CHARACTERIZATION OF PEANUT HULLS AND ADSORPTION STUDY ON BASIC DYE: ISOTHERM AND KINETIC ANALYSIS

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Abstract

The potential feasibility of peanut hull particle for removal of cationic dyes (methylene blue) from aqueous solution was investigated. The effects of various experimental parameters were examined and optimal experimental conditions were decided. The peanut hulls was characterized by using XRF, FTIR and SEM. FITR analysis showed that there were carbonyl and hydroxyl groups on the surface of the adsorbent which improve its surface for adsorption and contain capillaries tubes showed by SEM analysis. The equilibrium adsorption data of methylene blue on peanut hulls were analyzed using Langmuir, Tempkin and Freundlich models. The isothermal data for biosorption fitted the Langmuir, Freundlich and Tempkin model as R^2 values showed. The kinetic data were analyzed using the pseudo-first-order and pseudo-second-order adsorption kinetic models. According to these models, the rate constants were calculated for different initial dye concentrations. The biosorption processes conformed to the pseudo-second-order according to R^2 value. Also Intraparticle diffusion for peanut hulls were studied .The results in this study indicated that peanut hulls was an attractive candidate for removing cationic dye from dye wastewater.

Keywords: Peanut hulls, Methylene blue, Isotherm, Kinetics
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Introduction

Colour is considered as the first pollutant to be identified in wastewater and it is mostly caused by the effluents discharged from dyeing industries such as paper, rubber, cosmetics, textile and plastics. Approximately 10,000 different dyes and pigments are used for industries and over 7×10^5 tons of these dyes are annually produced worldwide [1]. Majority of dyes are visually detected even at the concentration of less than 1 mg/l. In addition, some dyes or their metabolites are either toxic or mutagenic and carcinogenic [2]. The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons [3]. Most of which are difficult to biodegrade due to their complex aromatic molecular structure and synthetic origin [4].

Methylene blue is the most commonly used substance for dying cotton, wood and silk. It can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [5]. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters. In industries, the methods employed for treating dye wastewaters include coagulation and flocculation [6], oxidation or ozonation [7, 8], membrane separation [9] and activated carbon sorption [10]. These technologies do not show significant effectiveness or economic advantage. Activated carbon is the most popular and widely used dye sorbent, but its relatively high price, high operating costs and problems with regeneration hamper its large-scale application. Therefore, there is a growing need to find low cost, renewable, locally available materials for the removal of dye colors. Some agricultural byproducts have been investigated for this purpose. There is a wide range of biomass natural fibres that are prevalent in commercial applications. We see them being utilised in industries producing ropes and canvases [11–13]. Industrial use of lignocellulose fibre is well established especially in the form of wood for paper pulp and the manufacture of fibreboard [14]. The annual global production of lignocellulosic fibres from crops is about 4 billion tonnes, of which 60% comes from agriculture and 40% from forests. In comparison, annual world production of steel is currently around 0.7 billion tonnes and plastic is about 0.1 billion tonnes [4].

In our laboratory, the work is in progress to evaluate the possibility of the use of waste biomass for industrial wastewater pollution management. The purpose of this work was to investigate the possibility of using peanut hulls as a biosorbent for removal of basic cationic dyes from aqueous solution. Peanut hulls is an abundant and low cost agricultural waste residue and is easily available in large quantity in Egypt. The effects of various operating parameters on

biosorption such as dye concentration, sorbent dosage, particle size and stirring speed were monitored and optimal experimental conditions were decided. The equilibrium adsorption data of methylene blue on peanut hulls were analyzed by Langmuir, Freundlich and Tempkin models. The kinetic data were analyzed using the pseudo-first-order and pseudo-second-order adsorption kinetic models. Finally Intraparticle diffusion of peanut hulls were studied

Materials and methods

Preparation of peanut hulls

Fresh biomass of peanut hulls was collected from its natural habitats in the farmland. The collected biomaterial was extensively washed with tap water to remove soil and dust, and washed with distilled water, next dried in an oven at 80 °C for complete dryness. Dry peanut husk was crushed into powder crusher and sieved to different particle sizes and then preserved in the desiccator for use. The major elements of peanut husk were analyzed using X-Ray Fluorescence, Rigaku Nexcg-Japan. FTIR of peanut hulls was performed to analysis the functional groups in the surface of peanut hulls. FTIR spectra were recorded on a (FTIR- 8400 S, Shimadzu-Japan) instrument in the absorption mode with a resolution of 4 cm^{-1}, in the range of 4000–400 cm^{-1}. Scanning electron microscope was used to study the surface morphology of peanut hulls using (SEM "JEOL JSM 6360LA"- Japan).

Preparation of MB solution

The MB used in this work was purchased from "NICE chemicals pvt. ltd company". The stock solution of 1000 mg/L was prepared by dissolving 1.00 g of MB in 1000 ml distilled water. The experimental solutions with different concentrations were prepared by diluting the stock solution with distilled water.

Experimental methods and measurements:

Biosorption experiments were carried out on a rotary shaker operated at 150 rpm and thermostatically controlled at (25±1) ℃. using 250 ml shaking flasks containing 100 ml of different concentrations and initial pH values of dye solutions. Different doses of sorbent were added to each flask and then the flasks were sealed to prevent change in volume of the solution during the experiments. After shaking the flasks for predetermined time intervals, the samples were taken out from the flasks and the dye concentration was analyzed using UV/VIS spectrophotometer (Ultrospec 2000 - Pharmacia Biotech), the samples were separated by decantation. All the measurements were made at wave length corresponding to the maximum absorbance of the dye at 655 nm. The amount of dyes sorbed by the biomass was calculated using the following equation:

$$q=(C_0-Ce)*V/W \qquad (1)$$

Where q (mg/g) is the amount of dye sorbed by biomass, C_0 and Ce (mg/l) are the initial and equilibrium liquid-phase concentrations of the dye, respectively, V (l), the initial volume of dye solution, and W (g), the weight of the biomass.

The percentage removal of dye from solution measured using the following equation:

$$\%Re=(C_0-C_e)/C_0*100 \qquad (2)$$

Where C_0 and Ce (mg/l) are the initial and equilibrium liquid-phase concentrations of the dye.

Results and discussion

The study of MB adsorption using peanut hulls was batch studies, the process was performed by kinetic and equilibrium studies.

Composition and physical properties of peanut hulls:

Table 1 gives the composition of the Peanut hulls which was determined by X-Ray Fluorescence, Rigaku Nexcg-Japan. As can be seen, potassium and calcium oxides were the main component in the Peanut hulls. The scanning electron micrograph of peanut hull were illustrated in figure 1 for surface and thickness. The figures illustrate that peanut hulls has roughness surface which cleared by increasing magnification factor from 150 to 650, also small pores with different sizes appeared with high magnification factor. While the thickness figures (figure 1 b) illustrate an irregular shape containing capillary tubes which help the dye to be entrapped inside it .

Al_2O_3	2.47
ZnO	0.175
SO_3	8.41
SiO_2	3.15
P_2O_5	4.98
CuO	0.104
K_2O	37.8
CaO	30.2
Cr_2O_3	0.0926
MnO	0.303
Fe_2O_3	2.05
NiO	0.0447

Table 1: Metallic ingredients of peanut hulls (mass %).

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(a)

(b)
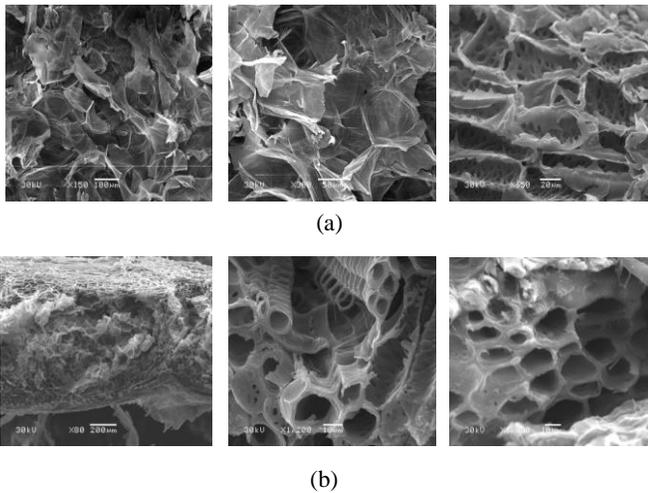
Figure 1: SEM for peanut hulls (a) surface (b) thickness

Figure2: FTIR spectrum of natural peanut hulls

FTIR spectrum of peanut hulls:

All vegetable biomass are composed of cellulose, hemi-cellulose and lignin. Peanut hulls, mainly consisted of poly-saccharides, proteins, and lipids, offer many polar this functional groups such as carboxyl, carbonyl, hydroxyl and amino which can be involved in metal and dye binding [15]. The FTIR technique was an important tool to identify functional groups, which are capable of adsorbing pollutant ions [16, 17]. FTIR spectroscopy was, therefore, done for preliminary quantitative analysis of major functional groups presented in native peanut hulls. Fig. 2 showed the FTIR spectrum of natural peanut hulls. The broad band around 3388 cm^{-1} was attributed to the surface hydroxyl groups, adsorbed water and amine groups. The O-H stretching vibrations occurred within a broad range of frequencies indicating the presence of "free" hydroxyl groups and bonded O-H bands of carboxylic acids. The peak at 2920 cm^{-1} was assigned to C–H asymmetrical stretching of methyl groups on the surface. These groups were present on the lignin structure [16]. The peak located at 1630 cm^{-1} was characteristics of the carbonyl group stretching from carboxylic acids and ketones. They could be conjugated or non-conjugated to aromatic rings. The peak at 1407 cm^{-1} was attributed to the stretch vibration of C–O from the carboxyl group [18]. The peak at 1271 cm^{-1} was due to the asymmetric bending vibration of the -CH3 group. The wave number observed at 1051 cm^{-1} was due to the C-O group in carboxylic and alcoholic groups [19]. The analysis of the FTIR spectrum showed the presence of ionizable groups (carboxyl and hydroxyl) able to interact with protons, metal or positive dye ions these functional groups may be the major biosorption sites for methylene blue removal.
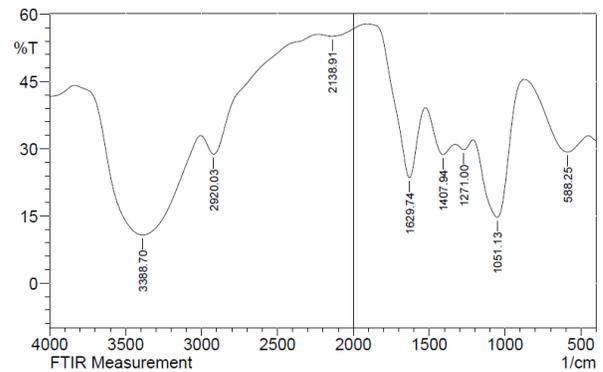
Influence of initial dye concentration:

The influences of dye concentration on adsorption percentages of dye were estimated. As shown in Fig. 3, when the dye concentration was increased from 5 to 25 mg/l, the percentages of dyes removal increased from 79.2% to 89.77 after 120 min. and by increasing adsorption time until 180 min. the curves seem to reach the equilibrium.
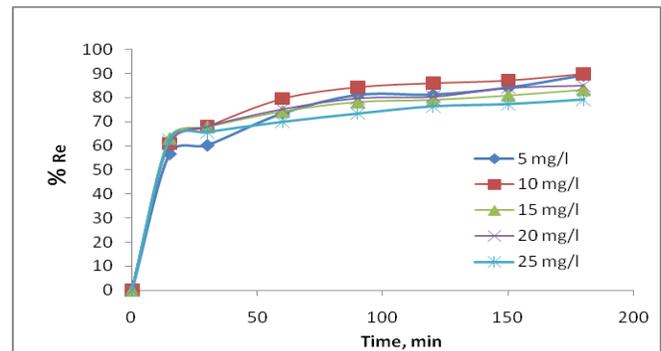
Figure. 3. Influence of dye concentration on adsorption of MB by peanut hulls (sorbent dose: 0.1 g; particle size: 1 mm; stirring speed; 200 r.p.m; contact time: 3 h).

Effect of sorbent dose:

The effects of sorbent dose on the removal ratios of dye were shown in Fig.4. The percentages of dyes sorbed increased as the sorbent dose was increased over the range 0.05–0.4 g. The adsorption ratios of dyes increased from 14.4 to 65.96%, in MB at the first 15 min. and increasing of dye removal still increase to reach nearly constant values after 120 min. for 0.05g, while for the other doses small increase in dye removal was obtained and seemed to be con-

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stant after 120 min. also above 0.3 g of sorbent. Increase in biosorption with the sorbent dose could be attributed to increased surface area and the availability of more sorption sites. Equilibrium time was lesser at higher adsorbent doses. So, in other parameter experiments, a peanut hulls biomass of 0.3 g was chosen.
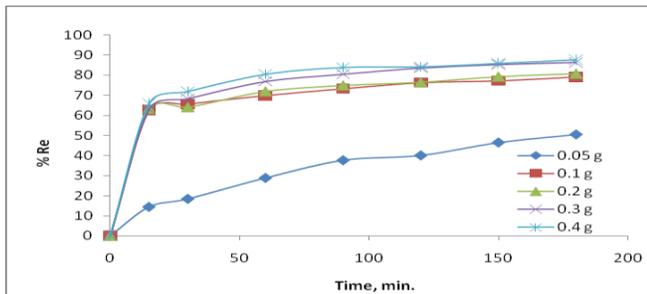
Figure 4. Effect of sorbent dose on adsorption of MB by peanut hulls (dye concentration: 25 mg/l; particle size 1mm; stirring speed 200 r.p.m; contact time: 3 h).

Effect of sorbent particle size:

Figure 5, showed the effects of sorbent particle size on adsorption percentages of dye. The ratios of dyes sorbed increased as the sorbent particle size was decreased from 74.5% at 4 mm to 92 % at 125 μm after 120 min, as the rapid increase in dye removal at the first 30 min, after that small increase was observed to reach equilibrium at 120 min. The ratios of dyes sorbed had neared the maximum values, this may be due to the increase of surface area by decreasing particle size which increase the contact surface between sorbent molecule and dye solution which improve the dye sorption process. For convenience of liquid–solid phase separation, the sorbent particle in 500μ m was used in all other parameter experiments.
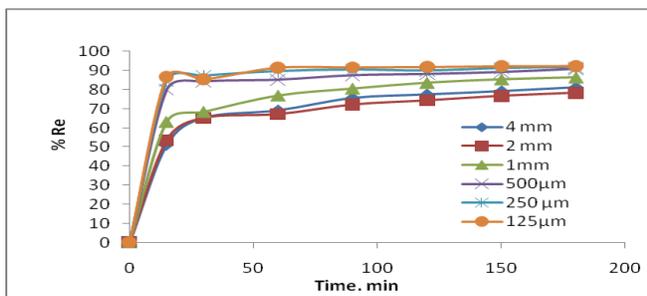
Figure . 5. Effect of sorbent particle size on adsorption of MB by peanut hulls (dye concentration: 25 mg/l; stirring speed: 200 r.p.m ; sorbent dose: 0.3 g; contact time: 3 h).

Effect of stirring speed:

The effects of stirring speed on adsorption percentages of dye were elucidated in Fig. 6. The dye removal ratios were minimum at the initial r.p.m. The ratios of dyes sorbed increased as the r.p.m was increased from 68.4 to 84.96 at the first 15 min, then the dye removal ratios were not significantly altered as after 60 min. dye removal percentage at all stirring speed seems to be the same value, so it concludes that stirring speed is not effective factor for dye removal for time more than 60 min.
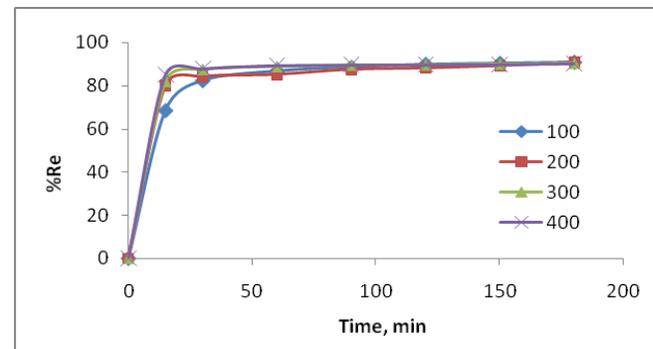
Figure . 6. Effect of stiring speed on adsorption of MB by peanut hulls (dye concentration: 25 mg/l; sorbent dose: 0.3g ; particle size: 500μm; contact time: 3 h).

Equilibrium of adsorption:

Adsorption isotherms used to determine the capacity and optimizing the use of the adsorbent at equilibrium. Therefore, the correlation of equilibrium data by either theoretical or empirical equations is essential to the practical design and operation of adsorption system.

Adsorption isotherms:

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose [20] .
As adsorption isotherm is basically important to describe how solutes interact with adsorbents, and is critical in optimizing the use of adsorbents. In order to investigate the adsorption isotherm, the experimental data of equilibrium isotherms were intercepted using three equilibrium models; Langmuir, Freundlich and Tempkin. Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane

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of surface [21] . While, Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage [21]. The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2.

Langmuir isotherm:

The linear form of Langmuir's isotherm model is given by the following equation:

$$C_e/q_e = 1/(Q_0*b) + (1/Q_0)*C_e \qquad (3)$$

Where C_e is the equilibrium concentration of the adsorbate (MB) (mg/l), q_e the amount of adsorbate adsorbed per unit mass of adsorbate (mg g^{-1}), and Q_o and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively.

When C_e/q_e was plotted against C_e, straight line with slope $1/Q_o$ was obtained (Fig. 7), indicating that the adsorption of MB on peanut hulls follows the Langmuir isotherm. The Langmuir constants 'b' and 'Q_o' were calculated from this isotherm and their values are given in Table 1.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) [22] , which is defined by:

$$R_L = 1/(1 + bC_0) \qquad (4)$$

Where b is the Langmuir constant and C_0 the highest dye concentration (mg l^{-1}). The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Value of R_L was found to be 0.108 and confirmed that the peanut hulls is favorable for adsorption of MB dye under conditions used in this study.
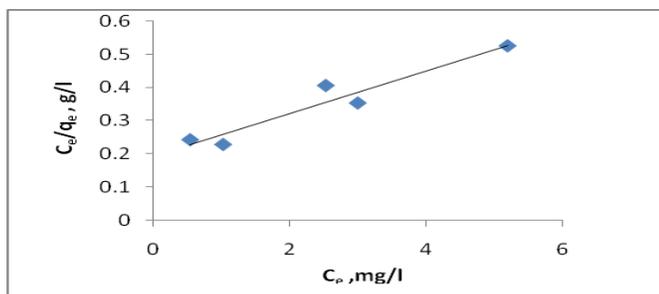
Figure 7. Langmuir isotherm of MB adsorption onto peanut hulls

Table (2): Isotherm parameters for removal of methylene blue by peanut hulls powder

Isotherm	Parameters	
Langmuir model	R^2	0.9212
	Q_0	15.625 mg/g
	b	0.33 mg-1
	R_L	0.108
Freundlich model	n	0.6395
	1/n	1.563
	K_f	20.84
	R^2	0.9497
Temkin model	A	2.195
	B	3.3207
	R^2	0.9569

Freundlich isotherm:

The well-known logarithmic form of Freundlich model is given by the following equation:

$$\text{Log } q_e = \log K_f + 1/n_f * \log Ce \qquad (5)$$

While the linear form:

$$q_e = (C_0-C_e)*(V/W) \qquad (6)$$

Where qe is the amount adsorbed at equilibrium (mg g^{-1}), Ce the equilibrium concentration of the adsorbate (MB) and K_F and n are Freundlich constants, n giving an indication of how favorable the adsorption process and K_F (mg g^{-1}(l mg^{-1})*, n is the adsorption capacity of the adsorbent. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for a unit equilibrium concentration.

The slope $1/n$ ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [23]. A value for $1/n$ below one indicates a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption [24]. The plot of log qe versus log$C$e gives straight lines with slope '$1/n$' (Fig. 8), which shows that the adsorption of MB also follows the Freundlich isotherm. Accordingly, Freundlich constants (K_F and n) were calculated and recorded in Table 2.
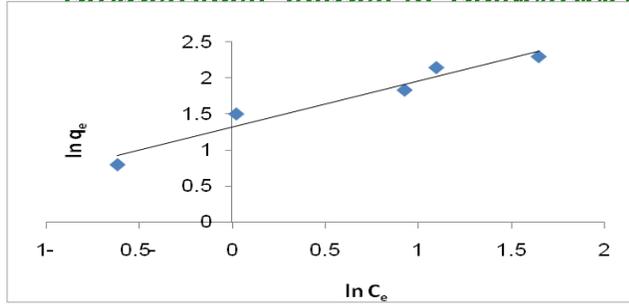
Figure. 8. Freundlich isotherm of MB adsorption onto peanut hulls

Tempkin isotherm:

Tempkin and Pyzhev considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The Tempkin isotherm has been used in the following form [25].

$$q_e = RT/b*(\ln AC_e) \qquad (7)$$

Eq. (7) can be expressed in its linear form as:

$$q_e = B\ln A + RT/b \ln C_e \qquad (8)$$

where

$$B = RT/b$$

The adsorption data can be analyzed according to Eq. (8). A plot of qe versus ln Ce enables the determination of the isotherm constants A and B as shown in fig (10) . The constant B is related to the heat of adsorption. The constant *A* and *B* together with the R^2 values are shown in Table 2.

As shown in Table 2 which summarizes the results of the isotherm constants for the three different equilibrium isotherms tested. On the basis of the correlation coefficients (R^2), Freundlich model yields ($R2 = 0. 9497$) while Langmuir model ($R2 = 0. 9212$) and Tempkin isotherm was($R^2 = 0. 9569$) which seemed to represent the equilibrium adsorption data with better fit as compared to the other isotherms.
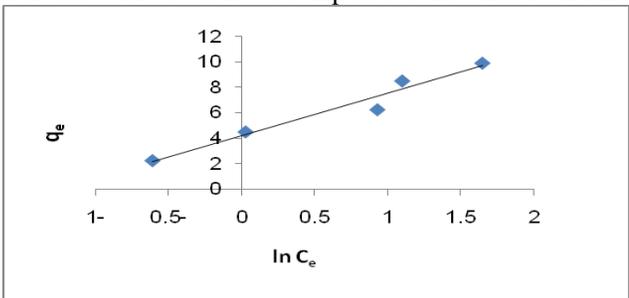
Figure. 9. Tempkin isotherm of MB adsorption onto peanut hulls

Adsorption kinetics:

Lagergren proposed a method for adsorption analysis which is the pseudo-first-order kinetic equation of Lagergren [26] in the form:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (9)$$

Integrating this for the boundary conditions t=0 to $t = t$ and q_t =0 to $q_t = q_t$, gives

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (10)$$

Where k_1 is the equilibrium rate constant (1/min), q_e the amount of dye adsorbed on the surface at equilibrium (mg/g), q_t the amount of dye adsorbed at any time (mg/g). The value of the adsorption rate constant (k_1) for MB sorption by peanut hulls powder was determined from the plot of log ($q_e - q_t$) against t. The parameters of pseudo-first-order model for different parameters studied in this work are summarized in Table 3

The pseudo-second-order kinetics may be expressed as [27,28]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (11)$$

Where k_2 is the rate constant of adsorption, q_e is the amount of dye adsorbed at equilibrium (mg/g) and q_t is the amount of dye adsorbed at time t (mg/g). Separating the variables in Eq. (13) gives:

$$\frac{dq_t}{(q_e - q_t)^2} = k_2\, dt \qquad (12)$$

Integrating this for the boundary conditions t=0 to $t = t$ and q_t =0 to $q_t = q_t$ gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad (13)$$

Which is the integrated rate law for a pseudo-second-order reaction. Eq. (13) can be rearranged to obtain:

$$q_t = \frac{t}{(1/k_2 q_e^2) + (t/q_e)} \qquad (14)$$

Which has a linear form of:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (15)$$

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Where the equilibrium adsorption capacity (q_e), and the second order constants k_2 (g/mg min) can be determined experimentally from the slope and intercept of plot t/q_t versus t.

Table 3 presents the coefficients of the pseudo-first- and second-order adsorption kinetic models. The R^2 values of the pseudo-second-order model exceeded 0.99 and the q values ($q_{e,cal}$) calculated from pseudo-second-order model were more consistent with the experimental q values ($q_{e,exp}$) than those calculated from the pseudo-first-order model. Hence, the pseudo-second-order model better represented the adsorption kinetics and this suggests that the overall rate of the MB adsorption process appeared to be controlled by chemical process.

Table (3) Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants and calculated and experimental q_e values obtained at different initial MB concentrations for different parameters studied

Dye system	$q_{e,exp}$ mg/g	Pseudo first order model K_1 min^{-1}	q_{e1} mg/g	R^2
1-Different concentrations W=0.1g n=200rpm P=1mm				
C0 = 5 mg/l	2.23	0.010	0.45	0.862
C0 = 10mg/l	4.489	0.025	1.375	0.962
C0 = 15 mg/l	6.235	0.016	1.655	0.9713
C0 = 20 mg/l	8.500	0.029	3.712	0.9872
C0 = 25 mg/l	9.900	0.025	4.03	0.9641
2- Sorbent dosage n= 200rpm P=1mm C0=25mg/l				
w0= 0.05g	12.600	0.0198	11.392	0.9591
w0= 0.1g	9.900	0.0256	4.033	0.9641
w0= 0.2g	5.043	0.0355	2.654	0.8812
w0= 0.3g	3.601	0.0242	0.792	0.9233
w0= 0.4g	2.744	0.0145	0.394	0.8608
3- Particle size W=0.2g n=200rpm C0=25mg/l				
P0= 2mm	3.384	0.024	3.765	0.9996
P0= 1mm	3.267	0.0355	2.654	0.8812
P0= 500µm	3.601	0.0228	1.756	0.9865
P0=250 µm	3.786	0.0161	1.047	0.09702
P0= 125 µm	3.8224	0.023	0.844	0.977
4- rpm W=0.2g P=1mm C0=25mg/l				
rpm0= 100	4.784	0.023	1.667	0.9649
rpm0= 200	4.788	0.0355	2.654	0.8812
rpm0= 300	4.767	0.0168	0.613	0.9078
rpm0= 400	4.759	0.0168	0.357	0.8635

Dye system	$q_{e,exp}$ mg/g	Pseudo second order model K_2 g/mg.min	q_{e2} mg/g	R^2
1-Different concentrations W=0.1g n=200rpm P=1mm				
C0 = 5 mg/l	2.23	0.109	2.043	0.9996
C0 = 10mg/l	4.489	0.042	4.583	0.9996
C0 = 15 mg/l	6.235	0.0285	6.693	0.9998
C0 = 20 mg/l	8.500	0.0158	9.381	0.9996
C0 = 25 mg/l	9.900	0.014	11.325	0.9994
2- Sorbent dosage n= 200rpm P=1mm C0=25mg/l				
w0= 0.05g	12.600	0.00336	21.186	0.9945
w0= 0.1g	9.900	0.014	11.325	0.9994
w0= 0.2g	5.043	0.184	5.663	0.9992
w0= 0.3g	3.601	0.0739	3.768	0.9993
w0= 0.4g	2.744	0.1149	2.82	0.9988
3- Particle size W=0.2g n=200rpm C0=25mg/l				
P0= 2mm	3.384	0.0083	5.6179	0.9992
P0= 1mm	3.267	0.032	5.663	0.9992
P0= 500µm	3.601	0.0278	5.477	0.9998
P0=250 µm	3.786	0.0465	5.462	0.9994
P0= 125 µm	3.8224	0.0653	5.350	0.9999
4- rpm W=0.2g P=1mm C0=25mg/l				
rpm0= 100	4.784	0.0326	5.663	0.9992
rpm0= 200	4.788	0.1527	5.580	0.9999
rpm0= 300	4.767	0.0871	5.663	0.9999
rpm0= 400	4.759	0.1527	5.580	0.9999

Sorption mechanism:

The kinetic studies help in predicting the progress of adsorption, but the determination of the adsorption mechanism is also important for design purposes. In a solid–liquid adsorption process, the transfer of the adsorbate is controlled by either boundary layer diffusion (external mass transfer) or intraparticle diffusion (mass transfer through the pores), or by both. It is generally accepted that the adsorption dynamics consists of three consecutive steps:

- Transport of adsorbate molecules from the bulk solution to the external surface of the adsorbent by diffusion through the liquid boundary layer.
- Diffusion of the adsorbate from the external surface and into the pores of the adsorbent
- Adsorption of the adsorbate on the active sites on the internal surface of the pores.

The last step, adsorption, is usually very rapid in comparison to the first two steps. Therefore, the overall rate of adsorption is controlled by either film or intraparticle diffusion, or a combination of both. Many studies have shown that the boundary layer diffusion is the rate controlling step in systems characterized by dilute concentrations of adsorbate, poor mixing, and small particle size of adsorbent. Whereas the intraparticle diffusion controls the rate of adsorption in systems characterized by high concentrations of adsorbate, good mixing, and big particle size of adsorbent [31][29]. Also, it has been noticed in many studies that boundary layer diffusion is dominant during the initial adsorbate uptake, then gradually the adsorption rate becomes controlled by intraparticle diffusion after the adsorbent's external surface is loaded with the adsorbate. The intraparticle diffusion parameter, k_i (mg/g min0.5) is defined by the following equation [32][30]:

$$q=k_i t^{0.5}+c \qquad (16)$$

where q is the amount of MB adsorbed (mg/g) at time t, k_i is intraparticle diffusion constant (mg/g min0.5), and c is the intercept. which can be evaluated from the slope of the linear plot of qt versus $t^{1/2}$ (Fig. 12). The k_{id} values were obtained from the slope of the linear portions of the curve of different initial concentrations and shown in Table 4. Theoretically, the plot of k_i versus $t^{0.5}$ should show at least four linear regions that represent boundary layer diffusion, followed by intraparticle diffusion in macro, meso, and micro pores [33][31]. These four regions are followed by a horizontal line representing the system at equilibrium. *Also,* the plot of uptake, q_t, versus the square root of time ($t^{1/2}$) should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and these further shows that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the

rate of adsorption, all of which may be operating simultaneously. The values of intercept give an idea about the boundary layer thickness such as the larger the intercept, the greater the boundary layer effect.

The intraparticle diffusion plots of the experimental results, q versus $t0.5$ for different initial MB concentrations using 0.1 g dose of 1mm particle size of peanut hulls are shown in Fig. 10. From the figure it is observed that there are three linear regions. At the beginning of adsorption there is a linear region representing the rapid surface loading, followed by the second linear region representing pore diffusion, and finally a horizontal linear region representing equilibrium.
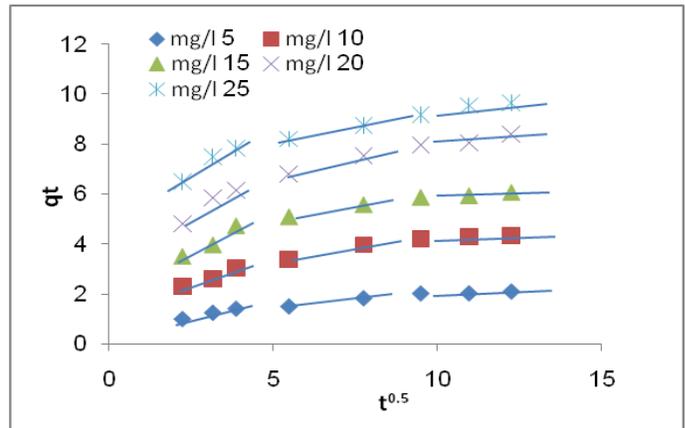
Figure. 10. Plots for evaluating intraparticle diffusion rate constant for sorption of MB onto peanut hulls

Table(4): Intraparticle diffusion constants for different initial MB concentrations

Initial concentration (mg/L)	k_{id} (mg/g min$^{1/2}$)	C	R^2
5	-0.0215	1.7475	0.7945
10	-0.0506	3.354	0.899
15	-0.0771	5.13	0.921
20	-0.1277	6.9522	0.946
25	-0.1369	8.624	0.972

Conclusions

The present study showed that the powdered peanut hulls is a promising biosorbent for the removal of cationic dye from aqueous solution, since the raw material peanut hulls was easily available in large quantity and the treatment method of biomaterial seemed to be economical.

The correlation coefficients (R^2) for Freundlich, Langmuir and Tempkin model were 0. 9497, 0. 9212 and 0. 9569 respectively which seemed to represent the equilibrium adsorption data with better fit as compared to the other isotherms. The R^2 values of the pseudo-second-order model exceeded 0.99 and the q values ($q_{e,cal}$) calculated were more consistent with the experimental q values ($q_{e,exp}$) than those calculated from the pseudo-first-order model. Hence, the pseudo-second-order model better represented the adsorption kinetics and this suggests that the overall rate of the MB adsorption process appeared to be controlled by chemical process. There were carbonyl and hydroxyl groups on the surface of peanut husk from FTIR analysis. Peanut husk may be suitable to remove MB from the aqueous solution.

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