Kinetics and Isotherm Studies on Methylene Blue Adsorption onto Ground Palm Kernel Coat

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Abstract

Palm kernel coat (PKC) was collected from an oil palm seed processing factory and the residual oil on the PKC was removed by saponification. The ability of the PKC to remove Methylene Blue (MB), a basic dye from waste stream, was studied by the method of continuous variation of 2 process variables: Initial MB concentration (mg/l) and PKC dosage (g/l). The amount of MB sorbed per gram of PKC (q_t mg/g) increased with increasing initial MB concentration while a reverse trend was observed when the PKC dosage was increased. The experimental data were fitted into the following kinetic models: Lagergren pseudo-first order, the chemisorptions pseudo-second order, Elovich kinetic model, and the intraparticle diffusion model. It was observed that chemisorptions pseudo-second order kinetic model described the sorption process with high coefficients of determination (r^2) better than any other kinetic models. The equilibrium isotherms, for the sorption of MB on PKC, were analyzed using 3 widely used isotherm models (Langmuir, Freundlich, and Temkin isotherm models). Error analysis, using the linear correlation coefficients (r^2), showed that the Langmuir isotherm best fits the MB adsorption data on PKC. The monolayer coverage capacity of the PKC, obtained from the Langmuir isotherm studies, was 277.77 mg/g. Thermodynamics showed that the adsorption of MB on PKC was most favorable and spontaneous.

Key Words: Palm kernel, Sorption, Methylene blue, Pseudo, Kinetics, Equilibrium.

Introduction

In recent years, the screening of sorbents of cellulosic origin, termed biosorbents, has continued to be a relentless exercise, embarked upon by environmental scientists and engineers, because of the inherent merits they posses. They have been found to be accessible, cheap, reliable, and possessing the ability to complete favorably with the conventional sorbents. It is of note that concerns over the task of sorbent regeneration and the mode of handling of the product of the sorption process (i.e. the used sorbent) has also been allayed by the fact that some of this sorbents got very cheap and need no regeneration hence they can end up as biofuels. It has also been reported (Nigam et al., 2000; Robinson et al., 2001) that once the dye has been adsorbed on the agricultural substrate, it is in a more treatable form and can then be treated through solid state fermentation (SSF). SSF of the dye adsorbed will degrade the dye and simultaneously enrich the nutritional value of the waste. This fermented substrate then has the potential to be used as soil conditioner or fertilizer. Consequent upon this, the use of biosorbents can find application in the developing world, remote sites in use for only short periods of the year, farm settlements, and cottage industries.

Dye contaminated wastewater originates from a number of industries, such as textile, metal plating, packaging, and paper industry. The need for the treatment of dye contaminated wastewater arose from the environmental impact. They impart objectionable color on water bodies and retard photosynthesis hence lead the aquatic life on the path of

extinction. Some dyes have been found to act as substrate for metal ions and may import contamination by heavy metals (Strivastava et al., 1984). It has also been reported that many dyes and pigments have toxic as well as carcinogenic, mutagenic, and teratogenic effects on aquatic life as well as humans (McKay et al., 1985; Gregory et al., 1991).

A number of biosorbents have been reported to have high sorptive capacity for dye in aqua systems (e.g. Waranusantiangul et al., 2003; Bhattacharyya and Sharma, 2005; Netpradit et al., 2004; Al-Ghouti et al., 2003; Oladoja et al., 2008a, 2008b, 2008c). Palm kernel coat (PKC), the sorbent used in the present study, is obtained from the oil palm tree (*Elais guineensis*). This tree is native to the west coast of Africa and widespread in the tropics. *Elais guineensis* and *Elaeis Oleifera* (i.e. the American oil palm) are members of the family *Arecaceae* (formerly: *palmae*). Virtually all parts of the oil palm tree have been utilized in one form or the other. Over 15,600 t of shell and fiber are generated annually and only about 5% of the waste is sometimes used as biofuel (Latey and Acquah, 1999).

The use of palm kernel coat in the treatment of lead contaminated water has been reported by Ho and Ofomaja (2005a, 2005b). They collected palm kernel coat that has been allowed to age or decay with residual oil, after processing, for about 2 months, and studied its potential for lead ion removal from aqueous solution. In the present study, the palm kernel coat was obtained as soon as the oil was extracted from it. The residual oil on it was not allowed to biodegrade but was removed by saponification. The ability of this sorbent (i.e. PKC) to remediate water contaminated with MB basic dye was investigated. The sorption capacity of PKC was evaluated using 3 equilibrium isotherm models (Langmuir, Freundlich, and Temkin isotherm models) and the sorption dynamics were analyzed using pseudo first order, pseudo second order, and Elovich kinetic models.

Materials and Methods

Preparation of sorbent

PKC was obtained from a small scale palm oil processing factory, situated in Akungba-Akoko (a university town), Nigeria. Raw PKC was steeped in warm deionized water, to melt the residual oil on the PKC. PKC was separated from warm deionized water and 0.5 M of NaOH was added to PKC for al-

kaline 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 a particle size of 53-74 μm. This fraction was then stored in an air tight plastic container pending usage.

Preparation of sorbate

MB (C_{16} H_{18} Cl N_3 S), the sorbate used in the present study, is a monovalent cationic dye. It is classified in dye classification as C.I. Basic blue 9, C.I. Solvent blue 8, and C.I. 52015. It has a molecular weight of 373.90. The Methylene Blue (MB) (BDH 85%) was used as supplied. A stock solution of 1000 mg/l was prepared and the working solutions were prepared by diluting the stock solution with deionized water as required.

Sorbate quantification The MB concentrations in the aqua medium were quantified by the determination of the absorbance at the characteristic wavelength using a double beam UV/Visible spectrophotometer. 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 ($\lambda_{max} = 661$ nm), as determined from this plot, was noted and the wavelength was used for the preparation of the calibration curve used in the present study.

Sorption studies

Sorption dynamics

i) Effect of initial concentration

The effect of initial concentration of MB was studied using a range of MB concentrations [50,500 mg/l]. A typical experimental procedure was conducted by measuring accurately a liter of the MB solution of known concentration, 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, centrifuged, and the supernatant was analyzed for residual MB using a UV/visible spectrophotometer. The amount of MB 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 2 g/l – 16 g/l of MB solution. The experiment was conducted by measuring a liter of 500 mg/l of MB solution into a 2 l conical flask. Appropriate dosage of the PKC was measured into it and agitated [200 rpm] for 120 min. Samples were withdrawn, at fixed intervals, and analyzed for residual MB and the amount of sorbate sorbed per unit mass of the PKC [q in mg/l] was calculated using the mass balance procedure.

Equilibrium isotherm studies The isotherm studies were carried out using a range of initial MB concentration of 50-500 ml. A typical experiment was conducted in a batch process by adding 0.1 g of the PKC to 50 ml of different concentrations of the MB solution. The mixture was agitated for a predetermined period of time at a constant speed. At the expiration of this period, the mixture was centrifuged and the residual MB concentration was determined using UV/visible spectrophotometer at the wavelength of 661 nm, which was found to be the $\lambda_{\max}$ of MB.

Results and Discussion

A proximate analysis of the saponified PKC was carried out using the recommended standard methods of analysis (AOAC, 1990). The results obtained from the analysis showed that the saponified PKC contained (in % dry weight): protein 18.72%, lipid 3.72%, ash 1.37%, fibre 24.9%, carbohydrate 51.29%, Ca 0.5%, Mg 0.14%, Na 0.21%, K 0.05%, P 0.03%, and 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/m^3). 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%), and <63 (3.60%).

Sorption dynamics

The dynamics of sorption describes the rate of MB uptake on PKC and this rate controls the equilibrium time. Information on the dynamics of sorption is required for selecting optimum operating conditions for the full scale batch process (Gupta et al., 1997). In order to study the mechanism of sorption and potential rate determining steps, different kinetic models have been used to test experimental data obtained from 2 process variables (initial MB concentration and PKC dosage). The sorption dynamics of the adsorption by PKC were tested with the Lagergren pseudo-first order, the chemisorptions pseudo-second order (Ho, 1995), Elovich kinetic model (Chien and Clayton, 1980), the intraparticle diffusion model (Weber and Morris, 1963), and liquid film diffusion model (Boyd et al., 1949).

The linearized form of the pseudo-first order equation of Lagergren is generally expressed as follows:

$$\log[q_e - q_t] = log[q_e] - [k_1/2.303]t \qquad (1)$$

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; k_1 and q_e can be calculated from the slope and intercept of the plot, respectively.

The pseudo second order kinetic model is represented by the following linear equation:

$$t/q_t = 1/kq_e + 1/q_e t \qquad (2)$$

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/qt against t of Eq. (2) should give a linear relationship; 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.

A simplified linearized form of Elovich kinetic equation is presented as follows:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \qquad (3)$$

If the sorption of MB on PKC fits the Elovich Model, a plot of qt versus ln (t) should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)$ ln $(\alpha\beta)$.

Several steps are involved in the sorption of sorbate by a sorbent. These involve transport of the solute molecules from the aqueous phase to the surface of the solid particulates and diffusion of the solute molecules into the interior of the pores, which is usually a slow process. The intra-particle diffusion rate constant (k_{id}) is given by the following equation:

$$q_t = k_{id}t^{0.5} \qquad (4)$$

When intra-particle diffusion plays a significant role in controlling the kinetics of the sorption process, the plots of qt versus $t^{0.5}$ yield straight lines passing through the origin and the slope gives the rate constant k_{id}.

However, when the transport of the solute molecules from the liquid phase up to the solid phase, boundary plays the most significant role in adsorption; the liquid film diffusion model may be applied as follows:

$$\ln(1 - F) = -k_{fd}t \qquad (5)$$

where F is the fractional attainment of equilibrium F = q_t/q_e and k_{fd} is the adsorption rate constant. A linear plot of –ln (1-F) vs. t with zero intercept would suggest that the kinetics of the sorption process is controlled by diffusion through the liquid film surrounding the solid sorbent.

Effect of initial MB concentration

The effect of initial concentration on the sorption of MB on PKC is presented in Figure 1. This result was obtained at the initial concentration range of 50-500 mg/l of MB at a fixed sorbent dosage (2 g/l) and fixed agitation speed (200 rpm). In the range of MB concentration studied, the uptake of the MB was rapid in the first 5 min. The rapid uptake then gave way to a much slower adsorption after 5 min (Figure 1). This initial rapid uptake can be attributed to the concentration gradient created at the start of the adsorption process between solute concentration in solution and that at the PKC surface. As the dye loading increases on the sorbent, this gradient reduces and gives way to a slower uptake.

The results presented in Table 1 were obtained from the sorption experiment were analyzed with the Lagergren pseudo-first order kinetic model. The val-

ues of log (q_e-q_t) were plotted against time (min). The linearity of the plots were not so high (R^2 = 0.738 - 0.8616). The first order rate constant ranged between 6.40×10^{-2} and 3.62×10^{-2}. The pseudo first order theoretical q_e values, obtained from the intercept of the linear plots, were compared with the experimental q_e values (Table 1). The pseudo first order kinetic model suffered from inadequacies when applied to MB sorption on RSS at varying MB concentrations. The experimental q_e values differ from the corresponding theoretical values. Discrepancies of this nature have been reported (Ho and McKay 1998 and 1999; Gupta and Bhattacharya, 2006). Owing to the low linearity of the plots obtained from this study and the discrepancies noted in the theoretical and experimental values of q_e, chemisorptions pseudo second order kinetic model was also used to test the data obtained from the same studies.
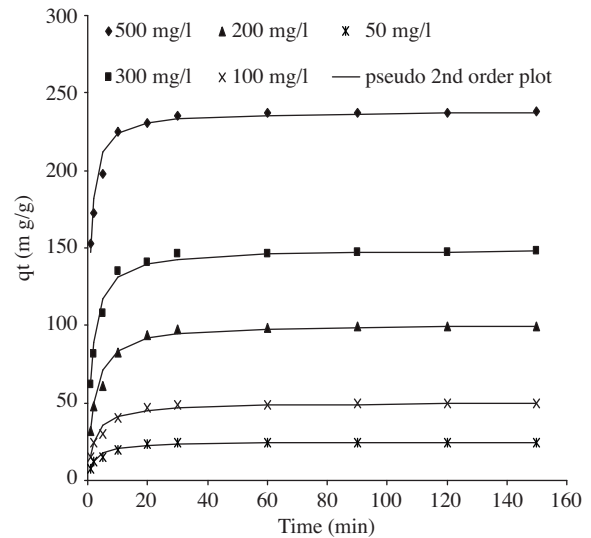
Figure 1. Effect of initial concentration (mg/l) and time on the sorption of MB by PKC.

Table 1. Pseudo first order kinetic parameters for the removal of MB by PKC at different initial MB concentrations (mg/l) and PKC dosages (g).

| Initial conc.(mg/l)	$q_{e(exp)}$	$q_{e(the)}$	$K_1 \times 10^{-2}$	r^2	Sorbent Dose(g)	$q_{e(exp)}$	$q_{e(the)}$	$K_1 \times 10^{-2}$	r^2 r^2
500	238.35	32.26	3.89	0.8236	0.1	238.35	32.26	3.89	0.8236
300	147.75	27.19	4.12	0.738	0.2	120.59	18.51	3.11	0.7967
200	99.28	23.26	6.40	0.7974	0.4	61.68	10.60	3.80	0.8501
100	49.55	13.14	4.17	0.7707	0.6	41.35	6.44	4.10	0.8029
50	24.80	8.09	3.62	0.8616	0.8	31.07	3.67	4.51	0.7673

It can be inferred from this plot (Figure 2) that the possibility of the chemisorptions playing a significant rule in the rate determining step cannot be rule out. This fact is attested to by the very high linearity of the plot (Table 2). The pseudo second order parameters, q_e, h, and k, obtained from the pseudo second order plot are presented in Table 2. The initial sorption rate, h, $(11.29 - 384.37$ mg/g) min varies directly with the initial MB concentration, while an inverse relationship exists between the overall sorption rate $(6.78 \times 10^{-3} - 1.78 \times 10^{-3})$ and initial MB concentration.

The data obtained from the sorption experiment were also tested with the Elovich kinetic model and the linearity values of the plots of qt versus ln (t) and the Elovich parameters are presented in Table 3. The results presented in Table 3 showed that this kinetic model described the sorption process better than the pseudo first order model but not as well as the pseudo second order kinetic model.

Effect of sorbent dosage

The effect of PKC dosage on the sorption of MB was studied at the PKC dosage range of 2-16 g/l, MB concentration of 500 mg/l, and a fixed agitation speed (200 rpm). The results obtained from this study are presented in Figure 3. The amount of MB sorbed per gram of the PKC (q_t mg/g) reduced
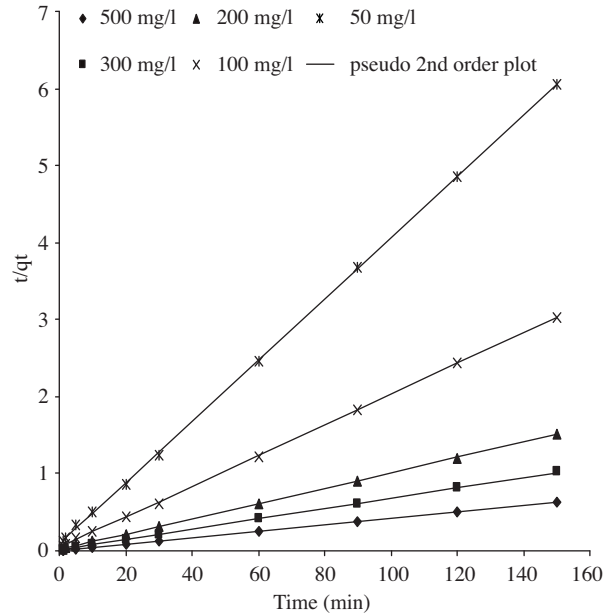
Figure 2. Pseudo second order plot of the effect of initial MB concentration (mg/l) on the sorption of MB by PKC.

Table 2. Pseudo second order kinetic parameters for the removal of MB by PKC at different initial MB concentrations (mg/l) and PKC dosages (g).

| Initial conc.(mg/l)	q_e	h	$K_2 \times 10^{-3}$	r^2	Sorbent Dose(g)	q_e	h	$K_2 \times 10^{-3}$	r^2
500	238.35	384.37	6.78	0.999	0.1	238.35	284.37	6.78	0.999
300	149.25	109.89	4.93	0.999	0.2	120.48	137.03	9.44	1.000
200	101.01	48.06	4.71	0.999	0.4	62.11	66.74	17.30	1.000
100	50.25	23.42	9.27	0.999	0.6	41.67	46.88	27.00	1.000
50	25.19	11.29	17.80	0.999	0.8	31.25	37.21	38.10	1.000

Table 3. Elovich kinetic parameters for the removal of MB by PKC at different initial MB concentrations (mg/l) and PKC dosages (g).

Initial conc.(mg/l)	β	α	r^2	Sorbent Dose(g)	β	α	r^2
500	0.060	3.58	0.8614	0.1	0.060	3.58	0.8613
300	0.060	1.66	0.8545	0.2	0.115	4.40	0.8798
200	0.074	1.17	0.8922	0.4	0.217	5.92	0.9022
100	0.147	1.56	0.8982	0.6	0.303	4.77	0.8716
50	0.294	2.42	0.8964	0.8	0.424	7.75	0.8898

with increase in the dosage of PKC. This reveals that the instantaneous and equilibrium sorption capacities of MB are functions of the PKC dosage. Increasing the dosage of the PKC and keeping the MB concentration constant makes a large number of sites available for a fixed concentration of sorbate, hence the reduction in the value of q_t and q_e. The analysis of the results obtained in the present study with different kinetic models is presented in Table 1. The conformance of this plot to the pseudo second order plot is extremely high (Figure 4), which shows that the sorption of MB on PKC at varying sorbent dosage obeys the pseudo second order chemisorptions kinetic model. The pseudo second order parameters, h, k, and q_e, are presented in Table 2.
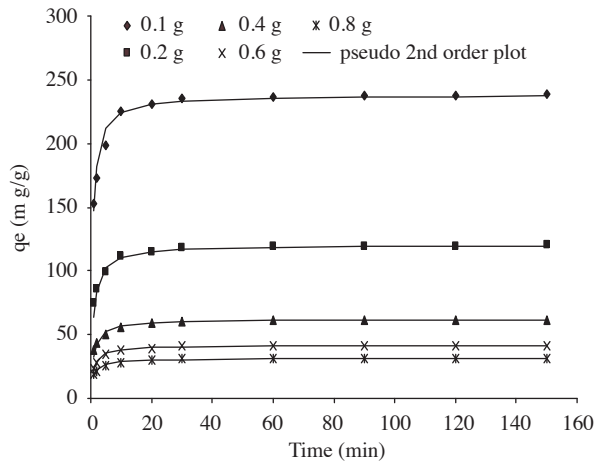
Figure 3. Effect of Sorbent dosage (g) and time on the sorption of MB by PKC.
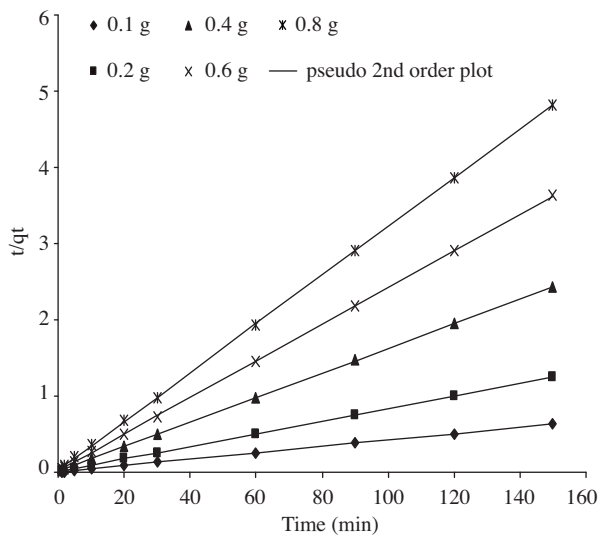
Figure 4. Pseudo second order plot of the effect of sorbent dosage (g) on the sorption of MB by PKC.

Macro and micro-pore diffusion

The mechanism of adsorption of a sorbate on a sorbent follows a series of steps. The slowest of these steps control the overall rate of the process. Generally, pore and intraparticle diffusion are often-rate limiting in a batch reactor while, for a continuous flow system, film diffusion is more likely the rate limiting step (Goswami and Gosh, 2005). Though there is a high possibility for pore diffusion to be the rate limiting step in a batch process, the adsorption rate parameter, which controls the batch process for most of the contact time, is the intraparticle diffusion (Weber and Morris, 1963; Allen et al., 1989)

The most widely applied intraparticle diffusion equation for sorption system is given by Weber and Morris (1963) as follows:

$$q_t = k_i t^{0.5} \tag{6}$$

where k_i is the intraparticle rate constant (mg/g mm$^{0.5}$).

According to Weber and Morris (1963) if the rate limiting step is intraparticle diffusion, a plot of solute sorbed against the square root of the contact time should yield a straight line passing through the origin. The plots obtained (results not shown for brevity) are related by 2 straight lines; the first straight portion depicting the macropore diffusion and the second representing the micropore diffusion (Allen et al., 1989). The deviation of the straight lines from the origin may be due to the difference in the rate of mass transfer in the initial and final stages of adsorption (Panday and Prasad, 1986; Mall et al., 2006). The values of K_{id1} and k_{id2} (Table 4) indicate that the pores are micropores and the intraparticle diffusional resistance is due to micropores only (Goswami and Gosh, 2005). The diffusion rate parameters indicate that the intraparticle diffusion controls the sorption rate, which is the slowest step of the sorption process.

Equilibrium isotherm studies

Equilibrium isotherm is described by a sorption isotherm, characterized by certain constants whose values express the surface properties and affinity of the sorbent sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that at the sorbent interface. In order to quantify the affinity of PKC for the basic

Table 4. Macro- and micro-pores diffusion parameters for the removal of MB by PKC at different initial MB concentrations (mg/l) and PKC dosages (g).

Initial conc.(mg/l)	K_{id1}	K_{id2}	r^2	Sorbent Dose(g)	K_{id1}	K_{id2}	r^2
500	33.78	0.842	0.9914	0.1	32.78	0.842	0.9914
300	33.05	0.705	0.9921	0.2	16.61	0.592	0.9838
200	22.46	0.582	0.9845	0.4	8.01	0.337	0.9731
100	10.81	0.317	0.9651	0.6	6.28	0.187	0.9651
50	5.45	0.155	0.9644	0.8	4.05	0.110	0.9787

dye studied, i.e. MB, 3 widely used isotherm models (Langmuir, Freundlich, and Temkin isotherm models) were used to analyze the data obtained from the sorption process.

The monolayer coverage of the sorbate on a sorbent surface at a constant temperature is represented by the Langmuir isotherm. The basic assumption is that the forces exerted by chemically unsaturated surface atoms do not extend further than the diameter of one sorbed molecule. The Langmuir isotherm hints towards surface homogeneity (Eq. (7)).

Langmuir Isotherm: $C_e/q_e = [1/K_d q_m] + [1/q_m]C_e$
(7)

where q_e is the amount of MB sorbed at equilibrium per mass of PKC (mg/g); C_e is the concentration of the dye in aqueous phase at equilibrium; K_d is the sorption equilibrium constant; q_m (mg/g) is the monolayer capacity.

The monolayer coverage is obtained from a plot of C_e/q_e versus C_e. The slope and the intercept of the linear graph obtained from this plot give the value of q_m and K. The Langmuir equilibrium adsorption curves relating solid and liquid phase concentration of MB at equilibrium is given as:

$$q_e \frac{75.83C_e}{1 + 0.273C_e}$$

The Freundlich Isotherm: $q_e = K_f C_e^n$ (8)

The Freundlich isotherm is an empirical equation that encompasses the heterogeneity of sites and the exponential distribution of sites and their energies (Eq. (8)). The Freundlich coefficients n and K_f are obtained from the plots of $\ln q_e$ versus $\ln C_e$. The Freundlich equilibrium adsorption curves relating the solid and liquid phase concentration of MB at equilibrium are given as follows:

$$q_e = 55.22C_e^{1.870}$$

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy (Temkin, 1940). The Temkin isotherm is given as:

$$q_e = BlnA + B\ln C_e \qquad (9)$$

where A (l/g) is the equilibrium binding constant, corresponding to the maximum binding energy, and constant B is related to the heat of adsorption. A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants B and A from the slope and intercept of the straight line plot. The Temkin equilibrium adsorption curves relating the solid and liquid phase concentration of MB at equilibrium are given as follows:

$$q_e = 69.514\ln 1.619C_e$$

The 3 isotherm model parameters along with the regression coefficients are listed in Table 5. The fitting of the data, obtained from the sorption of MB on PKC, to the 3 isotherm models showed that the linearity of the Langmuir isotherm models ($r^2 = 0.9968$) was higher than that of the other isotherm models (Table 5). This shows that the sorption of MB on PKC is more of monolayer sorption rather than sorption on a surface having heterogeneous energy distribution. The experimental adsorption capacity and the adsorption capacity predicted by the Langmuir isotherm model were compared and the results are presented in Figure 5. The results of the comparison of the value of q_m (mg/g) obtained from the present study with results from other studies are presented in Table 6.

Table 5. Equilibrium isotherm parameters for the removal of MB by PKC.

Langmuir parameters	Freundlich Parameters	Temkin parameters
q_{emax} = 277.77 mg/g	n = 1.870	A = 1.619
K_a= 0.273 dm^3/mg	K = 55.219 mg/g	B = 69014
r^2 = 0.9968	r^2 = 0.8937	r^2 = 0.989

Table 6. Comparison of the Langmuir Sorption Capacity (q_m in mg/g) of different sorbents for MB.

Sorbent	q_m(mg/g)	Reference
PKC	277.77	Present study
Carbonized spent bleaching earth	94.5	Low et al. (1995)
Coal	230	McKay et al. (1986)
Cotton waste	240	McKay et al. (1986)
Coconut husk	99	Low and Lee (1990)
Diatomaceous earth	198	Al Ghouti et al. (2003)
Hair	120	McKay et al. (1986)
Hexane extracted spent bleaching earth	120.5	
Hydrilla Verticillata	198	Low et al. (1993)
Spirodela polyrrhiza (at pH 7)	119	Waranusantigul et al. (2003)
Spirodela polyrrhiza (at pH 9)	144.93	Waranusantigul et al. (2003)
Water hyacinth root	128.9	Low et al. (1995)
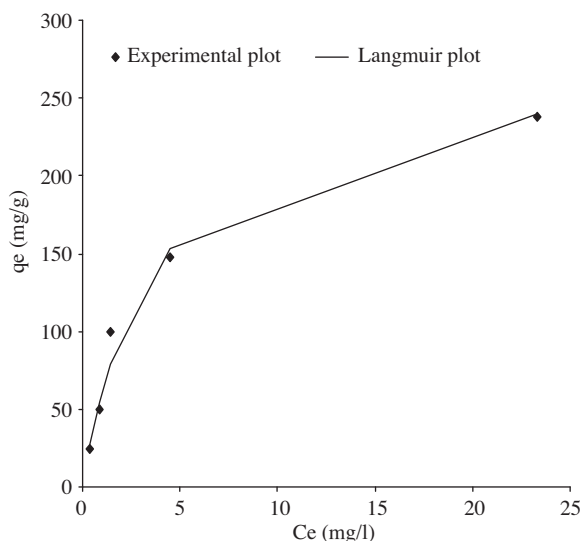
Figure 5. Langmuir equilibrium sorption isotherm plot of the sorption of MB by PKC.

Sorption thermodynamic

The thermodynamic parameter, the Gibbs free energy change (ΔG°), is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity. The free energy of adsorption was obtained from the Langmuir isotherm equations as follows:

$$-\Delta G^o_{ads} = RT\ln(K) \qquad (10)$$

where ΔG^o is the free energy change (kJ/mol), T is the absolute temperature (K), R is the universal gas constant (8.314 J mol/K) and K is the Langmuir constant. The Gibbs free energy of adsorption (ΔG) can be related with the equilibrium constant K (l/mol) corresponding to the reciprocal of the Langmuir constant b.

The Gibbs free energy of adsorption (ΔG°) of MB on PKC, as calculated from the Langmuir constant, was found to be -32.71 kJ/mol. Similar values have been reported for the sorption of Malachite green, a basic dye, on bagasse fly ash, commercial activated carbon, and laboratory grade activated carbon (-33.62; -33.51, and -33.08 kJ/mol, respectively) (Mall et al., 2005). The negative value of ΔG° confirmed the feasibility of the process and the spontaneous nature of sorption with a high preference of MB on PKC.

Conclusion

The time–concentration profile and the equilibrium isotherm studies showed that PKC can be effectively utilized for the removal of MB from solution. The effect of initial MB concentration and PKC dosage

on the sorption dynamics of MB on PKC was studied. The experimental data obtained from various studies were fitted to 4 different kinetic models but the results showed an extremely high coefficient of determination (r^2) when it was fitted to the pseudo second order kinetic models. The rate of sorption was also found not to be controlled by a singular rate limiting step. The equilibrium isotherm studies showed that the sorption of MB on PKC is more of monolayer sorption rather than sorption on a surface having heterogeneous energy distribution monolayer. The monolayer coverage capacity of the PKC was 277.77 mg/g, which is comparable with the monolayer coverage capacity of other sorbents previously studied by other researchers. The Gibbs free energy of adsorption ($\Delta G°$) of MB on PKC, as calculated from the Langmuir constant was found to be -32.71 kJ/mol. The negative value of $\Delta G°$ confirmed the feasibility of the process and the spontaneous nature of sorption of MB on PKC.

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