

Article

Dye Removal from Aqueous Solution Using Coconut Coir Dust Extract-modified Polyvinyl alcohol: A Novel Adsorbent

U. J. Etim^{1,*}, E. Inam¹, S. A. Umoren¹, U. M. Eduok²

¹ Department of Chemistry, University of Uyo, Nigeria

² King Fahd University of Petroleum and Minerals, Daharan, KSA

* Author to whom correspondence should be addressed; E-Mail: uje4sure2010@yahoo.com.

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Abstract: Coconut coir dust contains a large proportion of lignin and cellulosic groups which act as potential pollutants absorber in effluents. This study investigated the cross-linking of polyvinyl alcohol having one –OH group on its molecule with coconut coir dust in order to introduce functions to the polymer and increase its hydrophilicity by physical means. The application of the adsorbent to remove cationic dye malachite green from effluent was very feasibly. Adsorption was studied as a function of solution pH, contact time and initial dye concentration. Adsorption data were analysed using various isotherms models and was found to conform to the principle of Lagmuir, Freundlich and Flory-Huggins models with good correlation coefficients ($R^2 > 0.95$). The kinetics was also studied to elucidate the mechanistic pathway of the process. Results revealed that pseudo second order kinetic model provided better fit than the pseudo-first order in terms of adsorption capacity of the sorbent. Changes in Gibb's free energy (ΔG) as calculated from Langmuir and Flory-Huggins isotherms are +3.033 and +14.634 respectively indicating a non-spontaneous process at the temperature of study. Based on this report, coconut coir dust could be used to functionalize low molecular weight polymers for its applications in wastewater treatment.

Keywords: adsorption; coconut coir dust; polyvinyl alcohol; malachite green; kinetics; isotherm.

1. Introduction

Dye removal from wastewater has received considerable attention with several classes of dye being investigated. The presence of dyes even at a very low concentration is highly observable and undesirable. Therefore dye removal has been a very important area of wastewater treatment. Neglecting the aesthetics problem, the greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water, which interferes with the growth of bacteria, limiting it to levels insufficient to biologically degradable impurities in the water (Crini, 2008). It is evident; therefore, that removal of such coloured compounds from industrial wastewater before disposal is of significant environmental and technical importance.

Several physical, chemical and biological decolourization methods have been reported and applied for the removal of pollutants including dyes from industrial discharge of textile, paper, and pulp industries. These methods include coagulation and flocculation (Han et al., 2005), adsorption (Chen et al., 2010, 2011a & b; Deniz and Saygideger, 2011; El-Halwany, 2010; Mahmoodi et al., 2011a & b; Mital et al., 2009; Rafatullah et al., 2010; Rahchamani et al., 2011; Salleh et al., 2011; Santhi, et al., 2010a; Senthilkumar et al., 2010; Sharma and Uma, 2009), Ozonation (Ho et al., 2005), electrochemical techniques (Kumar, 2006) and electron beam radiation (Vahdat et al., 2010). Amongst the numerous techniques of wastewater decolourization, adsorption is widely adopted and certified efficient in the removal of colours from effluents and gives best results as it can be used to remove different types of colouring materials. For an efficient adsorption process, rapid removal of pollutants is needed. Consequently, kinetic studies, which give information for the rate of removal of pollutants from solution and the adsorption equilibrium data, are essential for the design of water treatment units involving adsorption process. Another is the choice of adsorbent. Though various commercially prepared activated carbons are available and researchers are developing novel sorbents for wastewater treatment, much work is still needed to be done to developing a super adsorbent with hyper properties. Most of the adsorption experiment nowadays is conducted with biomaterials, which are cheap and easily available; there is still need to test synthetic bio-materials blend for sorption applications. At the moment there is no literature documenting natural and synthetic blend for dye removal.

Therefore, this study investigated the use of blended polyvinyl alcohol (PVAL) as a model adsorbent for cationic dye (malachite green) removal from aqueous solution. The effects of operational parameters, isotherms and kinetic data were also evaluated.

2. Materials and Methods

2.1. Materials and Apparatus

The adsorbent coconut (*Cocos nucifera* L) coir dust was obtained from a local coconut processing mill in Ukanafun Local Area of Akwa Ibom State. Polyvinyl alcohol (PVAL) DP-1700 to 1800 MW: 74800-79200; Hydrolysis (mole %): 98-99; $-(C_2H_4O)_n$ was obtained from Burbidges Burgoyne & Co., Mumbai, India. The cationic dye used in this study as an adsorbate was malachite green (MG) purchased from Smerck fine chemicals, Onitsha, Nigeria. It was used without further purification. Other reagents include concentrated HCl and dilute NaOH solutions. All reagents were of analytical grade. Double distilled water was used throughout for the experiment.

2.2. Preparation of Adsorbent and Adsorbate

Coconut coir dust was washed with water to remove dirt and sand particles. It was air dried for 48 h in an oven at 60 °C to constant weight.

2.2.1. Extraction of Coir Dust in Water

Coir dust (10 g) was added to 200 mL of double distill water in a beaker on hot plate and stirred for 1 h at the boiling point (100 °C) of the solvent (Okon et al., 2012). At the end of the time, the mixture was filtered and the filtrate was evaporated to dryness. The weight of the extract was obtained. The extraction procedure was repeated to obtain sufficient quantity of the extracts.

2.2.2. Preparation of CCD-MPVAL

One gram (1.0 g) of the wet extract was mixed with 10 g of PVAL which has been soaked in hot water to gelation. The polymer blend was oven dried at 40 °C for 6 h to obtain CCD-MPVAL (Fig. 1). The particles sizes were reduced to increase its surface area. It was stored in a clean dry plastic container for use.



Figure 1. Photograph of modified PVAL.

2.2.3. Preparation of Dye Solution

The dye stock solution was prepared by dissolving accurately weighed dye in distilled water to the concentration of 1 g/L. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to needed initial concentrations. Fig. 2 shows the structure of the malachite green used in the study.

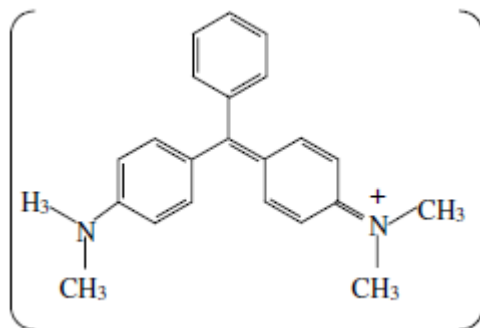


Figure 2. Structure of malachite green.

2.3. Batch Adsorption Experiments

Adsorption experiments were carried out in 250 mL conical flasks with volume of reaction solution kept at 100 mL. The flasks were shaken at 200 rpm for an equilibrium time of 6 h on a mechanical shaker. The effect of adsorbent dosage on the removal of MG was studied with different adsorbent dosages (1.0 – 4.0 g) in 100 mL dye solution and shaken till equilibrium time. The pH effect on the removal of MG was investigated over the pH range from 1.0 – 10.0. The initial solution pH was adjusted using 0.1 M HCl or 0.1 M NaOH. Effect of initial concentration was studied by shaking 1.0 g of the adsorbent at ambient temperature (27 ± 0.5 °C) and optimum pH (9.0) for different time interval and different initial concentrations. Adsorption equilibrium experiments were performed by stirring 100 mL of MG aqueous solution with initial concentration of (10 – 50) mg/L in each 100 mL flask containing 1.0 g of the adsorbents. The solutions were agitated at different time interval. Adsorption kinetic experiments were performed by keeping 1.0 g of adsorbent and 100 mL of MG aqueous solution of 50 mg/L in a series of 250 mL conical flasks, maintained at ambient temperature. Then the flasks were taken out at some intervals of time. After adsorption, the adsorbent and the supernatants were separated by centrifugation at 4000 rpm for 10 min. The supernatant were analyzed for residual dye concentration using UV–visible spectrophotometer (model He λ 105, Japan) by monitoring the absorbance changes at λ_{\max} (550 nm). The amount of dye adsorbed per gram of adsorbent (q_e) and the percentage adsorption (A) were calculated using equations (1) and (2), respectively.

$$q_e = \frac{V}{m}(C_o - C_e) \quad (1)$$

$$\% A = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

where C_o and C_e are initial and equilibrium MG concentrations, respectively (mg/L), V is MG solution volume (L), m is the mass of adsorbent (g). The instantaneous amount of dye adsorbed, q_t is given in equation 3, where C_t is the concentration of the dye in solution after time, t .

$$q_t = \frac{V}{m}(C_o - C_t) \quad (3)$$

3. Results and Discussion

3.1. Effect of Adsorbent Dosage

The adsorbent dosage determines the capacity of adsorbent for a given initial concentration of dye solution. Fig. 3 shows effect of adsorbent dosage on the adsorption capacity of MPVAL for MG. From the figure, it can be deduced that the adsorption capacity increases with decrease in adsorbent dosage. At dosage of 1.0 g the adsorption capacity is 37.25 mg/g which decreases to 11.5 mg/g at 4.0 g. This is due to greater availability of the exchangeable sites or surface area at a higher concentration of the adsorbent (Ahmad, 2009). However, with increase in the amount of adsorbent, percentage removal of the dye is found to increase (from 74.5 to 92.0%). Such a trend is mainly attributed to the fact that with increase in the amount of adsorbent the adsorptive surface area increases which provides a greater number of active sites for adsorption (Sonawane and Shrivastava, 2009).

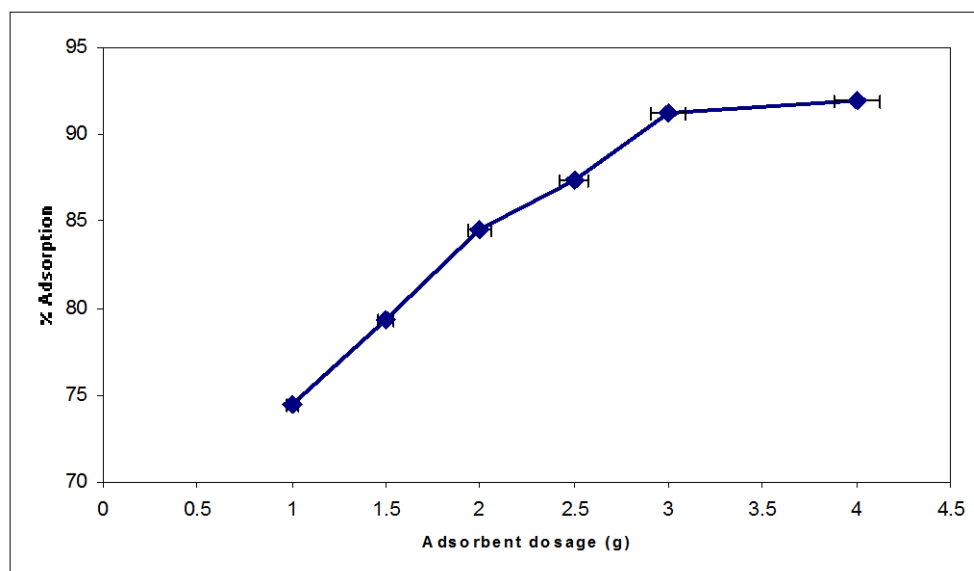


Figure 3. Variation of adsorbent dosage with percentage adsorption at pH = 9.0; temperature = 27 ± 0.5 °C, initial dye concentration = 50 mg/L and stirring rate of 200 rpm.

3.2. Effect of Initial Concentration

The effect of the initial dye concentration factor depends on the immediate relation between the dye concentration and the available binding sites on an adsorbent surface (Salleh et al., 2011). The adsorption capacity increases from 2.38 mg/g to 9.83 mg/g while the percentage removal of dye decreases from 95.1 to 78.8%. This value is greater than those obtained from other studies where PVAL mix was used as adsorbent (Gehlot et al, 2011; WanchantheuK and Thapol, 2011) or unmodified PVAL (Umoren et al., 2013). This trend is due to concentration providing the driving force to overcome the resistance to the mass transfer of dye between the aqueous and the solid phase. Again, at a fixed dosage of sorbent, fewer sites are available for greater molecules of the dye at higher concentration hence resulting to decrease in percentage adsorption. In other words, the residual concentration of dye molecules will be higher for higher initial dye concentrations. In the case of lower concentrations, the ratio of initial number of dye molecules to the available adsorption sites is low and subsequently the fractional adsorption becomes independent of initial concentration. Fig. 4 shows the effect of initial dye concentration.

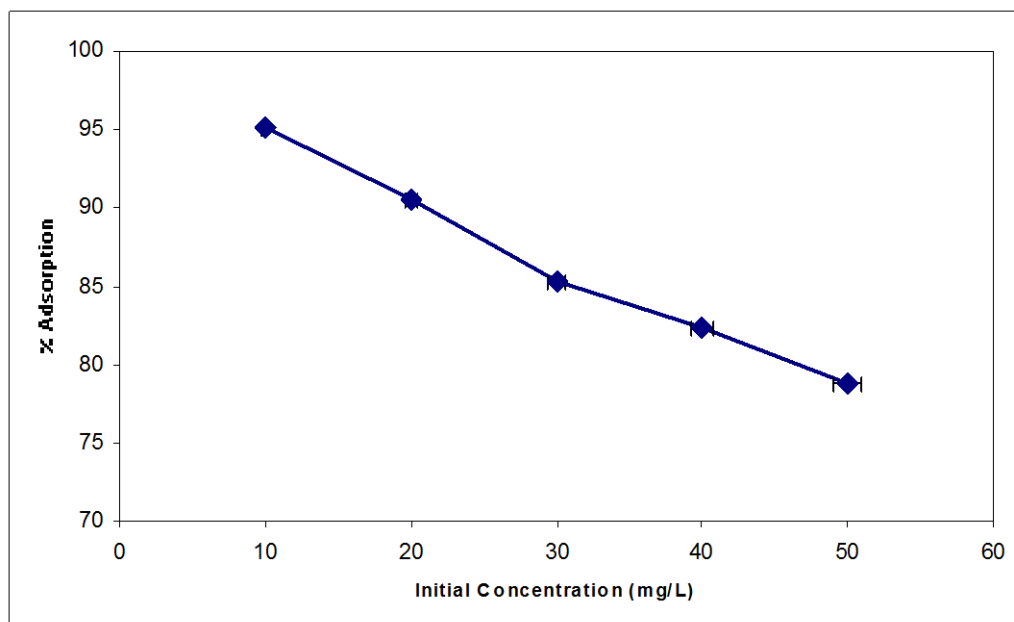


Figure 4. Variation of initial dye concentration with percentage adsorption at pH = 9.0; temperature = 27 ± 0.5 °C, adsorbent dosage = 1.0 g and stirring rate of 200 rpm.

3.3. Effect of pH Value

The pH of a medium which controls the magnitude of electrostatic charges imparted by the ionized dye molecules is critical in dye removal studies. As a result, the rate of adsorption will vary

with the pH of an aqueous medium (Onal et al., 2006). Fig. 5 shows the percentage adsorption of MG onto MPVAL at different pH (1.0-10.0) of the solution at room temperature. It can be seen from the curve that adsorption of the dye onto polymer blend is non-linear; the maximum removal is at the pH of 9.0. At low pH, there is protonation of the dye solution which tends to repel the cation of the dye molecules by electrostatic repulsion as a result of competition for available sorption sites. As the pH increases there is excess of the hydroxyl ions in solution. This forms strong intermolecular bond with the positive ions of the dye resulting in high uptake of the dye from the solution. The maximum adsorption of MG (94.8%) obtained in this study is greater than that obtained for PVAL coated carbon at pH 8.0 (62.3%) at a concentration of 40 ppm (Gehlot et al., 2011).

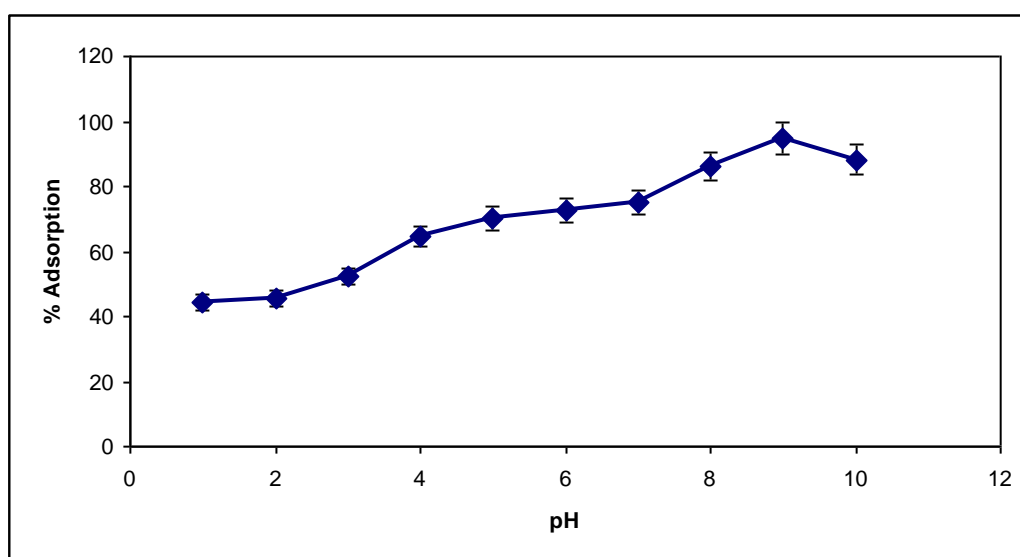


Figure 5. Variation of pH with % adsorption at initial dye concentration = 50 mg/L; adsorbent dosage = 1.0 g, temperature = 27 ± 0.5 °C and stirring rate of 200 rpm.

3.4. Adsorption Isotherm

To optimize the design of an adsorption system for the removal of adsorbate, it is important to establish the most appropriate correlation for the equilibrium curves. Fig. 6 shows the relationship between the adsorption amount at equilibrium with the equilibrium concentration pH, adsorbent dosage and initial dye concentration. At each condition, a linear curve is obtained this is an indication of a perfect correlation for adsorption at the chosen parameters at equilibrium.

Various isotherm equations have been used to describe the equilibrium nature of adsorption. Large numbers of researchers in the field of environmental science and engineering have used the most common Freundlich and Langmuir isotherm equations to represent equilibrium adsorption data (Dawood and Sen, 2012; Etim et al., 2012; Sen et al., 2011). It is significant for understanding the

adsorption behavior to identify the most appropriate adsorption isotherm model. In this paper, Langmuir, Freundlich and Flory-Huggins isotherms are employed to investigate the adsorption behaviour. Adsorption isotherm was studied at a temperature of 30 °C.

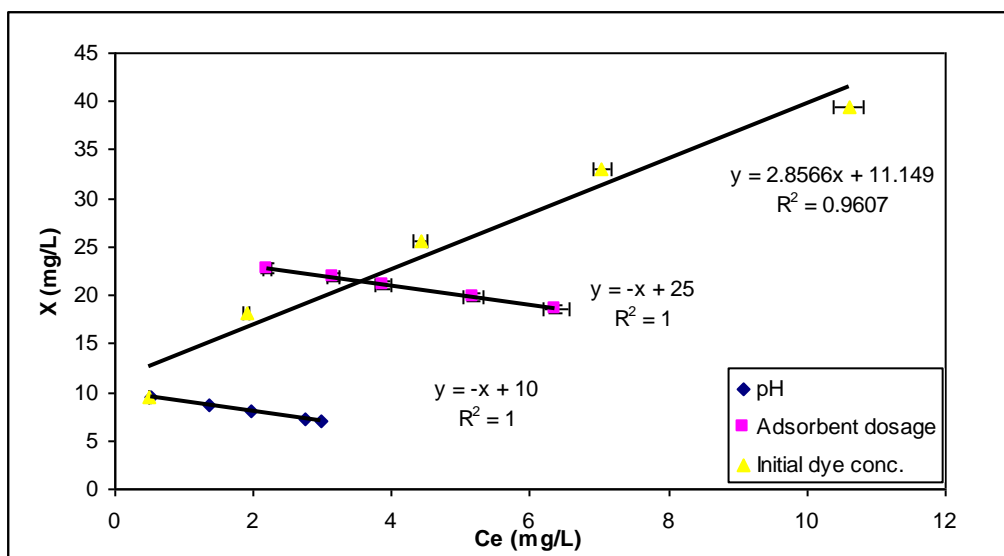


Figure 6. Equilibrium isotherm plot for adsorption at different conditions.

3.4.1. Langmuir isotherm

Langmuir isotherm can be expressed according to equation 4, which has been successful for the explanation of monolayer adsorption (Langmuir, 1916).

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \tag{4}$$

where q_{max} is the maximum or monolayer adsorption capacity of the adsorbent (mg/g) and K_L is the Langmuir adsorption constant (L/mg), which is related to the free energy of adsorption. Plot of C_e/q_e against C_e is shown in Fig. 7. The maximum adsorption capacity, q_{max} , and Langmuir constant, K_L are calculated from the slope and intercept of the plot respectively. Values obtained for the adsorption of malachite green onto the adsorbent (MPVAL) are presented in Table 1. The linear correlation coefficient value ($R^2 > 0.9805$) (Table 1) shows strong positive correlation indicating that adsorption follows Langmuir isotherm. The maximum adsorption capacity, q_{max} , obtained from the Langmuir plot is 37.17 mg/g at 30 °C. The value is about three times higher than reports in literature for modified polyvinyl alcohol (Gehlot et al., 2011; Umoren et al., 2013). At times R^2 value is insufficient to prove the fit of this model. It can be predicted whether an adsorption system is favourable or unfavourable using the essential characteristic of the Langmuir isotherm expressed by means of R_L , a dimensionless constant referred to as separation factor or equilibrium parameter defined by:

$$R_L = \frac{1}{1 + K_L C_o} \tag{5}$$

where C_o is the initial concentration. The parameter suggests the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$). As can be seen from Table 1, the value of R_L is less than 1 (0.063) which suggest that adsorption is favourable with Langmuir isotherm.

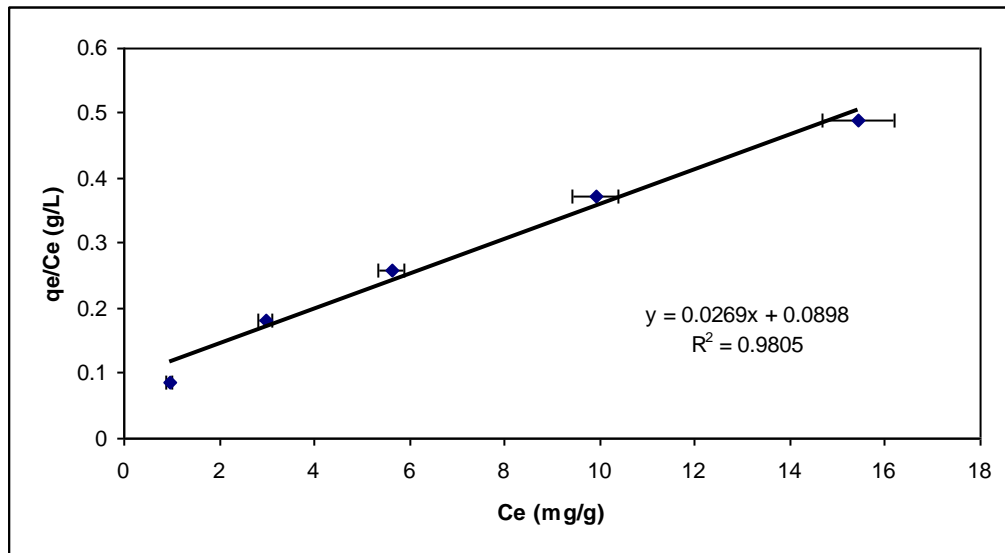


Figure 7. Langmuir isotherm plot at 30 °C

Table 1. Isotherm parameters

Langmuir isotherm		Freundlich isotherm		Flory-Huggins isotherm	
q_{max} (mg/g)	37.17	n (no unit)	2.61	n_{FH} (no unit)	-1.22
K_L (L/mg)	0.30	K_F ($mg^{1-1/n}L^{1/n}g^{-1}$)	11.08	K_{FH} (L/g)	0.00259
R_L (no unit)	0.063				
R^2	0.9805	R^2	0.9983	R^2	0.9898

3.4.2. Freundlich isotherm

The Freundlich isotherm is an empirical model used to describe heterogeneous adsorption process isotherm, and is expressed by the equation:

$$q_e = K_F C_e^{1/n} \tag{6}$$

This can be linearized to

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \tag{7}$$

where k_F ($mg^{1-1/n}L^{1/n}g^{-1}$) is adsorption capacity and n , a dimensionless constant, can be used to explain the extent of adsorption and the adsorption intensity between the solute concentration and adsorbent

respectively. The values of k_F and n are calculated from the intercept and slope of the plot of $\log q_e$ versus $\log C_e$ and values are shown in Table 1. The value of ‘ n ’ is larger than 1 which indicates the favourable nature of adsorption and a physical process (Dawood and Sen, 2012). The plot of the linear form of Freundlich isotherm is presented in Fig. 8. Accordingly, the Freundlich constants (K_F and n) 11.08 and 2.61 respectively and R^2 presented in Table 1 shows that Freundlich model could also be used to explain adsorption process.

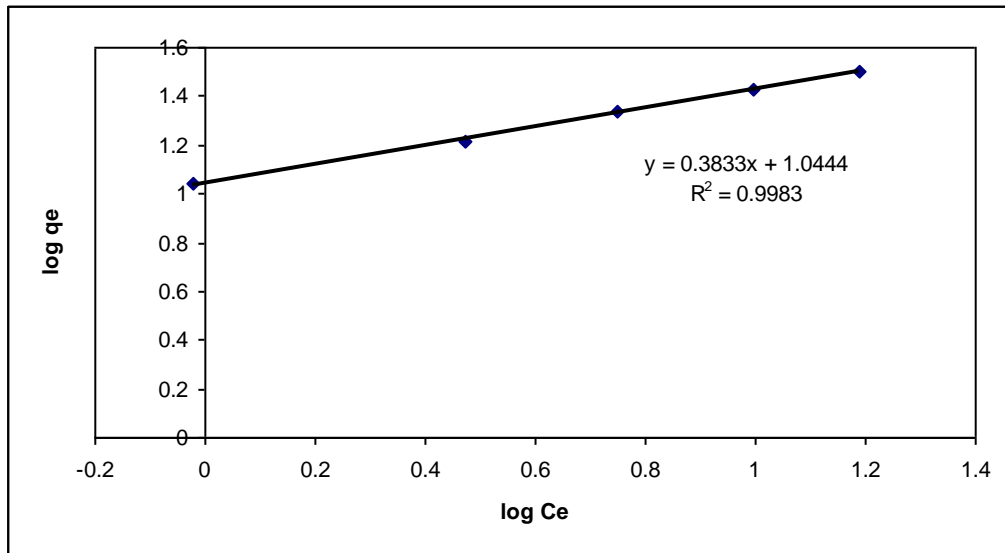


Figure 8. Freundlich isotherm plot at 30 °C.

3.4.3. Flory-Huggins isotherm

Flory–Huggins isotherm model (Foo and Hameed, 2010), which occasionally deriving the degree of surface coverage characteristics of adsorbate onto adsorbent, can express the feasibility and spontaneous nature of an adsorption process. The Flory-Huggins equation is expressed as equation 8.

$$\text{Log} \left(\frac{\theta}{C_o} \right) = \text{Log} K_{FH} + n_{FH} \text{Log} (1 - \theta) \tag{8}$$

where, θ is the degree of surface coverage, and is defined by equation 9.

$$\theta = \frac{C_o - C_e}{C_o} \tag{9}$$

K_{FH} and n_{FH} are the indication of its equilibrium constant and model exponent respectively. The equilibrium constant, K_{FH} is used for the calculation of spontaneity free Gibbs energy, according to the equation 10 (Vijayaraghavan, 2006).

$$\Delta G^\circ = -RT \ln(K_{FH}) \tag{10}$$

where R is the molar gas constant (8.314 J/mol K) and T is the absolute temperature. Plot of $\text{Log} \left(\frac{\theta}{C_o} \right)$

against $\text{Log}(1-\theta)$ is shown in Fig. 9 from where the values of n_{FH} and K_{FH} are obtained from slope and intercept respectively.

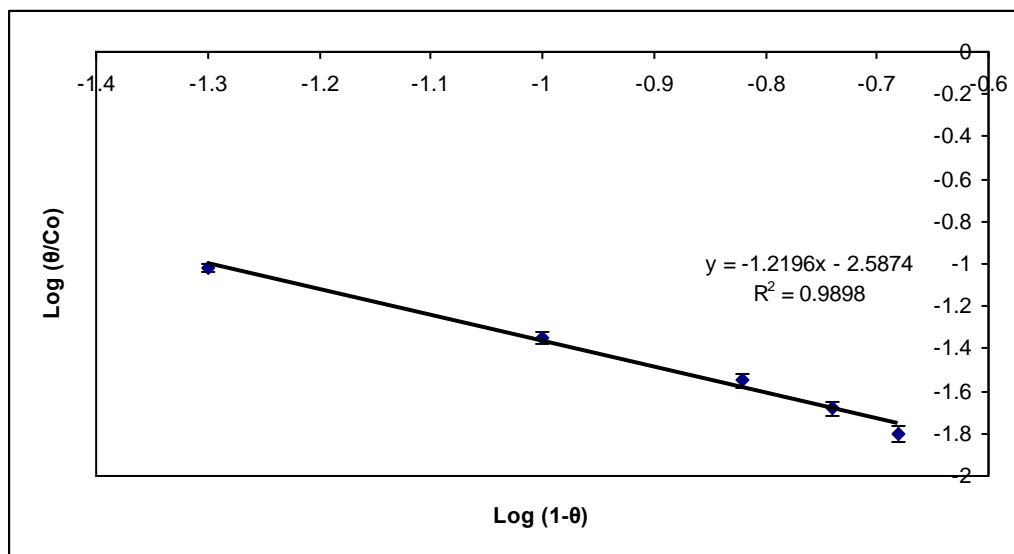


Figure 9. Flory-Huggins isotherm plot at 30 °C.

3.5. Effect of Temperature of Adsorption

Previous study on the used of PVAL as adsorbent for methylene blue indicated that the process was exothermic (Umoren et al., 2013). Based on this, a temperature of 30 °C was selected for the study in order to determine the mechanism, type of adsorption and spontaneity of the adsorption process. The change in standard Gibb's free energy, ΔG is given as:

$$\Delta G = -RT \ln K_L \quad (11)$$

where K_L is a constant obtained from Langmuir plot. ΔG as obtained from both Langmuir and Flory-Huggins isotherm models are +3.033 and +14.634 KJ/mol respectively. Values of ΔG are positive indicating non spontaneity of the process. Reports of non-spontaneous process have been documented for removal of Congo red by pine biomass (Dawood and Sen, 2012), Congo red dye adsorption onto activated carbon prepared from coir pith (Namasivayam and Kavitha, 2002) and adsorption of copper using pine cone (Ofomaja et al., 2009).

3.6. Adsorption Kinetics

Adsorption kinetics provides valuable information about the reaction pathways and mechanism of the reactions. Pseudo first-order (Largergrén, 1898) and pseudo second-order (Ho and McKay, 1998) models are employed to elucidated the mechanism embedded in this process. The conformity between

experimental data and the model predicted values are expressed by the correlation coefficients (R^2) and the q_e values.

The pseudo-first order kinetic model can be represented by Lagergren rate equation (Lagergren, 1898),

$$\text{Log}(q_e - q_t) = \text{Log } q_e - \frac{K_1}{2.303}t \tag{12}$$

where q_e and q_t represent the amounts of dye adsorbed (mg/g) at equilibrium and at any time, t (min), k_1 is the rate constant (min^{-1}). The values of q_e and k_1 are deduced from the intercept and slope of the linear plot of $\log (q_e - q_t)$ against t (Fig. 10). For the present study however, Lagergren pseudo-first order kinetics parameters (Table 2) does not prove effective in representing the experimental kinetic data with a good R^2 value. Calculated values of $q_{e,\text{cal}}$ has deviated largely from that of the experimental values $q_{e,\text{exp}}$. Similar trend has been reported for adsorption of methyl orange and methyl violet (Chen et al., 2010).

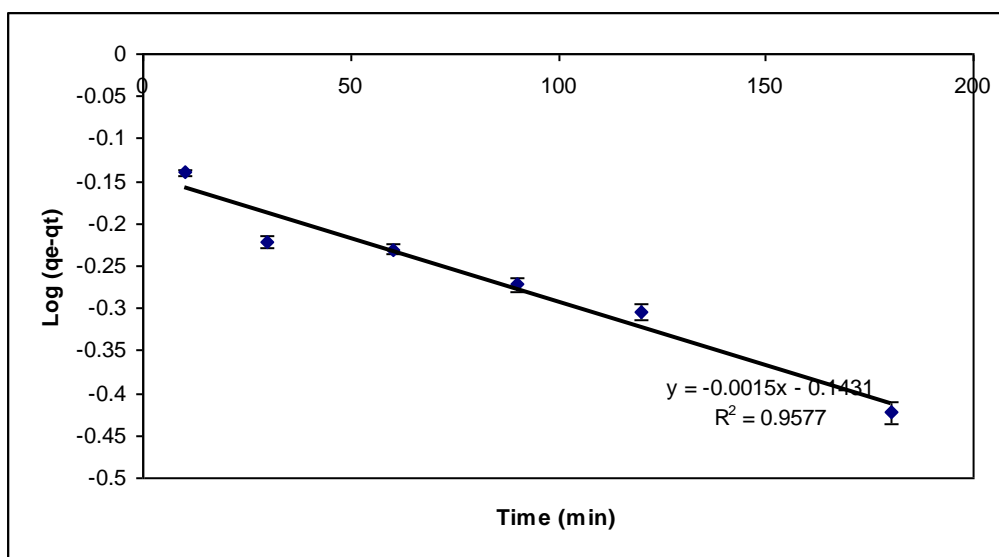


Figure 10. Psuedo first order kinetic plot.

Table 2. Adsorption kinetics parameter

Pseudo 1st order		Pseudo 2nd order		Intra-particle diffusion	
K_1	3.45×10^{-3}	K_2	7.08×10^{-3}	K_{id}	3.06×10^{-1}
q_e	7.19×10^{-1}	q_e	2.39×10^1	I	2.98×10^0
R^2	0.9577	R^2	0.9988	R^2	0.9632

The pseudo-second order kinetic model can be represented with the following equation (Ho and Mackay, 1998):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \tag{13}$$

where k_2 is the rate constant of pseudo-second order kinetics (g/mg min). Fig. 11 shows pseudo-second order plot for the adsorption of malachite green onto MPVAL. K_2 and q_e values are determined from the intercept and slope of the linear plots of equation 13. Calculated value of the adsorption capacity $q_{e,cal}$ (23.9 mg/g) agrees well with that of the experimental values $q_{e,exp}$ (22.6 mg/g) and correlation coefficient ($R^2 > 0.99$) (Table 2). Based on this it can be concluded adsorption process follows pseudo-second order kinetic model. The applicability of the pseudo-second order model suggested that chemical reaction might be also responsible for adsorption of MG onto MPVAL. The kinetics of adsorption of many dye species onto various bio-materials have earlier been reported to conform to pseudo-second order kinetic model (Chiou et al., 2004; Dawood and Sen, 2012; Ofojama and Ho, 2007).

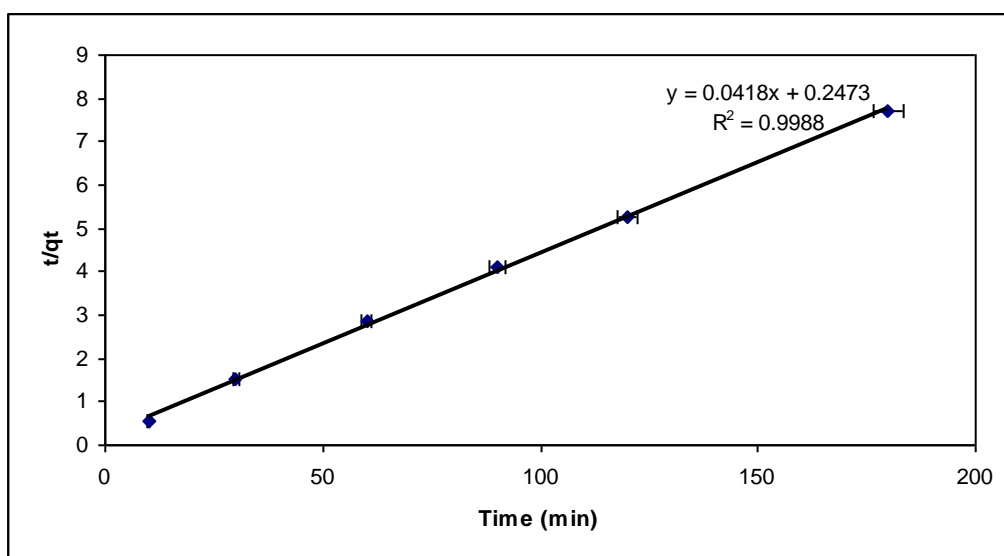


Figure 11. Pseudo-second order kinetic plot.

3.7. Adsorption Mechanism

Intra-particle diffusion model is commonly used to identify the adsorption mechanism for design purpose. The adsorbate species are most probably transported from the bulk of the solution in to the solid phase through intra-particle diffusion process, which is often the rate limiting step in many adsorption processes. According to Weber and Morris (1963), for most adsorption processes, the removal varies almost proportionally with $t^{1/2}$ rather than with the contact time and can be represented as follows:

$$q_t = K_{id} t^{1/2} + I \tag{14}$$

where q_t is the amount adsorbed at time t . $t^{1/2}$ is the square root of the time, I is the intercept and K_{id} ($\text{mg/g min}^{1/2}$) is the rate constant of intra-particle diffusion. The value of intercept I (Table 2) provides information about the thickness of the boundary layer and the resistance to the external mass transfer increases as the intercept increases (Santhi et al., 2010b). Fig. 12 shows intra-particle diffusion plot for adsorption of malachite green onto MPVAL. It is obvious from the figure that adsorption shows multi-mechanism which could be through the steps: (i) migration of the dye molecules from the bulk solution to the surface of the sorbent, (ii) diffusion through the boundary layer to the surface of the sorbent, (iii) adsorption at sites and intra-particle diffusion into the interior of the sorbent (Nandi et al., 2009; Oladoja et al., 2008; Vadivelan and Kumar, 2005; Vimonses et al., 2009), and others such as chemical reaction and hydrogen bonding (Umoren et al., 2013). However, The R^2 value (Table 2) is close to unity indicating the applicability of this model. This may confirm that the involvement of the intra-particle diffusion process in the overall sorption mechanism.

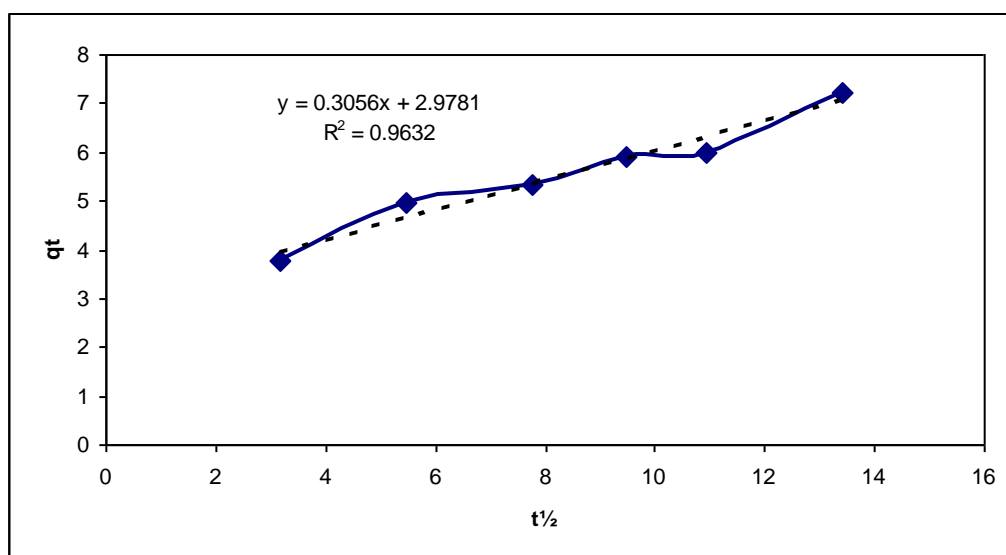


Figure 12. Intra-particle diffusion plot.

4. Conclusions

The results of analysis of the sorption behaviour of a novel adsorbent made from the modification of a synthetic polymer polyvinyl alcohol (PVAL) with coconut coir dust, a natural polymer by physical means revealed the feasibility of its application as adsorbents for treating wastewater in terms of decolourization. Process exhibited optimal activity at pH 9.0, adsorbent dosage 4.0 g and lowest concentration under study. Maximum percentage adsorption of 95.1% was obtained from 10 mg/L malachite green at pH 9.0 at room temperature. Adsorption was modeled with Langmuir, Freundlich and Flory-Huggins isotherms and all gave good correlation coefficient at 30 °C.

The kinetic models indicated the pseudo second model to fit better to adsorption data than the first order model. The sorption process was non-spontaneous at 30 °C with positive change in Gibb's free energy. On the whole adsorption was a physico-chemical process with intra-particle diffusion defining its mechanism.

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