

Full Length Research Paper

Kinetics and thermodynamic studies of adsorption of malachite green onto unmodified and EDTA-modified groundnut husk

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Accepted 20 November, 2012

A batch experiment was applied to study the adsorption of malachite green from aqueous solution by unmodified and ethylene diamine tetraacetic acid (EDTA)-modified groundnut husk. The effect of initial dye concentration, temperature, contact time and pH on the sorption process was investigated. The Langmuir and Freundlich adsorption isotherms were applied to test the experimental data. The chemically modified groundnut husk agreed well with both the Langmuir and Freundlich models at the temperature below the room temperature (25°C) and above the room temperature. Unmodified groundnut husk showed poor agreement with the isotherm at temperature below the room temperature but fits well into the model at higher temperature. Kinetics of the adsorption with respect to the initial dye concentration and temperature was also investigated. The pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to test the kinetic data. Obtained data were fitted properly in the pseudo-second-order kinetic model. The thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also determined and the results obtained confirmed that the sorption process is feasible, spontaneous, and endothermic.

Key words: Adsorption capacity, ethylene diamine tetraacetic acid (EDTA)-modified, groundnut husk, diffusion, Kinetic modelling.

INTRODUCTION

There has been increasing scientific concern about the hazardous effects of coloured dyes which are widely used in industries such as textile, leather, paper, plastics, and food technology etc. to colour their final products (Mohamed, 2004). These industries are the important sources of contaminants responsible for the continuous pollution of the environment. Reactive dyes exhibit a wide range of different chemical structures, primarily based on substituted aromatic and heterocyclic groups. A large number of reactive dyes are azo compounds that are linked by an azo bridge (Change et al., 2001). Many reactive dyes are toxic to some organisms and cause direct destruction of aquatic creatures (Schnick, 1998). In addition, since reactive dyes are highly soluble in water,

their removal from effluent is difficult by conventional physicochemical and biological treatment methods (Ozacar and Sengil, 2003).

Malachite green (4-[(4-dimethylaminophenyl)phenylmethyl]-N,N-dimethylaniline) is a basic dye that is mostly used in industries (Khaltri et al, 1997 and Papinulti et al, 2006). Though the use of this dye has been banned in several countries and has not been approved by the US Food and Drug Administration (Raymond et al, 1984). Nevertheless, it is still being used in many parts of the world due to its lack of a proper alternative (Pacic et al., 2004). When malachite green is discharged into receiving streams, it affects the aquatic life and causes detrimental effects in the liver, gill, kidney, intestine and the pituitary gland of living organism (Srivastava et al., 2004). Therefore, the treatment of effluent containing such dye is desirable due to its aesthetic impacts on receiving waters.

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Table 1. Some important properties of dye (malachite green) used.

Item	Detail
Name of dye	Malachite green (MG ⁺)
CI name	Basic green 4 (BG4)
Colour index number	42,000
Empirical formula	C ₂₃ H ₂₅ N ₂ Cl
Molecular weight	365
Dye contents	90%
Maximum wavelength of absorption	619 nm

Various techniques have been employed for the removal of dyes from wastewaters. These methods include adsorption, nano-filtration, electro-kinetic coagulation, coagulation and precipitation, advanced chemical oxidation, electrochemical oxidation, ozonisation, supported liquid membrane, liquid-liquid extraction, and biological process (Mahmoud et al., 2007). The adsorption process is one of the efficient methods to remove dyes from effluent due to its low initial cost, simplicity of design, ease of operation, and insensitivity to toxic substance (Robinson et al., 2001). Activated carbon is the most widely used adsorbent with great success due to its large surface area, micro-porous structure, high adsorption capacity etc. However, its use is limited because of its high cost. This has led to research for cheaper substitutes (Allen and Koumanova, 2005). Many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk, date pits, saw dust, wool waste, coconut shell, rice to remove dyes and metal ions in effluents (Arivoli et al., 2007a, b; Sekaran et al., 1995; Selvarani, 2000).

Other materials including fly ash, tree bark, and human hair have been tested and are reported to give good results in several areas of application (Malik, 2003). However, the adsorption capacities of the above adsorbents are not very high. In order to improve the efficiency of the adsorption processes, it is necessary to develop cheap and easily available adsorbent with high adsorption capacities. Research for a low-cost and easily available adsorbent has led to the investigation of materials of biological origin as potential adsorbent.

Groundnut husk, an agricultural waste material, that is widely cultivated in both Northern and South-western Nigeria and indiscriminately litters around Nigeria urban areas has attracted the attention of many researchers as a potential adsorbent to concentrate and adsorb metal ions. Groundnut husk is cellulose that contains polysaccharide with carboxyl acid functional groups, hydroxyl groups, carboxyl groups of alginate and amino groups. It has been observed that biosorbent needs further modification to increase the active binding site and also make them available for sorption (Huang et al., 1996). Treatment of biomass removes the surface impurities on the biosorbent and exposed the available

binding site for sorption (Cabuk et al., 2005). This research is targeted at using natural biomass (groundnut husk) both unmodified and ethylene diamine tetraacetic acid (EDTA)-modified groundnut husk to remove malachite green from aqueous solution.

MATERIALS AND METHODS

Groundnut husk was collected locally from popular Lafenwa market in Abeokuta, Ogun state, Nigeria. The groundnut husk was washed with distilled water to remove the attached dust and impurities and then sun-dried. The washed groundnut husk was ground in a mechanical grinder to form powder. The biomass was sieved to particles with size less than 0.1 mm diameter and soaked in 7% v/v aqueous H₂SO₄ for 4 h for hydrolysis. The mixture was filtered and the residue washed with distilled water several times to remove any acid content and dried at 50°C for 8 h. The dried biomass was stored in an air tight glass bottles to protect it from moisture.

Malachite green was obtained from Bektoh (Germany) and used without further purification. It was characterized by its visible spectrum, which gave a molar extinction coefficient which is in agreement with the literature value at λ_{max} of 619 nm (Green, 1990). The summary of the properties of malachite green used is presented in Table 1. Other chemicals and reagents used in this study were analar grade and used without further purification.

EDTA-modification of groundnut husk

A mixture of 17 g of the hydrolyzed husk, 0.3 dm³ of pyridine and 56.7 g EDTA was heated under reflux for 3 h. The reaction mixture was filtered, diluted with 0.03 dm³ of distilled water and filtered again. EDTA-modified husk was washed several times with distilled water until it is free of pyridine odour and then air-dried. The modified husk was stored in air tight glass bottles for use (Okieimen et al., 1991).

Batch kinetic studies

In experiment of batch kinetic adsorption, 0.2 g of EDTA-modified groundnut husk and unmodified groundnut husk of 0.1 mm diameter particles size and 50 cm³ of dye solution was poured in a 100 ml flask and agitated with a maximum speed of 500 rpm using a shaker with a water bath to control temperature (Haake Model K-F3). At particular time intervals, the aqueous sample (5 cm³) was taken and the concentration was analyzed. The concentrations of dyes were measured with ultraviolet (UV)/visible spectrophotometer (Hitachi Model U-2000). The experimental parameters included contact-time, initial dye concentration, temperature and pH. All of the experiments were carried out in duplicate and the average values were used in calculations. The maximum deviation was

found to be $\pm 2\%$. The amount of adsorption at time t , q_t (mg/g), equilibrium adsorption, q_e (mg/g) and percentage dye removal at time t , and at equilibrium was obtained as follows:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

$$\% \text{ Dye removal} = \frac{(C_0 - C_e)100}{W} \quad (3)$$

Where C_o , C_t and C_e (g/m^3) are the liquid-phase concentrations of solutes at initial, any time t , and at equilibrium, respectively. M is the dosage of adsorbent in the solution (kg/m^3) and V is the volume of the dye used in (cm^3).

Kinetic models of adsorption

Pseudo-first and second-order equations

In order to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, several kinetic models were used to test experimental data. The large number and array of different functional groups on the groundnut husk both modified and unmodified ($-\text{NH}_2$, $-\text{COOH}$, $-\text{OH}$) imply that there are many types of adsorbent-solute interactions. From a system design viewpoint, a lumped analysis of adsorption rate is thus sufficient to practical operation. A simple kinetic analysis of adsorption is the pseudo-first order equation in the form (HO and Mackay, 1998, 2000):

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (4)$$

Where K_1 is the rate constant of pseudo-first order adsorption and q_e denotes the amount of adsorption at equilibrium.

In addition, a pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the form of (HO and Mckay 1998; HO and Mckay, 2000);

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

Where k_2 is the rate constant of pseudo-second order adsorption. The intra-particle diffusion equation (Furusawa and Smith, 1997) can be written by the following equation:

$$q_t = K_{ipd} t^{1/2} + C \quad (6)$$

Where q_t is the amount of dye adsorbed onto adsorbent at various time $t^{1/2}$ (mg/g), C is the intercept and K_{ipd} is the intra-particle diffusion rate constant (mg/g/min).

Thermodynamic parameters such as change in free energy (ΔG°) (kJ/mol), enthalpy (ΔH°) (kJ/mol) and entropy (ΔS°) (J/K/mol) for the adsorption process were determined using the following equation (Vadivelan and Vasanthakumar, 2005):

$$\Delta H^\circ = \frac{R[(T_2 T_1)]}{(T_2 - T_1)} \ln \left(\frac{K_2}{K_1} \right) \quad (7)$$

$$\Delta G^\circ = -RT \ln K_o \quad (8)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (9)$$

$$K_o = \frac{C_{solid}}{C_{liquid}} \quad (10)$$

$$\log K_o = \frac{(\Delta S^\circ)}{2.303R} - \frac{(\Delta H^\circ)}{2.303RT} \quad (11)$$

Adsorption isotherm: The adsorption isotherm is an equation relating the amount of solute adsorbed onto the solid and equilibrium concentration of solute in solution at constant temperature. Several isotherm equations are available. In this study, the adsorption data correlated with the Freundlich (Freundlich, 1906) and Langmuir (Ozacar and Sengil, 2003) models. The following linearized Freundlich adsorption isotherm is employed.

$$\ln q_e = \ln K_f + \left(\frac{1}{n} \right) \ln C_e \quad (12)$$

Where q_e the amount is adsorbed at equilibrium (mg/g), K_f the Freundlich constant, $\left(\frac{1}{n} \right)$ is the heterogeneity factor which are related to the capacity and intensity of the adsorption, respectively and C_e is the equilibrium concentration (mg/L). The value of K_f and $\left(\frac{1}{n} \right)$ can be obtained from the slope and intercept of the plots of $\ln q_e$ against $\ln C_e$.

A well-known linear form of the Langmuir equation can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{(q_m \times b)} + \frac{C_e}{q_m} \quad (13)$$

Where, C_e and q_e has usual meaning and q_m and b are the Langmuir constant related to the capacity and energy of adsorption, respectively. According to the Equation 13, a plot of $\frac{C_e}{q_e}$ versus C_e

should be a straight line with a slope $\frac{1}{q_m}$ and intercept $\frac{1}{(q_m \times b)}$

when the adsorption obeys the Langmuir equation.

The important characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless factor, R_L (Ozacar and Sengil, 2003) which is defined as:

$$R_L = \left(\frac{1}{(1 + b C_e)} \right) \quad (14)$$

The R_L values indicate the type of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

RESULTS AND DISCUSSION

Kinetic and the thermodynamic studies of the adsorption of malachite green onto unmodified and EDTA-modified groundnut husk have been investigated and the results presented.

Effect of contact time

The contact time between the dye molecules and the sorbent is significant in the dye treatment by sorption process. The effect of contact time on the adsorption of malachite green (MG^+) was investigated at initial dye concentration of 50 mg/L , a sorbent mass of 0.2 g , a

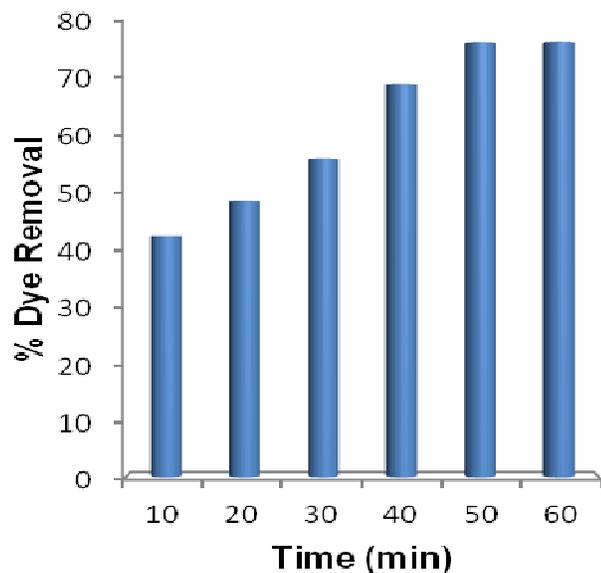


Figure 1a. Effect of contact time on adsorption of malachite green by unmodified groundnut husk.

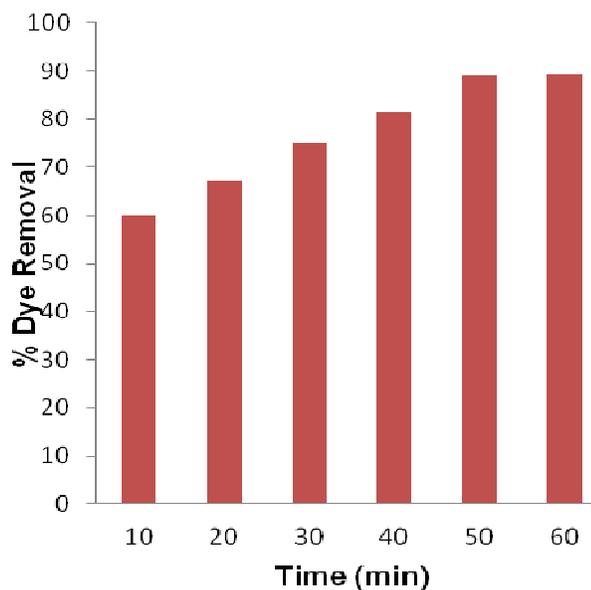


Figure 1b. Effect of contact time on adsorption of malachite green by EDTA-modified groundnut husk.

solution volume of 50 ml, an agitation speed of 250 rpm and temperature of 25°C. Figures 1a and b present the effect of contact time on the adsorption of malachite green (MG⁺) onto unmodified groundnut husk and EDTA-modified groundnut husk, respectively. The figures reveal that the uptake of sorbate species is fast at initial stage of the contact time (30 min) and thereafter it becomes slower near the equilibrium. Between these two stages of

the uptake, the rate of sorption is found to be nearly constant. This is clear from the fact that a large number of vacant binding sites are available for sorption during the initial stage and after a lapse of time, the remaining vacant surface site are difficult to be occupied due to repulsive forces between the solute molecule on the solid and bulk phases. Equilibrium was established at exactly 50 min for both adsorbents, the corresponding percentage dye removed at this time by each adsorbent stood at 78.6% for unmodified groundnut husk, but there was significant increase in the percentage dye removed by the EDTA-modified groundnut husk at equilibrium contact time which is 92.4%, suggesting an increased in the sorption efficiency of the modified adsorbent.

At this point, the amount of dye sorbed by the adsorbent is in dynamic equilibrium with the amount of dye desorbed from the sorbent. Additionally, the chart is single, smooth, and continuous leading to equilibrium which indicates the possible monolayer coverage of the surface of the adsorbent.

Effect of initial dye concentration

The experimental results of adsorption of malachite green (MG⁺) onto both unmodified and the chemically modified groundnut husk at various initial concentrations of 50, 100, 150, 200 and 250 mg/L at different temperatures are presented in Tables 2a and b. These tables reveal that the percentage adsorption decreased with increasing initial dye concentration but adsorption capacity of the adsorbent increased with increase in dye concentration. This indicates that the initial dye concentration plays an important role in the adsorption capacity of malachite green on the groundnut husk that is, highly dependent on the initial concentration of the dye. At lower concentration, the ratio of initial number of dye molecules to the available surface area is low. Subsequently, the fractional adsorption becomes independent of initial dye concentration. However, at high concentration the available sites of adsorption become fewer and hence the percentage removal of dye is dependent upon initial concentration (Namasivayam et al., 1997; Namasivayam and Yamuna, 1995).

Effect of temperature

The effect of temperature on the adsorption of malachite green onto unmodified and EDTA-modified ground nut husk was studied at different temperatures of 20, 25, 30 and 35°C and the results shown in Tables 2a and b. The results show an increase in the adsorption capacity of malachite green onto groundnut husk with increasing temperatures. The chemically modified groundnut husk had the highest percentage dye removal across all the

Table 2a. Effect of initial concentration on adsorption of malachite green by unmodified groundnut husk.

C_o (mg/L)	C_e (mg/L)				Q_e (mg/L)				% Dye removal			
	20°C	25°C	30°C	35°C	20°C	25°C	30°C	35°C	20°C	25°C	30°C	35°C
50	10.70	7.950	4.25	2.75	9.83	10.5	11.4	11.8	78.6	84.1	91.9	94.5
100	29.20	23.70	19.5	13.8	17.7	19.1	20.1	21.6	70.8	76.3	80.5	86.2
150	84.38	44.25	37.1	29.4	16.4	26.4	28.2	30.2	62.5	70.5	75.3	80.4
200	87.20	75.40	57.0	46.4	28.2	31.2	35.8	38.4	56.4	62.3	71.5	76.8
250	124.8	106.5	89.8	71.3	31.3	35.9	40.1	44.7	50.1	57.4	64.1	71.5

Table 2b. Effect of initial concentration on adsorption of malachite green by EDTA-modified groundnut husk.

C_o (mg/L)	C_e (mg/L)				Q_e (mg/L)				% Dye removal			
	20°C	25°C	30°C	35°C	20°C	25°C	30°C	35°C	20°C	25°C	30°C	35°C
50	7.40	3.95	2.05	0.45	10.7	11.5	11.9	12.4	85.2	92.1	95.9	99.1
100	19.5	13.5	9.80	5.50	20.1	21.6	22.6	23.6	80.5	86.5	90.2	94.5
150	39.3	28.2	22.4	15.3	27.7	30.5	31.9	33.7	73.8	81.2	85.1	89.8
200	69.6	49.0	39.0	33.0	32.6	37.7	40.3	41.8	65.2	75.5	80.5	83.5
250	98.8	72.0	59.5	51.3	37.8	44.5	47.6	49.7	60.5	71.2	76.2	79.5

Table 3a. Equilibrium constant (K_o) and thermodynamic parameters of adsorption of malachite green by unmodified groundnut husk.

C_o (mg/L)	K_o				ΔG° (kJ/mol)				ΔH° (kJ/mol)	ΔS° (J/molK ¹)
	20°C	25°C	30°C	35°C	20°C	25°C	30°C	35°C		
50	3.67	5.29	10.8	17.2	-2.98	-4.43	-5.89	-7.35	82.39	291.35
100	2.43	3.22	4.13	6.25	-2.04	-2.88	-3.72	-4.56	47.30	168.39
150	0.78	2.39	3.05	4.10	-0.03	-1.33	-2.70	-4.06	79.80	272.26
200	1.29	1.65	2.51	3.31	-0.53	-1.40	-2.26	-3.12	50.06	172.67
250	1.00	1.35	1.79	2.51	-0.04	-0.76	-1.56	-2.36	46.79	159.57

temperatures. Therefore, the sorption of malachite green onto groundnut husk (both modified and unmodified) is temperature-dependent. This may be due to the fact that increase temperature may produce swelling effect within the internal structure of the groundnut husk thereby enlarged its pore size.

Equilibrium and thermodynamics of adsorption of Malachite green by modified and unmodified groundnut husk

The values of K_o , ΔG° (kJ/mol), ΔH° (kJ/mol), and ΔS° (J/mol K¹) were calculated from the slope and intercept of Van't Hoff plots of Equation 11 and the results are presented in the Tables 3a and b above. The results indicate that K_o decreased with increase in the concentration of dye but increased with increase in temperature. The positive values of ΔH show the endothermic nature of the adsorption and the possibility

of physisorption. In the case of physical adsorption, while increasing the temperature of the system, the extent of dye adsorption increases, this ruled out the possibility of chemisorption.

The negative values of ΔG° show that the adsorption is highly favourable and spontaneous. The positive values of ΔS° indicate an increased disorder and randomness at the solid-solution interface of the adsorbent. The adsorbed water molecules, which are displaced by the adsorbate (dye) species, gain more translational entropy than it is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system (Namasivayam et al., 1997; Namasivayam and Yamuna, 1995). From the results, we could conclude that more efficient is the physisorption.

Langmuir and Freundlich isotherms

The isotherms in Figures 2a, b and 3a, b were fitted in the linear Langmuir and Freundlich equations.

Table 3b. Equilibrium constant (K_o) and thermodynamic parameters of adsorption of malachite green by EDTA-modified groundnut husk.

C_o (mg/L)	K_o				ΔG (kJ/mol)				ΔH (kJ/mol)	ΔS (J/molk ¹)
	20°C	25°C	30°C	35°C	20°C	25°C	30°C	35°C		
50	5.76	11.7	23.4	110	-3.79	-6.35	-8.91	-11.5	146.35	512.41
100	4.13	6.41	9.20	17.2	-3.35	-4.62	-5.89	-7.16	71.10	254.10
150	2.82	4.32	5.71	8.80	-2.53	-3.54	-4.55	-5.56	56.68	202.09
200	1.87	3.08	4.13	5.06	-1.69	-2.58	-3.47	-4.36	50.31	177.49
250	1.53	2.47	3.20	3.88	-1.21	-2.03	-2.85	-3.66	46.78	163.78

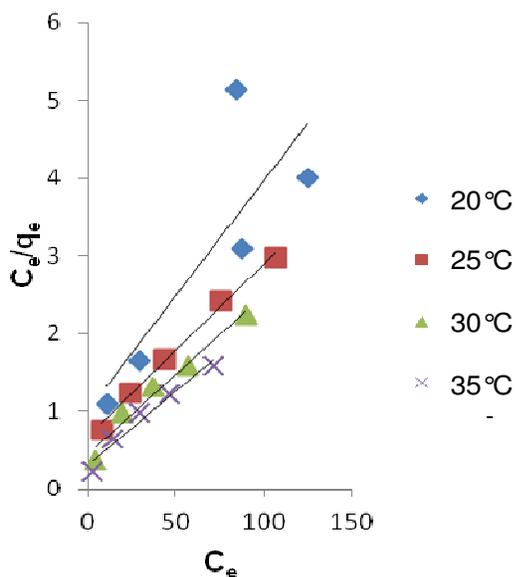


Figure 2a. Langmuir adsorption Isotherm for unmodified adsorbent.

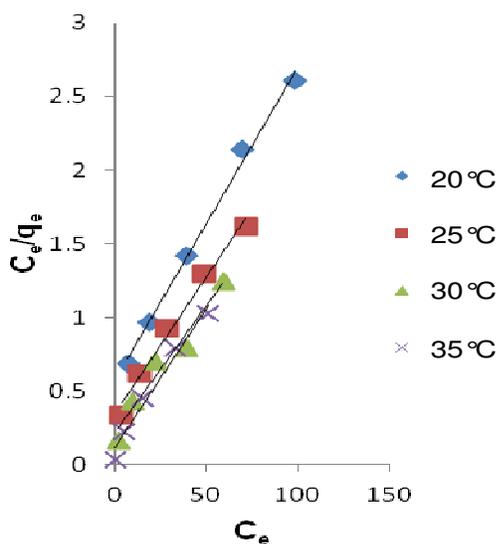


Figure 2b. Langmuir adsorption Isotherm for modified adsorbent.

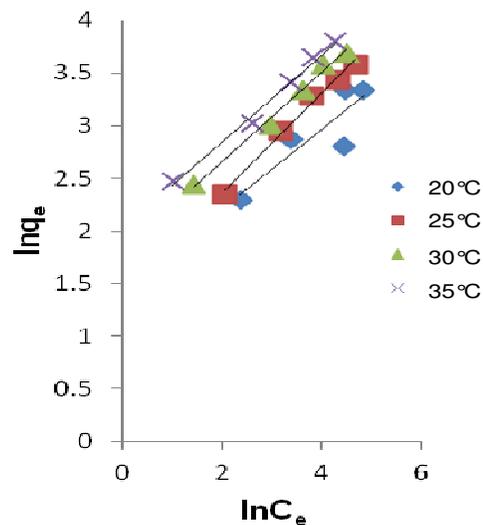


Figure 3a. Freundlich isotherm for adsorption of malachite green onto unmodified adsorbent.

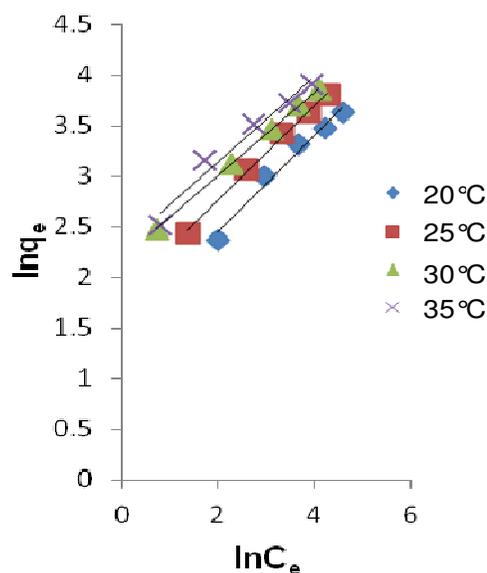


Figure 3b. Freundlich Isotherm for adsorption of malachite green onto modified adsorbent.

Table 4a. Langmuir isotherm constant for adsorption of malachite green by unmodified groundnut husk.

Temperature	20 °C	25 °C	30 °C	35 °C
q_m	33.90	44.84	48.08	52.91
b	0.029	0.034	0.047	0.061
R^2	0.6821	0.9938	0.9713	0.9631

Table 4b. Langmuir isotherm constant for adsorption of malachite green by EDTA-modified groundnut husk.

Temperature	20 °C	25 °C	30 °C	35 °C
q_m	46.73	54.05	58.14	52.36
b	0.038	0.054	0.081	0.181
R^2	0.9948	0.9845	0.9576	0.9778

Table 5a. Dimensionless separation factor (R_L) for unmodified groundnut husk.

Temperature/ C_o (mg/L)	R_L			
	20 °C	25 °C	30 °C	35 °C
50	0.408	0.370	0.299	0.247

Table 5b. Dimensionless separation factor (R_L) for EDTA-modified groundnut husk.

Temperature/ C_o (mg/L)	R_L			
	20 °C	25 °C	30 °C	35 °C
50	0.345	0.270	0.198	0.0995

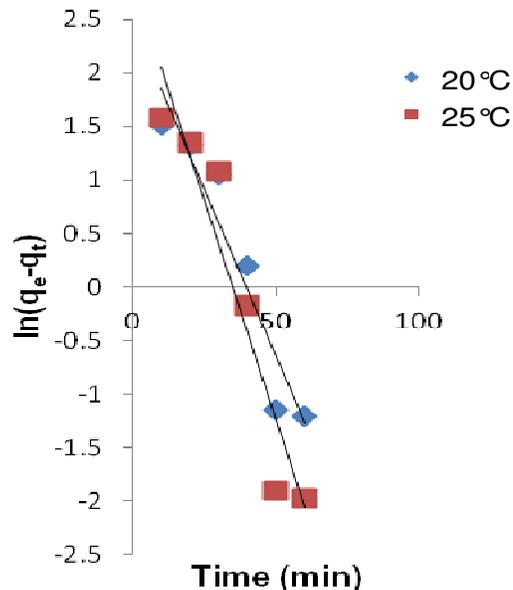
Table 6a. Freundlich Isotherm constant for the adsorption of malachite green by unmodified groundnut husk.

Temperature	20 °C	25 °C	30 °C	35 °C
K_f	4.27	4.10	6.07	7.49
n	2.64	2.11	2.36	2.41
R^2	0.7698	0.9889	0.9913	0.9921

Table 6b. Freundlich Isotherm constant for the adsorption of malachite green by EDTA-modified groundnut husk.

Temperature	20 °C	25 °C	30 °C	35 °C
K_f	4.46	6.22	8.88	10.01
N	2.10	2.14	2.43	2.38
R^2	0.976	0.997	0.999	0.9649

Tables 4a, b and 6a, b show the computation results. The Langmuir and Freundlich fit quite well with the experimental data for the EDTA-modified groundnut

**Figure 4a.** Pseudo-first-order kinetics of unmodified groundnut husk.

husk both below the room temperature (20 °C) and above room temperature as its correlation coefficient $R^2 > 0.9523$ but for the unmodified groundnut husk it shows poor agreement of both the Langmuir and Freundlich isotherm with the experimental data at lower temperature (below room temperature) as its correlation coefficient $R^2 < 0.7898$, but agreed well at the temperature above room temperature. The calculated n -values are greater than unity, suggesting favourable adsorption (Freundlich, 1906). Also, the dimensionless factor (R_L) values presented in Tables 5a and b lies in between 0 and 1. This suggested the favourability of the sorption process.

Pseudo-first-order, pseudo-second-order and the intraparticle diffusion Models

The pseudo-first-order, pseudo-second-order and the intraparticle diffusion model of the adsorption process at 20 and 25 °C are plotted in Figures 4a, b, 5a, b and 6a, b, respectively.

Tables 7a and b presented the rate constant and correlation coefficient of the pseudo-first-order, pseudo-second-order and the intraparticle diffusion model at 20 and 25 °C. The correlation coefficient R^2 for the pseudo-second-order adsorption model has extremely high values ($R^2 > 0.9614$), and its calculated equilibrium adsorption capacities q_{ecal} fit well with the experimental data. These suggest that the pseudo-second-order adsorption mechanism is predominant and the overall rate of this sorption process appears to be controlled by the chemical process (Mckay, 1983).

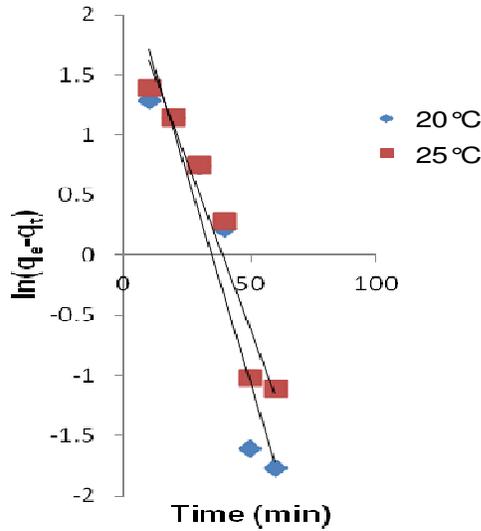


Figure 4b. Pseudo-first-order kinetics of EDTA-modified groundnut husk.

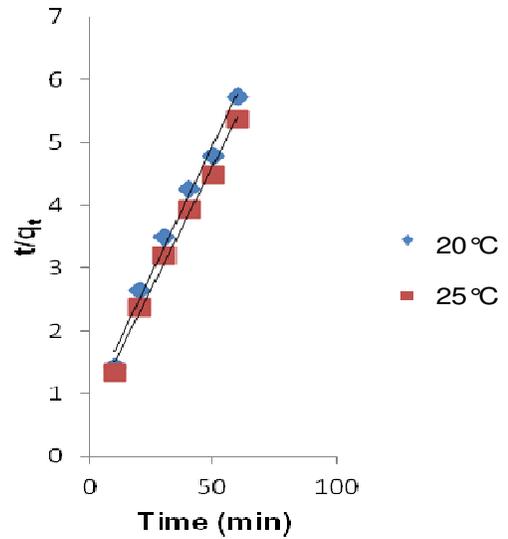


Figure 5b. Pseudo-second-order kinetics of EDTA-modified groundnut husk.

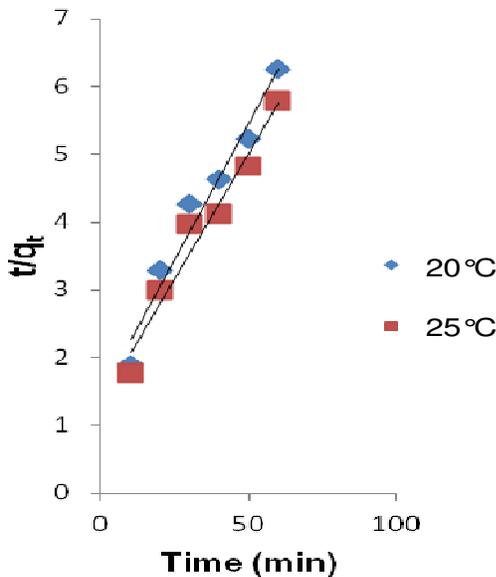


Figure 5a. Pseudo-second-order kinetics of unmodified groundnut husk.

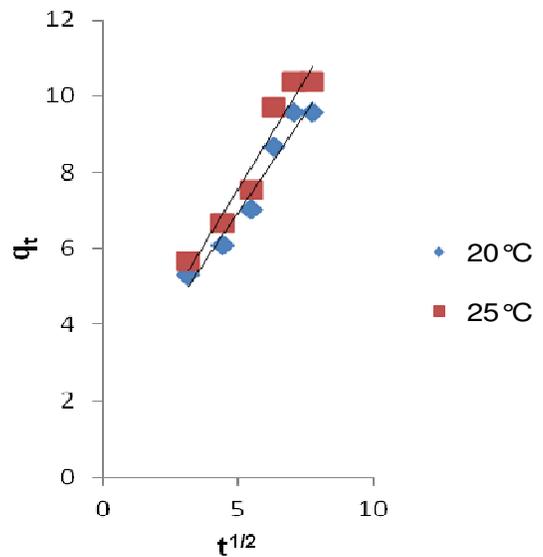


Figure 6a. Intraparticle diffusion of adsorption of malachite green onto unmodified groundnut husk.

The results in Tables 6a and 6b above describe the rate constant studied at two different temperatures calculated by the three models. For the pseudo-second-order, both the rate constant and the initial adsorption rate increased with increasing temperatures. This may be explained that higher temperature increases the reaction rate and also decreases the particle density thereby enlarging the pore sizes for dye molecules to diffuse. The correlation coefficient for the intraparticle diffusion is lower than pseudo-second-order kinetics, which indicates the present system may be followed by intraparticle

diffusion.

Effect of pH

The effect of pH on adsorption of malachite green onto unmodified and EDTA-modified groundnut husk was investigated, while the initial concentration, shaking time, amount of adsorbent and temperature were fixed at 50 mg/L, 250 min, 0.2 g and 25°C, respectively.

pH affects not only the adsorption capacity but also the

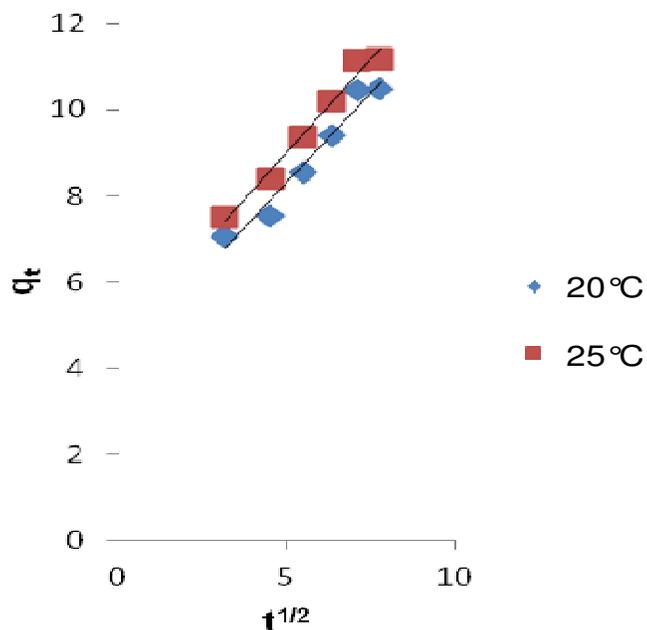


Figure 6b. Intraparticle diffusion of adsorption of malachite green onto EDTA-modified groundnut husk.

Table 7a. Pseudo-first-order, pseudo-second-order and the intraparticle diffusion models for unmodified adsorbent.

C_o (mg/L)	Pseudo-first-order					
	20 °C			25 °C		
	50	100	150	50	100	150
k_1	0.0625	0.0891	0.0909	0.0823	0.0798	0.0923
q_e	11.93	35.28	51.32	17.80	30.51	57.24
R^2	0.9169	0.8972	0.8674	0.908	0.9038	0.9022
	Pseudo-second-order					
k_2	0.0044	0.0025	0.0542	0.0040	0.0028	0.0556
q_e	12.48	22.73	30.12	13.62	23.53	34.13
R^2	0.965	0.9758	0.9582	0.9625	0.9831	0.9799
	Intraparticle diffusion					
K_{ipd}	1.0512	1.9345	2.51	1.669	1.975	2.9263
R^2	0.9578	0.9732	0.9577	0.948	0.9832	0.9803

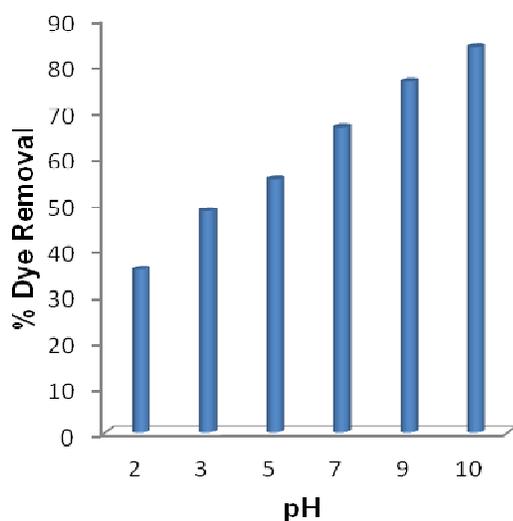
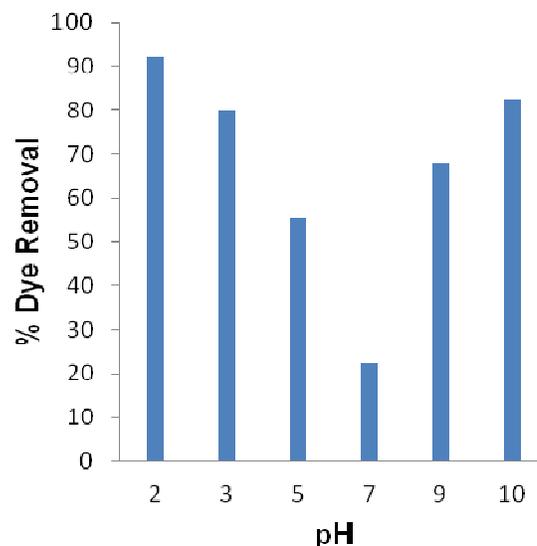
colour of the dye and the solubility of some dye. Therefore, the pH value of solution was an important controlling factor in the adsorption process (Waranusantigul et al, 2003). The effect of pH on malachite green adsorption by unmodified and chemically modified groundnut husk is shown in Figures (7a) and (7b), respectively.

Figure (7a) shows that the equilibrium sorption capacity is minimum at pH 2 and increases monotonically up to pH

5. A further increase in pH leads to an appreciable increase in percentage adsorption. The absence of sorption at low pH can be explained by the fact that at this acidic pH, H^+ may compete with dye ions for the adsorption sites of the adsorbent, thereby inhibiting the adsorption of dye. At higher pH, the groundnut husk may get negatively charged, which enhances the adsorption of positively charged dye cations through electrostatic forces of attraction. Moreover, a change of solution pH

Table 7b. Pseudo-first-order, pseudo-second-order and the intraparticle diffusion models for EDTA-modified adsorbent.

Pseudo-first-order						
C_o (mg/L)	20 °C			25 °C		
	50	100	150	50	100	150
k_1	0.0556	0.0907	0.0909	0.0686	0.0903	0.0923
q_e	11.05	35.66	58.67	8.88	39.40	68.17
R^2	0.8902	0.842	0.8674	0.9311	0.8289	0.9022
Pseudo-second-order						
k_2	0.0079	0.0825	0.0658	0.0084	0.0808	0.0687
q_e	12.18	23.75	33.78	12.85	25.45	37.59
R^2	0.9859	0.9814	0.9617	0.9921	0.9678	0.982
Intraparticle diffusion						
K_{ipd}	0.835	1.7633	2.659	0.8671	1.8262	3.0053
R^2	0.9622	0.9457	0.9468	0.9821	0.9367	0.9691

**Figure 7a.** Effect of pH on the adsorption of malachite green onto unmodified groundnut husk.**Figure 7b.** Effect of pH on the adsorption of malachite green onto EDTA-modified groundnut husk.

affects the adsorptive process through dissociation of functional groups on the surface of the adsorbent. Such behaviour leads to a shift in the equilibrium characteristics of the adsorption process. A similar report on effect of pH was also reported for the adsorption of malachite green onto rattan saw dust (Hameed et al, 2008). But for the chemically modified groundnut husk, the sorption process was minimal at pH 7 and maximum at acidic pH (Figure 7b). At pH 7, the interaction between the carboxylic groups of the modified groundnut husk and water predominates over the interaction between the adsorbent and the dye, hence the reduced adsorption.

However, when the pH of the solution was increased

(above pH 7), the uptake of malachite green was also increased. It appears that change in pH solution results in the formation of different ionic species, and different adsorbent surface. When the pH value is lower than 6, the malachite green ions were able to enter into the pore of the adsorbent by forming complex $[MGEDTA]^{3-}$ with the EDTA on the adsorbent surface.

But at pH 7, the zwitter ions form of malachite green in water raise the aggregation of malachite green to form bigger molecule (dimer) and was unable to enter the pore structure of the adsorbent. At pH value higher than 8, the existence of OH^- groups on the adsorbent surface

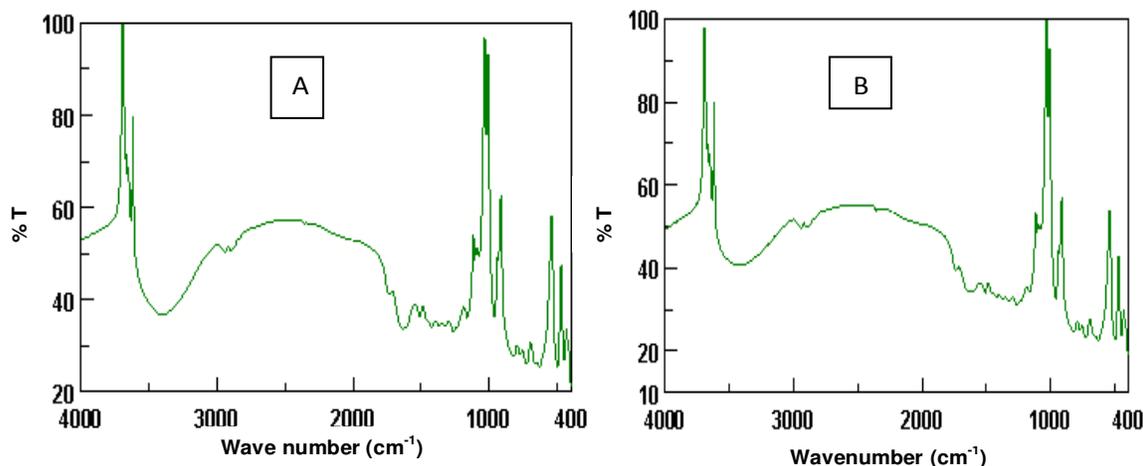


Figure 8. FTIR Spectrum of (A) unmodified groundnut husk and (B) modified groundnut husk.

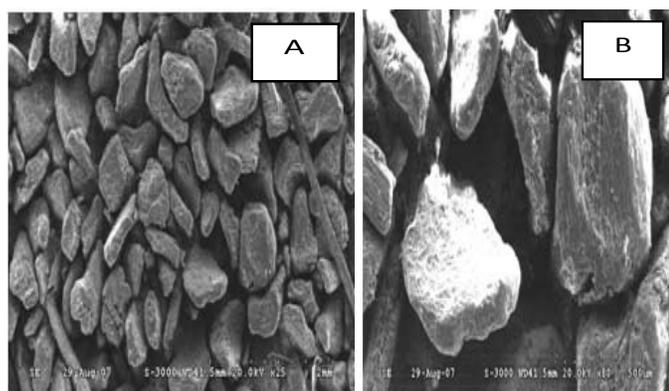


Figure 9. Scanning electron micrograph of (A) unmodified and (B) EDTA-modified groundnut husk.

enhances the adsorption of positively charged dye cations through electrostatic forces of attraction. Hence the increase in adsorption capacity (Arivoli et al., 2007a, b; Kalpana et al., 2007; Yupeng et al., 2005).

The FTIR spectrum and SEM micrographs of groundnut husk

The FTIR spectrum of groundnut husk is shown in Figure 8a. Broad peak at 3400 cm^{-1} is the indicator of -OH and -NH groups. The stretching of the -OH groups bound to methyl groups presented a signal between 2950 and 2887 cm^{-1} . The peaks located at 1737 and 1633 cm^{-1} are characteristics of carbonyl group stretching from aldehydes and ketones. The presence of -OH group, along with carbonyl group, confirms the presence of carboxylic acid groups in the adsorbent. The peaks at 1508 cm^{-1} are associated with the stretching in aromatic rings. The peaks observed at 1071 and 1024 cm^{-1} are

due to C-H and C-O bonds. The -OH, -NH, carbonyl and carboxylic groups are important sorption sites (Volesky, 2003). The FTIR spectra of the EDTA modified Groundnut husk, is presented in Figure 8b. As compared to simple groundnut husk, the broadening of -OH peak at 3400 cm^{-1} and carbonyl group peak at 1633 cm^{-1} was observed. This indicates the involvement of hydroxyl and carbonyl groups in the adsorption of malachite green. The SEM micrographs of groundnut husk and EDTA-modified groundnut husk are shown in Figure 9. These micrographs represent a porous structure, with large surface area, and large morphological changes in the modified groundnut husk with increased pore sizes and surface area. The results of surface area analysis further confirmed the porous nature and high surface area of the adsorbent.

Conclusion

The study investigates the dynamics of the adsorption of malachite green on the unmodified groundnut husk and EDTA-modified groundnut husk. The chemically modified groundnut husk shows a higher adsorption capacity than unmodified groundnut husk.

The Langmuir and Freundlich isotherm agree well with the equilibrium isotherm for the two adsorbents. The initial dye concentration and temperature also significantly affect the adsorption capacity of malachite green onto both the modified and unmodified groundnut husks. The pseudo-second-order kinetic model agrees very well with the dynamical behaviour for the adsorption of malachite green onto unmodified and EDTA-modified groundnut husks under several different initial dye concentrations and temperatures.

This study shows that groundnut husk can be used as an adsorbent in the treatment of waste water by sorption system but that its potency can be improved by chemical

modification. Groundnut husk is a better and cheaper adsorbent when compared with most adsorbents used for dye removal, and it is found abundantly in nature.

ACKNOWLEDGEMENT

The authors are grateful to the Department of Chemistry and the Central Laboratory of University of Agriculture Abeokuta, Nigeria for providing the facilities and the chemicals used for this work.

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