first-order. Earlier workers have shown that the adsorption of CR onto activated biomass carbon follows a first-order kinetics [9].

Removal Efficiency and Fractional Attainment to Equilibrium

The removal efficiency (E) of CR on the adsorbent can be calculated from Equation (7) [14]. Another related quantity, the fractional attainment to equilibrium (α), also was used to analyze the equilibrium data (Equation 8).

$$E = C_t/C_o \qquad (7)$$

$$\alpha = C_t/C_\infty \qquad (8)$$

...where C_t is the concentration of CR at any time t, C_o is the initial concentration, and C_∞ is the concentration at equilibrium.

A plot of *α* (fractional attainment to equilibrium) against time for the adsorption of CR onto KPC, KPHT, KPNA, and KPAC is as shown in Fig. 3, while the removal efficiency (E) of CR on the unmodified and modified KPCs are
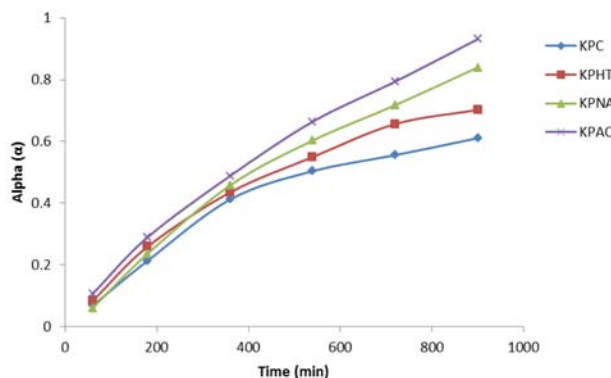

Fig. 3. Alpha (α) against time (min). (Experimental conditions: mass of KPC samples = 1.0 g, volume of CR solution = 100 ml, stirring speed = 200 rpm, temperature = 25ºC, particle size ≤ 0.5 mm)

Table 1. Pseudo first-order, second-order rate equation constants and rate coefficient for CR adsorption onto unmodified and modified KPCs.

Pseudo first-order			
Carbon type	k_1/min	q_e (mg/g)	R^2
KPC	$1.15 \cdot 10^{-3}$	57.98	0.9682
KPHT	$1.61 \cdot 10^{-3}$	61.56	0.9999
KPNA	$2.30 \cdot 10^{-3}$	72.88	0.9763
KPAC	$3.92 \cdot 10^{-3}$	99.04	0.9921
Pseudo second-order				
Carbon type	h_o/min	q_e (mg/g)	k_2 (mg/g min)	R^2
KPC	0.0914	84.75	$1.27 \cdot 10^{-5}$	0.8972
KPHT	0.1057	99.01	$1.07 \cdot 10^{-5}$	0.9732
KPNA	0.0809	285.71	$9.91 \cdot 10^{-7}$	0.3560
KPAC	0.1211	133.33	$6.81 \cdot 10^{-6}$	0.8619
Intraparticle diffusivity			
Carbon types	k_p/min		R^2
KPC	$1.0 \cdot 10^{-3}$		0.9644
KPHT	$1.4 \cdot 10^{-3}$		0.9911
KPNA	$2.0 \cdot 10^{-3}$		0.9873
KPAC	$2.8 \cdot 10^{-3}$		0.9387

Experimental conditions: mass of KPC samples = 1.0 g, volume of CR solution = 100 ml, stirring speed = 200 rpm, temperature = 25ºC, particle size ≤ 0.5 mm

Table 2. Fraction of the amount of adsorbed CR onto unmodified and modified KPCs.

Time (min)	Kola nut carbon (C_t/C_o)			
	KPC	KPHT	KPNA	KPAC
60	0.045	0.055	0.040	0.070
180	0.140	0.170	0.155	0.190
360	0.270	0.285	0.300	0.320
540	0.330	0.360	0.395	0.435
720	0.364	0.430	0.470	0.520
900	0.400	0.460	0.550	0.610

Experimental conditions: mass of KPC samples = 1.0 g, volume of CR solution = 100 ml, stirring speed = 200 rpm, temperature = 25ºC, particle size ≤ 0.5 mm

presented in Table 2. The percentage of CR adsorbed onto KPC, KPHT, KPNA, and KPAC at different contact time can therefore be easily calculated from Table 2.

Intraparticle Diffusivity

The adsorption rate is controlled by several factors, including the diffusion of the solute from the solution to the film surrounding the particle, diffusion from the film to the particle surface (external diffusion), diffusion from the surface to the internal sites (surface diffusion or pore diffusion) and the uptake that can involve several mechanisms such as physico-chemical sorption, ion exchange, precipitation or complexation [15, 16]. The first, second, and third factors are referred to as bulk diffusion, external mass transfer resistance, and intraparticle mass transfer resistance, respectively. Mass transfer is governed by several relationships that take into account the diffusion mechanisms and
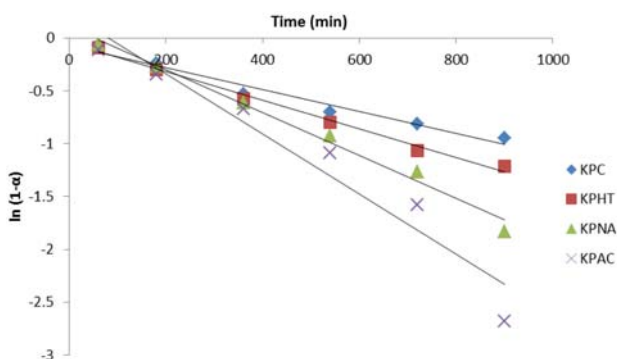
Fig. 4. Intraparticle diffusivity plot for CR adsorption. (Experimental conditions: mass of KPC samples = 1.0 g, volume of CR solution = 100 ml, stirring speed = 200 rpm, temperature = 25ºC, particle size ≤ 0.5 mm)

their related equations, the coupling between liquid and solid phases, and the initial and boundary conditions. Therefore, the rate of attainment to equilibrium may either be film-diffusion controlled or particle-diffusion controlled [17]. The linear driving force concept was used to develop the relationship for particle-diffusion controlled adsorption as shown by Equation (9).

$$\ln (1 - \alpha) = -K_p t \qquad (9)$$

K_p is the rate coefficient for the particle-diffusion controlled process corresponding to the particle size of the adsorbent; t is time and ln (1-α) is a measure of the intraparticulate diffusivity. If a plot of ln (1-α) versus time results in a linear relationship, the adsorption process is particle-diffusion controlled and the diffusivity of CR onto the adsorbent surface is independent of the extent of adsorption. As shown in Fig. 4, it was observed that the adsorption process tested was particle diffusion controlled.

The values of K_p from the slope of the graphs and the coefficient of regression (R^2) are also shown in Table 1.

The experimental data gave linear plots to the fractional attainment to the equilibrium concept. Hence, the adsorption process followed the particle diffusion process.

Conclusion

The results presented in our paper clearly suggest that the unmodified and modified kola nut pod carbon can be efficiently used for the removal of CR dye. The kola nut pod carbon modified with NH_4Cl thus proved more efficient as compared to the unmodified and other modified forms of kola nut pod carbon. An amount of 1.0 g of unmodified (KPC), heat modified (KPHT), nitric acid modified (KPNA), and ammonium chloride modified (KPAC) kola nut pod carbons could remove about 40%, 46%, 55.0%, and 61.0% of CR dye, respectively, from an aqueous solution of 100 mg/g at a stirring speed of 200 rpm and a contact time of 900 min. The interactions were tested for both pseudo first-order and second-order kinetics and it was observed that the adsorption process of all the KPCs follows a first-order kinetics. The mechanism of sorption was also found to obey the particle-diffusion model. The use of kola nut carbon to clean up CR-bearing effluents from textile industries is cheap, feasible, and environmentally friendly, and also will provide an affordable technology for small- and medium-scale industries.

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