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Congo Red Biosorption on Palm Kernel Seed Coat

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Palm kernel coat (PKC), a waste product of oil palm production, was studied as a biosorbent for Congo Red (CR) (an anionic dye) attenuation in an aqueous stream. A batch sorption system was used, and the system variables studied included initial CR concentration and PKC dosage. A batch sorption model, based on the assumption of pseudo-first-order and pseudo-second-order mechanisms, was applied to understand the sorption dynamics of CR onto PKC and to predict the rate constant of sorption, the equilibrium sorption capacity, and the initial sorption rate when the two process variables were optimized. The linear coefficient of determination (r^2) and the nonlinear chi-square test (χ^2) were used to assess the fitting of the sorption dynamics to either model. An equation was developed using the pseudo-second-order model, which predicts the amount of CR at any contact time and initial concentration within the given range. The rate-limiting step of the sorption reaction was also determined using the intraparticle diffusion, liquid film diffusion, and Boyd kinetic models. The results obtained showed that intraparticle diffusion becomes rate controlling at low concentration while at high concentration film diffusion is the main rate-controlling parameter. The results of the batch desorption studies showed that chemisorption played a prominent role in the sorption process. The elution curve obtained from the continuous desorption studies showed that the elution rate was fast and high elution efficiency could be obtained with 0.1 M CH_3COOH as an eluting solvent.

Introduction

Adsorption is a unit process that is used in the tertiary treatment stage of water and wastewater. It is used to polish already-treated water to an acceptable standard. The most commonly used sorbent in this regard is activated carbon. However, it is an expensive material and the process of regeneration, for reuse, is tedious. Litanies of sorbents of biological origin have been investigated by different researchers and the performances were found to be on a par with the conventional sorbent (i.e., activated carbon). Some of these biosorbents are peat,^{1,2} cotton waste, rice husk, bark,³ palm fruit bunch,⁴ jackfruit peel,⁵ wood,⁶ castor seed shell,⁷ rubber seed shell,^{8,9} and *Mansonia* wood sawdust.¹⁰

Dyes can be classified as anionic (direct and reactive dyes), cationic (basic dyes), and nonionic (disperse dyes). Colored dye wastewater arises as a direct result of the production of the dye and also as a consequence of its use in the textile and other industries.¹¹ There are more than 100 000 commercially available dyes, with over 7×10^5 metric tons of dyes produced annually.¹² Congo Red (CR) [1-naphthalenesulfonic acid, 3,3'-(4,4'-biphenylenebis(azo)bis(4-amino-)) disodium salt] is a benzidine-based anionic bisazo dye. This dye is known to metabolize to benzidine, a known human carcinogen.¹³ Effluents containing CR are generated from the textile, printing and dyeing, paper, rubber, plastic, etc. industries. Owing to structural stability, CR is difficult to biodegrade. Physicochemical or chemical treatment of such wastewater is, however, possible.¹⁴

In the present study, the use of palm kernel coat (PKC) in the attenuation of a model anionic dye (CR) in an aqueous stream shall be explored. Palm kernel coat (PKC), the sorbent

used in the present study, is obtained from the oil palm tree (*Elaeis guineensis*). This tree is native to the west coast of the Africa and is widespread in the tropics. *E. guineensis* and *E. oleifera* (i.e., the American oil palm) are members of the family Arecaceae (formerly Palmae). Before 1971, Nigeria was the world's largest exporter of palm oil. This tree serves as a vast resource of materials of industrial importance (e.g., palm wine, palm kernel oil, palm kernel cake). Virtually all parts of the oil palm tree have been utilized in one form or another. Palm oil, used in the manufacture of soap, liniment, ointments, margarine, soap, West African and Brazilian cooking, etc., is extracted from the fruit pulp. Palm kernel oil is obtained from the seed kernels of the fruits. Palm kernel shell and palm kernel coat (i.e., the fiber) are the major waste materials produced from the extraction of palm kernel oil and palm oil, respectively. Over 15 600 metric tons of shells and fiber are generated annually, and only about 5% of the waste is sometimes used as biofuel.¹⁵

The use of palm kernel coat in the treatment of 4-bromoaniline-azo-1,8-dihydronaphthalene-3,6-disodium sulfate (an anionic dye) contaminated water has been reported.¹⁶ Ofomaja and Ho¹⁶ collected palm kernel coat that has been allowed to age or decay with the residual oil, after processing, for about 2 months, and studied its potential for dye removal from aqueous solution. In the present study, the palm kernel coat was obtained immediately the oil was extracted from it. The residual oil on it was not allowed to biodegrade but was removed by saponification, and the ability of this sorbent (i.e., the PKC) to remediate water contaminated with CR was investigated. The sorption of CR by PKC was studied and the data obtained, when two process variables (i.e., initial concentration (mg/L) and sorbent dosage (g)) were optimized, was fitted into pseudo-first-order and pseudo-second-order kinetic models. The step that limits the rate of sorption of CR on PKC was determined by also analyzing the data with the intraparticle diffusion model,

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liquid film diffusion, and the kinetic model proposed by Boyd et al.¹⁷ The prospects of PKC regeneration were examined in different eluting solvents (deionized water, HCl, NaOH, and CH₃COOH), using a batch method. The solvent that gave optimum CR desorption was used in fixed bed desorption, to obtain a desorption curve, from which relevant information was generated.

Materials and Methods

Sorbent Preparation. The PKC was obtained from a small-scale palm oil processing factory, situated in Akungba-Akoko (the university town), Nigeria. The raw PKC was steeped in warm deionized water, to melt the residual oil on it. The PKC was separated from the warm deionized water and 0.5 M NaOH was added to the PKC for alkaline hydrolysis (saponification) of any residual oil on it. The saponified PKC was thoroughly washed until it stopped foaming and the pH of the washings was equal to the pH of the deionized water used in washing the PKC. The PKC was oven-dried, ground, and screened through a set of sieves to obtain particle size 53–74 μm . This fraction was then stored in an airtight plastic container pending usage.

Sorbate Preparation. The dye used in the present studies, CR (C.I. 2212, chemical formula = C₃₂H₂₂N₆Na₂O, λ_{max} = 500 nm), was accurately weighed and dissolved in distilled–deionized water to prepare the stock solution (500 mg/L). Different working solutions were prepared from the stock solution by serial dilution.

Sorbate Quantification. The CR concentrations in the aqueous medium were quantified by the determination of the absorbance at the characteristic wavelength using a double beam UV/visible spectrophotometer. A standard solution of the dye was taken and the absorbance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to the maximum absorbance (λ_{max}), as determined from this plot, was noted and the wavelength was used for the preparation of the calibration curve used in the present studies.

Sorption Dynamics Studies. (i) Effect of Initial Concentration. The effects of initial concentrations on the sorption of CR by PKC were studied using a range of CR concentrations [30–150 mg/L]. Owing to the pH-dependent nature of dye sorption onto biosorbents and the CR structural stability (i.e., the color intensity), the sorption experiment was carried out at the natural pH of the dye (pH 6.7).

A typical experimental procedure was conducted by measuring, accurately, 1 L of the CR solution of known concentration and 2 g of PKC was added and agitated [at 200 rpm] for 120 min, based on the results obtained from the equilibrium time studies, carried out as a preliminary study [results not shown]. Samples were withdrawn, at fixed time intervals and centrifuged, and the supernatant was analyzed for residual CR using the UV/visible spectrophotometer. The amount of CR sorbed per unit mass of the PKC [q in mg/g] was calculated using the mass balance procedure.

(ii) Effect of Sorbent Dosage. The effect of PKC dosage on the adsorption process was investigated by varying the sorbent dosage from 0.1 g/50 mL to 0.8 g/50 mL of CR solution. The experiment was conducted by measuring 1 L of 150 mg/L CR solution into a 2 L conical flask. Appropriate dosage of the PKC was measured into it, with agitation [200 rpm] for 120 min. Samples were withdrawn, at fixed time intervals, and analyzed for residual CR, and the amount of sorbate sorbed per unit mass of the PKC [q in mg/g] was calculated using the mass balance procedure.

Desorption Studies. (i) Batch Desorption Studies. The PKC (1 g) was loaded with the CR (200 mg/L) and dried in the oven at 60 °C overnight. This CR-loaded PKC was then placed in Erlenmeyer flasks containing 50 mL of the desorbing agent solution. The sample was agitated for 120 min and then the PKC was filtered. The desorbed CR concentration was quantified using the UV/visible spectrophotometer. Four different eluting solvents were used: deionized water, HCl (0.1 M), NaOH (0.1 M), and CH₃COOH (0.1 M).

(ii) Fixed Bed Desorption Studies. The fixed bed desorption studies were carried out in a fixed bed of CR-loaded PKC in a glass column (40 × 1 cm). The glass column was packed with a known weight (50 g) of the biomass (fixed bed height = 10 cm), and it was regenerated using the best eluting solvent obtained from the batch desorption studies. The effluent was collected at fixed time intervals (flow rate = 20 mL/min) until the CR concentration in the effluent was less than 0.02 mg L⁻¹. The experiment was conducted at ambient temperature (30 °C).

Error Analysis. The optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the different kinetic models to the experimental data.¹⁸ In the present study, the linear coefficient of determination and nonlinear chi-square were examined. The coefficient of determination, r^2 , represents the percentage of variability in the dependent variable that has been explained by the regression line. The linear coefficient of determination, r^2 , found from evaluation of data by linear model, was calculated with the aid of the equation

$$r^2 = \frac{S_{xy}^2}{S_{xx}S_{yy}} \quad (1)$$

where S_{xx} is the sum of squares of x :

$$S_{xx} = \frac{\sum x_i^2 - \sum x_i^2}{n}$$

S_{yy} is the sum of squares of y :

$$S_{yy} = \frac{\sum y_i^2 - \sum y_i^2}{n}$$

and S_{xy} is the sum of squares of x and y :

$$S_{xy} = \frac{\sum x_i y_i - (\sum x_i)(\sum y_i)}{n}$$

The chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models. The equivalent mathematical statement is

$$\chi^2 = \frac{\sum (q_{\text{e,exp}} - q_{\text{e,mod}})^2}{q_{\text{e,mod}}} \quad (2)$$

If data from models are similar to the experimental data, χ^2 will be a small number, and if they are different, χ^2 will be a bigger number. Therefore, it is necessary to also analyze the

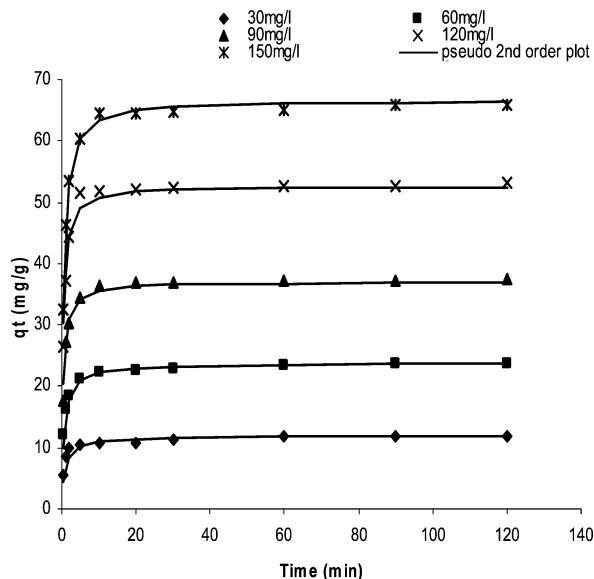


Figure 1. Effect of initial CR concentrations (mg/L) on time–concentration profile of sorption of CR by PKC. Sorbent mass, 2.00 g; sorbate volume, 1.00 L; agitation speed, 120 rpm.

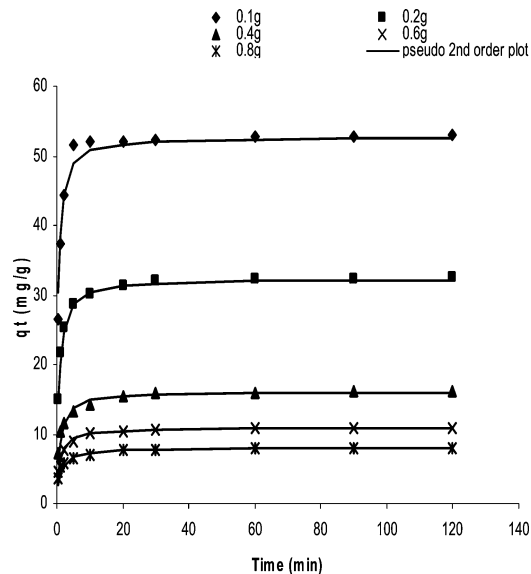


Figure 2. Effect of PKC dosage (g) on time–concentration profile of sorption of CR by PKC. MB concentration, 150 mg/L; sorbate volume, 1.00 L; agitation speed, 120 rpm.

data set on the nonlinear chi-square test to confirm the best-fit model for the sorption of CR by PKC.

Results and Discussion

A proximate analysis of the saponified PKC was carried out, using the recommended standard methods of analysis.¹⁹ The results obtained from the analysis showed that the saponified PKC contained (in % dry weight): protein, 18.72%; lipid, 3.72%; ash, 1.37%; fiber, 24.9%; carbohydrates, 51.29%; Ca, 0.5%; Mg, 0.14%; Na, 0.21%; K, 0.05%; P, 0.03%; N, 3.00%. (The results presented herein were obtained from the mean of triplicate determinations.) The bulk density of the PKC used was 497.28 kg/m³. The results of the particle size analysis showed that the PKC used for the present study was made up of the following particle sizes (μm): >90 (54.18%); 90–63 (42.22%); <63 (3.60%).

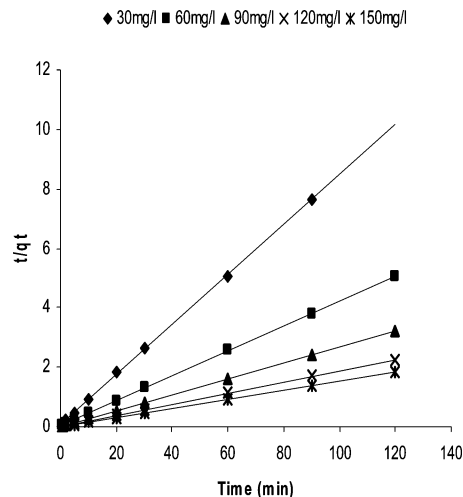


Figure 3. Pseudo-second-order kinetic plots for the removal of CR by PKC at different initial CR concentrations (mg/L). Sorbent mass, 2.00 g; sorbate volume, 1.00 L; agitation speed, 120 rpm.

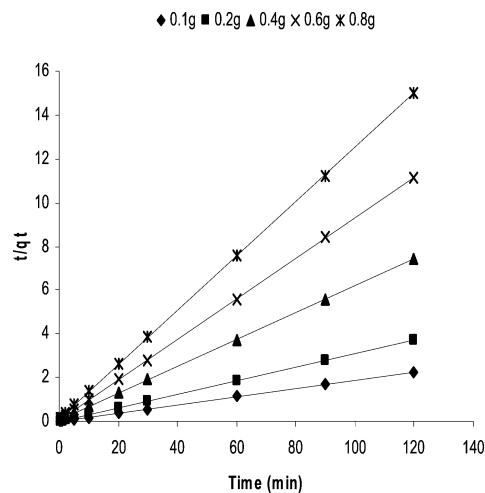


Figure 4. Pseudo-second-order kinetic plots for the removal of CR by PKC at different PKC dosages (g). MB concentration, 150 mg/L; sorbate volume, 1.00 L; agitation speed, 120 rpm.

The abstraction of CR from solution by PKC leads to the transfer of CR molecules to the surface of the PKC, where the concentration of the dye builds up until a dynamic equilibrium is reached between the CR in the PKC and CR in solution. Studies on the time–concentration profile of the sorption process are required to determine the optimum operating conditions for the full-scale batch process.²⁰ The sorption dynamic parameter, which is helpful for the prediction of adsorption rate, gives important information for designing and modeling the processes. Consequent upon this, the effects of initial CR concentration and PKC dosage were analyzed from the kinetic point of view.

Effect of Initial Concentration. The results presented in Figure 1 show the effects of initial CR concentrations (mg/L) on the amount of CR (mg) sorbed by the PKC (g). It was noted that the amount of CR sorbed per gram of PKC increased with the time of contact between the CR solution and the PKC until a time was reached when the rate of sorption became immeasurably slow. At this point an almost constant value of the amount of CR was abstracted by the PKC and a state of dynamic equilibrium was attained. For the entire period of sorption process (120 min), adopted in the present study, a greater amount of CR was sorbed per gram of PKC at higher initial concentration than at lower concentration. It was noted that the sorption

Table 1. Pseudo-First-Order Kinetic Parameters for the Removal of CR by PKC at Different Initial CR Concentrations (mg/L)

initial concn	k_1	$q_{e,exp}$	$q_{e,mod}$	r^2	χ^2
30	0.044	11.92	2.636	0.8837	32.6983
60	0.055	23.65	4.856	0.9163	72.7377
90	0.043	37.41	4.486	0.6462	241.6384
120	0.040	53.09	5.409	0.5873	420.3139
150	0.033	65.99	8.104	0.5404	413.4735

Table 2. Pseudo-First-Order Kinetic Parameters for the Removal of CR by PKC at Different PKC Dosages (g)

PKC dosage	k_1	$q_{e,exp}$	$q_{e,mod}$	r^2	χ^2
0.1	0.040	53.09	5.409	0.5873	420.3139
0.2	0.057	32.41	6.109	0.8532	113.2334
0.4	0.075	16.11	4.818	0.9192	26.4652
0.6	0.057	10.77	2.205	0.8026	33.2695
0.8	0.060	8.01	2.340	0.8892	13.7388

reaction was rapid at all initial CR concentrations. This could be seen from the gradual approach of the state of dynamic equilibrium, after the first 5 min.

Effect of Sorbent Dosage. The results presented in Figure 2 show the effects of PKC dosage (g) on the amount of CR (mg) sorbed per gram of the PKC. It was observed that the amount of the CR sorbed per gram of the PKC reduced with increase in the dosage of the PKC while a reverse trend was noticed when the amounts of CR (%) abstracted by the PKC dosages were compared. The sorption rate for a particular dose was initially rapid and then reduced as equilibrium was approached. It is apparent that, by increasing the dose of the PKC, the number of sorption sites available for sorbent–sorbate interaction is increased, thereby resulting in the increasing percentage of dye removal from the solution. The reduction in sorbent capacity could be ascribed to two reasons. First, the increase in sorbent dose at constant dye concentration and volume will lead to unsaturation of sorption sites through the sorption process,^{21,22} and second, the reduction in sorbent capacity may be due to particle interaction such as aggregation, resulting from high sorbent dose.²³ Such aggregation would lead to a decrease in total surface area of the sorbent and an increase in diffusional path length.²¹

Sorption Dynamics Studies. The dynamics of the sorption of CR by PKC were studied using two different kinetic models (pseudo-first-order and pseudo-second-order kinetic models). Chemical sorption has been reported to be an active process in the sorption of dyes on biosorbents.^{24,25} Chemical reaction may occur between the organic functional groups on the biosorbent surface and the ionized acid dye anion in aqueous solution via complexation or anion exchange due to the positive charge on the sorbent surface. Chemical reaction may therefore control the reaction rate. Other processes present, which may also control the sorption process, include transport in the bulk liquid phase, diffusion across the liquid film surrounding the solid particles, diffusion in the liquid film, and diffusion in liquid-filled macropores.²⁶

(i) Pseudo-First-Order Model. In the case of sorption preceded by diffusion through the boundary layer, the kinetics most likely follows the pseudo-first-order equation of Lagergren.^{27,28} The linearized form of the pseudo-first-order equation of Lagergren is generally expressed thus:

$$\log[q_e - q_t] = \log[q_e] - [k_1/2.303]t \quad (3)$$

where q_e and q_t are the sorption capacity at equilibrium and at time t , respectively (mg/g). k_1 is the rate constant of pseudo-first-order adsorption.

The plot of $\log(q_e - q_t)$ versus t should give a linear relationship from which k_1 and q_e can be calculated from the slope and intercept of the plot, respectively.

The pseudo-first-order constants, the correlation coefficients, r^2 , and the chi-square test statistic, χ^2 , were deduced from the plot of $\log(q_e - q_t)$ versus time (t), and the respective values obtained are presented in Table 1. The correlation coefficients of the pseudo-first-order plots were poor and ranged from 0.5404 to 0.9163. The calculated q_e values ($q_{e,mod}$) for all the CR concentrations obtained from the first-order kinetic model were lower than the values of the q_e obtained from the sorption experiment ($q_{e,exp}$). The disparities were very high (Table 1).

The pseudo-first-order constants, r^2 and χ^2 , obtained from the pseudo-first-order analysis of the data, obtained from the optimization of the PKC dosage by the method of continuous variation, are presented in Table 2. The r^2 values were also poor.

In order to further assess the applicability of this kinetic model, to effectively describe the sorption of CR by PKC, when the two process variables were optimized, the nonlinear chi-square test statistic was used to correlate the q_e values obtained from the theoretical prediction ($q_{e,mod}$) and the actual sorption process ($q_{e,exp}$) (Tables 1 and 2). The results presented in Tables 1 and 2 showed that the χ^2 values were very high, which is an indication that the pseudo-first-order model cannot describe the sorption process and that the sorption of CR by PKC is not diffusion controlled. Hence, the process does not follow the pseudo-first-order sorption rate expression of Lagergren.

(ii) Pseudo-Second-Order Model. The pseudo-second-order kinetic model is represented by the linear equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e t} \quad (4)$$

where q_e , q_t , and t have the same meaning as explained above. k_2 is the overall rate constants of pseudo-second-order sorption [g/(mg min)]. If pseudo-second-order kinetics is applicable, the plot of t/q_t against t of eq 4 should give a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot.

The initial sorption rate can be obtained from the pseudo-second-order linear plots, as q_t/t approaches zero:

$$h = k_2 q_e^2 \quad (5)$$

where h = initial sorption rate; then eq 4 becomes

$$q_t = \frac{1}{\frac{1}{h} + \frac{t}{q_e}} \quad (6)$$

The applicability of the pseudo-second-order kinetic model to the sorption of CR by PKC, when the two process variables (i.e., initial CR concentration and PKC dosage) were optimized, is presented in Figures 3 and 4, respectively. When the initial

Table 3. Pseudo-Second-Order Kinetic Parameters for the Removal of CR by PKC at Different Initial CR Concentrations (mg/L)^a

initial concn	h	k_2	$q_{e,exp}$	$q_{e,mod}$	r^2	χ^2
30	13.68	9.63×10^{-2}	11.92	11.92	0.9997	0.0000
60	34.86	6.18×10^{-2}	23.65	23.75	1.0000	0.0004
70	87.66	6.25×10^{-2}	37.41	37.45	1.000	0.0000
120	135.23	4.78×10^{-2}	53.09	53.19	1.000	0.0002
150	131.59	3.00×10^{-2}	65.99	66.23	1.000	0.0009

^a Units: h , mg/(g min); k_2 , g/(mg min); q_e , mg/g.**Table 4. Pseudo-Second-Order Kinetic Parameters for the Removal of CR by PKC at Different Sorbent Dosages (g)^a**

PKC dosage	h	k_2	$q_{e,exp}$	$q_{e,mod}$	r^2	χ^2
0.1	135.23	4.78×10^{-2}	53.09	53.19	1.0000	0.0002
0.2	51.77	4.88×10^{-2}	32.41	32.57	1.0000	0.0008
0.4	18.54	7.04×10^{-2}	16.11	16.23	1.0000	0.0009
0.6	14.58	12.43×10^{-2}	10.77	10.83	1.0000	0.0003
0.8	8.08	12.38×10^{-2}	8.01	8.08	0.9999	0.0006

^a Units: h , mg/(g min); k_2 , g/(mg min); q_e , mg/g.

CR concentration was optimized, the initial sorption rate, h , the pseudo-second-order rate constant, k_2 , the amount of CR sorbed at equilibrium, q_e , the linear coefficient value, r^2 , and the chi-square test statistic function, χ^2 , obtained are presented in Table 3. The values of h and q_e increased with the increase in the initial concentration of CR, but the overall sorption rate decreased (from 9.63×10^{-2} at 30 mg/L to 3.00×10^{-2} at 150 mg/L) with the increase in the initial concentration.

The results presented in Figure 4 were obtained when the data obtained from the PKC dosage optimization were fitted into the pseudo-second-order model. The values of q_e and h decreased with the increase in the PKC dosage, while the overall reaction rate, k_2 , increased with the increase in the PKC dosage (from 4.78×10^{-2} at 0.1 g PKC to 12.38×10^{-2} at 0.8 g PKC) (Table 4).

The analysis of the results obtained when the two process variables were optimized, and the two error functions r^2 and χ^2 are presented in Tables 3 and 4. The linearities of the plots were very high (0.9999–1.000). The value of the chi-square error function (χ^2) was negligible. The extremely high values of r^2 and the negligible values of χ^2 confirm that the sorption process follows a pseudo-second-order mechanism. Mall et al.^{13,29} and Ho and McKay²⁴ have also reported the applicability of the pseudo-second-order kinetic model to the sorption of anionic dye from the aqueous phase by different sorbents of biological origin.

According to Ho and McKay,²⁴ if the dye uptake is chemically rate controlled, the pseudo-second-order rate constant will be independent of particle diameter and flow rate and will depend on concentration of the ions in solution. Logarithmic plots of pseudo-second-order constants, k_2 , and, h , versus initial CR concentration were made, and the plots were found to give straight lines whose linear regression values, r^2 , were given as 0.9186 and 0.887, respectively. Mathematical expressions were therefore drawn relating the two pseudo-second-order constants and initial CR concentrations as follows:

$$k_2 = 0.0038C_o^{-0.9168}$$

and

$$h = 0.0085C_o^{1.0077}$$

The corresponding linear plots of the values of q_e , k_2 , and h in terms of the initial CR concentrations were regressed to obtain expressions for these values in terms of the initial CR concentrations with high correlation coefficients: $A_q = 0.4602$,

$$B_q = 2.91, r^2 = 0.998; A_k = 5.000 \times 10^{-4}, B_k = 0.1037, r^2 = 0.9047; A_h = 1.1206, B_h = 20.253, r^2 = 0.9261.$$

Therefore, it is further considered that q_e , k_2 , and h can be expressed as a function of C_o for CR as follows:

$$q_e = \frac{C_o}{A_q C_o + B_q} \quad (7)$$

$$k = \frac{C_o}{A_k C_o + B_k} \quad (8)$$

$$h = \frac{C_o}{A_h C_o + B_h} \quad (9)$$

Substituting the values of q_e and h into eqs 7 and 9 and then into eq 6, the rate law for a pseudosecond order and the relationship of q_e , C_o , and h can be represented thus:

$$q_t = \frac{t}{1/(1.1206C_o + 20.253) + 1/(0.4602C_o + 2.91)t} \quad (10)$$

Equation 10 represents the generalized predictive model for CR sorbed at any time and the initial CR concentration within the given range.

The relationship between the equilibrium sorption capacity, q_e , and PKC dosage was linearized over the PKC dosage that was examined, and this relationship was found by linear regulation. A low coefficient of determination (0.7337) was obtained, possibly due to continuous increase in the sorption site, provided by the increase in sorbent dosage, at a fixed and relatively low sorbate concentration. The mathematical expression of this relationship is

$$q_e = S_{sd} + Y = -70.625 + 56.903 \quad (11)$$

where the constant Y , at 56.903 m/g, is the maximum sorption capacity. The fiber dose approaches 0, and S at -70.625 is related to the sorption potential of the fiber. The negative value of S shows that, with the increase in fiber dose, the equilibrium sorption capacity q_e is reduced. A comparison of the monolayer equilibrium capacity of some adsorbents for CR and other anionic dyes from aqueous solution from the literature is made with that obtained from this study in Table 5.

Dye Diffusion Mechanisms. The prediction of the rate-limiting step is an important factor to be considered in the adsorption process. It is governed by the adsorption mechanism,

Table 5. Comparison of Monolayer Equilibrium Capacity for Some Anionic Dyes with Other Biosorbents

q_m (mg/g)	adsorbent	adsorbate	reference
38.60	palm kernel fiber	4-bromoaniline-azo-1,8-dihydronaphthalene-3,6-disodium sulfate	16
30.50	spent brewery grains	Acid Orange 7	35
22.40	orange peel	Congo Red	36
19.88	orange peel	Acid Violet 17	37
14.40	peat	Acid Blue 25	1
4.42	banana pith	Acid Brilliant Blue	38
4.26	sugar cane dust	Rhodamine B	39
3.23	orange peel	Rhodamine B	39
1.33	orange peel	Procion Orange	36
66.23	palm kernel seed coat	Congo Red	thiswork

Table 6. Intraparticle Diffusion Parameters for the Removal of CR by PKC at Different Initial CR Concentrations (mg/L)

initial concn	K_{id1}	K_{id2}	I_1	I_2
30	2.9481	0.169	4.6171	10.243
60	5.5026	0.1801	9.6891	21.842
90	9.5086	0.1065	14.696	36.264
120	15.153	0.1511	19.625	51.428
150	16.485	0.2144	26.088	63.621

Table 7. Liquid Film Diffusion Parameters for the Removal of CR by PKC at Different Initial CR Concentrations (mg/L)

initial concn	$K_{fd} \times 10^{-2}$	I
30	4.30	-1.5156
60	5.31	-1.5978
90	4.36	-2.1166
120	3.94	-2.2826
150	4.62	-1.9549

which is generally for design purposes. Abstraction of dye from aqueous solution by a biosorbent is usually characterized by external mass transfer (boundary layer diffusion), intraparticle diffusion, or both. This process can be described by four consecutive steps:

- (I) transport of the solute from bulk solution through liquid film to the adsorbent exterior surface
- (II) diffusion across the liquid film surrounding the sorbent particle
- (III) particle diffusion in the liquid contained in the pore and in the sorbate along the pore walls
- (IV) sorption and desorption within the particle and on the external surface

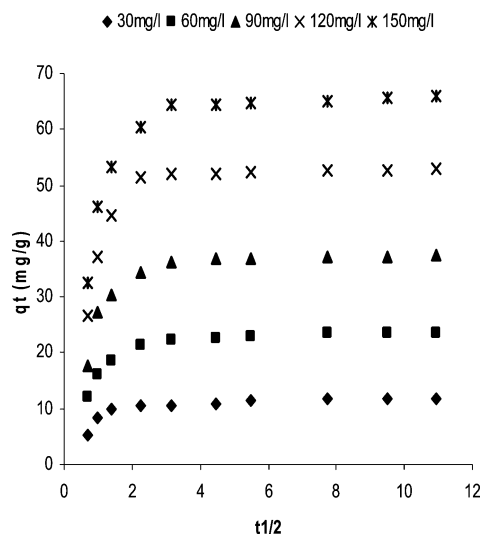


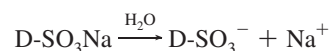
Figure 5. Intraparticle diffusion plots for the kinetics of sorption of CR by PKC at different initial CR concentrations (mg/L). Sorbent mass, 2.00 g; sorbate volume, 1.00 L; agitation speed, 120 rpm.

The first step and the last step are not considered as rate-limiting steps because the hydrodynamic condition outside the particle can easily be influenced by the agitation of the reacting mixture. This helps to avoid a concentrated gradient in the solution. Uptake of solution on the active site is regarded as a quasi-instantaneous mechanism. The overall rate of sorption is usually controlled by the slowest step, which could be either liquid film diffusion or pore diffusion (i.e., steps I and II).

(i) Intraparticle Diffusion. In order to investigate the possibility of CR being transported within the pores of PKC, the experimental data, obtained from the initial CR concentration optimization, were fitted into an intraparticle diffusion plot. The results in Figure 5 show the plots of the amount of CR sorbed, q_t (mg/g), versus $t^{0.5}$ ($\text{min}^{0.5}$). The deviation of straight lines from the origin (Figure 5) may be due to the difference in the rate of mass transfer in the initial and final stages of adsorption.³⁰ Further, such deviation of straight lines from the origin indicates that the pore diffusion is not the sole rate-controlling step.³¹

The results presented in Figure 5 show that two separate regions are found in the plot: the first straight portion is attributed to the micropore diffusion and the second linear portion is attributed to micropore diffusion.³² An attempt was made to determine the rate-controlling step between these two steps by determining the rate of intraparticle diffusion (K_{id}) from the intraparticle diffusion plots. A comparison of the K_{id} values, for the two stages, shows that the rate-limiting step is the micropore diffusion stage (Table 6). The boundary layer effects, as obtained from the intercepts of the plots, were also of greater effect at this stage than at the macropore diffusion stage (Table 6).

In the aqueous solution, the acid dye dissolved and the sulfonate groups of the acid dye ($\text{D-SO}_3\text{Na}$) are dissociated and converted to anionic dye ions, thus:¹³



Dye ions tend to aggregate (or self-associate) in aqueous solution. Due to aggregation, the adsorption of dye ions takes place in the macropores. CR is a relatively large molecule. Consequent upon this, rapid adsorption kinetics takes place at the macropores of the PKC, hence the high K_{id1} and low K_{id2} values obtained from the macropore and micropore diffusion stages, respectively.

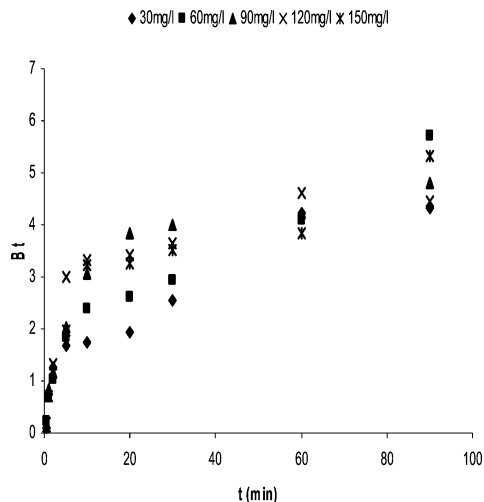


Figure 6. Boyd kinetics plots for the kinetics of sorption of CR by PKC at different initial CR concentrations (mg/L). Sorbent mass, 2.00 g; sorbate volume, 1.00 L; agitation speed, 120 rpm.

The lower K_{id2} values may also be attributed to a very slow diffusion of the adsorbate (CR) from the surface film into the micropores, which are the least accessible sites of adsorption. This also stimulates a very slow rate of migration of adsorbate from the liquid phase onto the adsorbent surface.

(ii) Liquid Film Diffusion. In order to understand the mechanism of CR uptake by the PKC, diffusion from the bulk liquid phase to the surface of an adsorbent was assumed; i.e., liquid film diffusion might also play a significant role in determining the rate processes. The plot of $-\ln(I - F)$ versus t , when the initial concentration was optimized in accordance with the liquid film diffusion model, yielded linear plots ($r^2 = 0.5856-0.9102$) with intercepts of $r^2 = -1.5156$ and -2.2826 . The rate constant for liquid film diffusion, K_{fd} , is in the range $3.94 \times 10^{-2}-5.31 \times 10^{-2}$ (Table 7).

The inability of the plots to pass through the origin (i.e., zero intercept) shows that the prediction of this model will have only limited applicability in the adsorption of CR by PKC.

In order to characterize what the actual rate-controlling step involved in the CR sorption process is, the sorption process was further analyzed by the kinetic expression given by Boyd et al.¹⁷

$$F = 1 - (6/\pi^2) \exp(-Bt) \quad (12)$$

where F is the fraction of solute sorbed at different times, t , and Bt is a mathematical function of F :

$$F = q/q_\infty \quad (13)$$

where q and q_∞ represent the amount sorbed (mg/g) at any time, t , and at infinite time. Substituting eq 12 into eq 13, the kinetic expression becomes

$$Bt = -0.498 - \ln(1 - q/q_\infty) \quad (14)$$

Thus the value of Bt can be calculated for each value of F using eq 14. The calculated Bt values were plotted against time (Figure 6), and the linearity test of the Bt versus t plot for different initial CR concentrations was employed to distinguish between the film diffusion and particle diffusion controlled adsorption. At low concentrations, the Bt versus t plot moves toward the origin, which indicates that intraparticle diffusion becomes rate controlling, while at high concentrations the plots do not pass

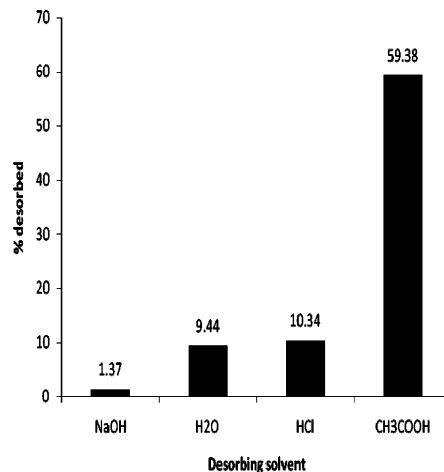


Figure 7. Batch desorption of CR from PKC using different eluting solvents. Desorbing solvent concentration, 0.1 M; agitation time, 120 min.

through the origin; this shows that film diffusion is the main rate-controlling parameter.

Desorption Studies. (i) Batch Desorption Studies. Batch desorption studies were carried out to explore the possibilities of PKC regeneration for reuse and the recovery of the sorbed dye. Mall et al.³³ opined that desorption studies could be used to elucidate the mechanism of an adsorption process. If the dye adsorbed on the adsorbent can be desorbed by water, it can be said that the attachment of the dye onto the adsorbent is by weak bonds. If strong acid or strong base can desorb the dye, the attachment of the dye to the sorbent is regarded as ion exchange. If organic acid can desorb the dye, the adsorption of the dye onto the adsorbent is taken to be chemisorption.³³

Different eluting solvents (deionized water, HCl, NaOH, and CH_3COOH) that cut across these classifications were used in the desorption of the CR from the biomass used. The results obtained are presented in Figure 7. A very low desorption of the dye was observed when NaOH, HCl, and deionized water were used, while an appreciable amount of the dye was desorbed when CH_3COOH was used. The appreciable amount of dye desorbed with the use of CH_3COOH could be ascribed to the role of chemisorptions in the uptake of CR by PKC. The undesorbed portion of the dye in the sorbate could be ascribed to the complex formation between the CR and the active sites on the PKC, hence the inability of the eluting solvents to completely desorb the dye.

Fixed Bed Desorption. In a typical batch desorption system, the desorbed pollutants remain in the batch system, making a complete desorption difficult. Moreover, the applicability of the data to most treatment systems, where contact time is not sufficient for the attainment of equilibrium, is limited. Fixed bed desorption allows a more efficient use of the biosorbent, as a consequence of the enhanced use of the pollutant concentration difference between solution and sorbent.

The desorption procedure in a fixed bed is described using the concept of an elution curve, which is also known as a desorption step. The elution curve normally has an unsymmetrical frequency distribution, with a rapid increase of the released sorbate concentration followed by a flat diminution.³⁴ This produces the appearance of a peak that provides two important parameters: C_p , the maximum concentration peak, which measures the eluted sorbate at this point, and t_p , the time passed until the effluent concentration peak reaches its maximum value (it gives an idea of the elution rate). The elution curve can be described by the elution efficiency (E). This parameter

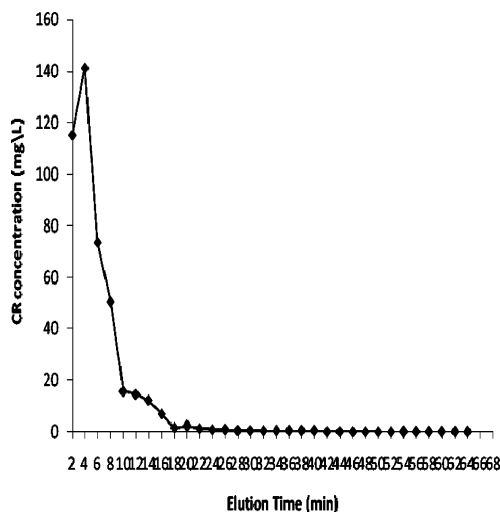


Figure 8. Elution curve for CR desorption in a fixed bed of PKC. Sorbent mass, 50 g; bed height, 10 cm; flow rate, 20 mL/min.

was obtained by dividing the sorbate mass desorbed (m_d) by the sorbate mass bound to the sorbent in the previous adsorption step (m_{ad}):

$$E (\%) = \frac{m_d}{m_{ad}} \times 100 \quad (15)$$

where m_d is calculated from the numerical integration of the regeneration curves from $t = 0$ to t_e with the following equation:

$$m_d = 0.06F \int_{t=0}^{t=t_e} C_d dt \quad (16)$$

where t_e is the time passed until residual sorbate concentration (less than 0.02 mg L^{-1}) was found in the effluent.

In the present studies desorption was carried out in a fixed bed of previously CR loaded PKC using $0.1 \text{ M CH}_3\text{COOH}$, the best eluting solvent, from the batch desorption studies. The elution curve, obtained from the desorption of CR from PKC, is presented in Figure 8. A rapid desorption of the sorbed CR was obtained at the inception of the studies, and this was followed by a flat diminution. The C_p was 141.46 mg L^{-1} and the t_p was 4 min. The elution efficiency, E , was 85.67. An elution efficiency of 85.67% could be considered to be high for any desorption process.

Consequent upon the copiousness of the PKC, as an agricultural waste with little or no great value, at present, except for the cost to be incurred in its collection and transportation, the cost of PKC will be relatively paltry compared with that of the conventional adsorbent (i.e., activated carbon). The cost of activated carbon makes the recovery of the dye and the regeneration of the adsorbent compulsory.³³ Premised on this fact, the exhausted PKC along with the adsorbed dye could be dried and used as a fuel in boilers/incinerators, or could be used for the production of fuel briquettes. The bottom ash may be blended with clay to make firebricks or with a cement–concrete mixture to make colored building blocks, thus disposing of dyes through chemical and physical fixation.³³

Conclusion

The ability of PKC to abstract CR, an anionic dye, from an aqueous system was studied in a batch adsorption system. The two process variables optimized were the initial CR concentration and PKC dosage. Studies on the effect of initial concentra-

tion on the dynamics of the adsorption process showed that an increase in dye concentration results in an increase in the amount of dye sorbed per unit mass of adsorbent. The initial uptake of dye was found to be rapid at the inception of the sorption reaction, i.e., the first 5 min. It slows down with time as the sorption process proceeds and equilibrium is attained. The results obtained when the PKC dosage was optimized shows that the amount of CR sorbed per unit (g) of PKC decreased with an increase in PKC dosage while the amount of CR (%) sorbed increased with an increase in PKC dosage.

The data obtained from the sorption dynamics studies were fitted into two kinetic models (i.e., pseudo-first-order and pseudo-second-order kinetic models). Linear coefficients of determination and nonlinear chi-square test statistics were used to test the fitting of these kinetic models. The pseudo-second-order kinetic model was found to best fit the experimental data within the time range of sorption. Intraparticle diffusion was found to be the rate-controlling parameter at low concentration, while at high concentration film diffusion is the main rate-controlling parameter. The results of the batch desorption studies showed that chemisorption played a prominent role in the sorption process. The elution curve, obtained from the continuous desorption studies, showed that the elution rate was fast and a high elution efficiency could be obtained with $0.1 \text{ M CH}_3\text{COOH}$, as an eluting solvent.

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