

Study of the removal of basic dye on raw and pretreated barley straw from aqueous solution and its kinetic behavior

A.A. Amer ^a, Azza El-Maghraby ^b, M. El-Khaiary ^c and Nahla A. Taha ^d

^a Alexandria Petroleum Company,

^b Fabrication Technology Dept., Institute of Advanced technology and New Materials, Mubarak City for Scientific Research and Technology Applications, Alexandria, Egypt,

^c Chemical Eng. Dept., Faculty of Eng., Alexandria University, Alexandria, Egypt

^d Institute of Advanced technology and New Materials, Mubarak City for Scientific Research and Technology Applications, Alexandria, Egypt

e-mail: maghrabyazza@yahoo.com

Barely straw as a low-value agriculture by-product can be converted to sorbent materials which can be used for dyes removal. The removal of the basic dye (Methylene blue) from an aqueous solution has been studied by adsorption onto a low cost agricultural residue (barley straw). The thermal pretreatments were carried out in order to delignify, or to increase the surface area of the sorbents, and to study their effect on the rate and effective adsorption of dyes. The effect of experimental parameters; dye concentration, contact time, time of carbonization, and adsorbent particle size were studied. Optimum adsorption capacity of dye was achieved with samples treated at 200°C for 1/2 hr. Maximum dye was sequestered within 30 min after the beginning for every experiment. The equilibrium data were analyzed using the Freundlich isotherm model for raw and thermally activated barely straw. The equilibrium process described well by the Freundlich isotherm model; for Barley straw at 500 °C heating temperature. Two simplified kinetics models including Pseudo-first-order and second-order equation were selected to follow the adsorption processes and intraparticle diffusion kinetic models. The kinetic parameters of this best-fit model were calculated and discussed. The adsorption of methylene blue fit the Lagergren equation well.

يعتبر قش الشعير من المخلفات الزراعية منخفضة القيمة والتي يمكن تحويلها لمادة مازة تستخدم في إزالة الصبغات. يتضمن هذا البحث اجراء معالجة للقش حراريا وذلك لزيادة المساحة السطحية للقش ودراسة تأثير ذلك علي معدل امتزاز الصبغة كما تم ايضا دراسة تأثير العوامل المختلفة علي معدل امتزاز الصبغة وذلك من حيث تركيز الصبغة، زمن التلامس، فترات الكربنة وحجم الحبيبات للمادة المازة وكان افضل معدل امتزاز للصبغة للعينات التي تم كربنها عند 200 °م لمدة نصف ساعة. اعلي معدل ازالة للصبغة كان خلال بداية عملية الامتزاز لمدى زمني قوامه نصف ساعة من بداية التجارب. تم تحليل نتائج الاتزان باستخدام معادلات فريندلش وذلك للقش قبل وبعد المعالجة الحرارية. وقد وجد انها تعبر جيدا عن عملية الامتزاز وذلك للقش الذي تم معالجته عند 500 °م كما تم اختيار نموذجين لمعادلات الدرجة الاولى والثانية لاتباع عملية الامتزاز ووجد ان امتزاز صبغة الميثيلين الزرقاء متناسبة مع معادلة لاجريجران.

Keywords: Methylene blue, Pretreatments, Adsorption, Barley straw, Kinetics

1. Introduction

Environmental policy in the UK, since 1997, has required that zero synthetic chemicals should be released into the marine environment. This legislation is in line with similar EU measures affecting all member states [1]. The effluents from textile, leather, food processing, cosmetics, paper and dye manufacturing industries are important sources of dye pollution [2]. Many dyes and their break down products are toxic for living organisms [3], therefore, decolorization of dyes

is an important aspect of waste water treatment before discharge. Generally biologic aerobic waste water systems are not successful for decolorization of majority of dyes [3], and thus color removal was extensively studied with physico-chemical methods such as coagulation, ultra-filtration, electro-chemical adsorption, and photo oxidation [3,4]. Other methods for removing dyes from waste water include flocculation, electroflotation, precipitation, electrokinetic coagulation, ion exchange, membrane filtration, electrochemical destruction,

irradiation and ozonation. Among these methods, adsorption is widely used for dye removal from waste water [4, 5].

Adsorption technology has been used extensively in industrial processes for many purposes of separation and purification. The removal of colored and colorless organic pollutants from industrial wastewater is considered as an important application of adsorption process using suitable adsorbents [6]. Highly functional porous materials with high surface areas are generally used for such applications as they show excellent efficiency [7]. Granular and powder activated carbon are commonly used for dye removal [8-9]. However, they are expensive and the regeneration or disposal of them has several problems. Thus the removal of dyes from waste waters using several low cost and biodegradable adsorbents has been studied by many researchers such as rice husk [10], bentonite clay [11], waste orange peel [12], bamboo dust, and coconut shell [3].

Egypt produces 47 million tons of agricultural waste annually which include rice husk, rice straw, bagasse, cotton waste, and barley straw. Burning of this waste releases large quantities of smoke, ash and carbon dioxide into the air with detrimental environmental effects.

The objective of the present work is study the adsorption of basic dye (Methylene blue) from aqueous solution onto raw barley straw (BS) and also onto thermally activated barely straw (TABS) at different temperatures; and the effects of TABS particle size, solution pH were also investigated and isotherm analysis was carried out. The kinetics of adsorption was fitted by conventional models, and the mechanism of adsorption was explained in terms of the pore-diffusion model.

2. Materials and methods

2.1. Barely straw

Sun dried BS was obtained from El-Beheyra farms. It was crushed in wiley mill to different particle sizes. BS was studied as raw material for its morphology [13] and also it was treated to carbonize the straw by heating at 200, 300, 400, and 500°C for 0.5, 1, 2, and

3 hours. The carbonization was carried out in a closed stainless steel tube with length of 12.5 cm and inner diameter 2.5 cm, the tube had a hole in the top for venting gases produced during carbonization.

2.2. Methylene blue

Methylene blue ($C_{16}H_{18}N_3SCl_3 \cdot 3H_2O$) from NICE chemicals pvt. ltd company, was used without further purification. Methylene blue (MB) was dried at 110°C for 2 hr before use. 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.

2.3 Adsorption kinetic experiments

Kinetic adsorption experiments were carried out to study the effect of time on adsorption process. Batch adsorption experiments were carried out by shaking constant mass (100 mg) of 2000-1000 μm particle size of raw or carbonized barley straw with a constant volume (50 ml) of MB solution of increasing initial dye concentration from (5-25 mg/l) to maintain constant mass to volume ratio. The pH of the solution was adjusted to the required value by adding either NaOH or HCl solutions. The samples were placed on a rotary shaker operated at 150 rpm and thermostatically controlled at (25 \pm 1) °C. The dye concentration was analyzed using UV/VIS spectrophotometer (Ultrospec 2000 - Pharmacia Biotech), the sample was separated by decantation. All the measurements were made at wave length corresponding to the maximum absorbance of 655 nm. The dye removal percentage can be calculated as follows:

$$\text{Removal percentage} = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (1)$$

where C_0 and C_e (mg/l) are the liquid-phase concentrations of dye at initial and equilibrium, respectively.

The effect of contact time was investigated for 30, 60, 90, 120, 150, and 180 min at room temperature, 100 mg of adsorbent dosage, for

different initial concentrations of dye and 0.5 hr carbonization time. Also in these experiments, different MB concentrations were used in conjunction with samples at 25 ± 1 °C in the presence of 100 mg of BS samples. The adsorption time was held constant at 30 min, at a constant methylene blue concentration 5 mg/l for different carbonization time of TABS samples between 30-180 min. Different particle sizes (250, 500, 1000, and 2000 μm) of adsorbent were used at a constant MB concentration, 5 mg/l, contact time of 0.5 hr and carbonization temperature 200 °C for 30 min, at temperature (25 ± 1) °C were studied.

2.4. Equilibrium studies

Adsorption experiments were carried out with same conditions mentioned before, the beakers were placed for 7 days to ensure equilibrium was reached, the amount of adsorption at different time t , q_t (mg/g), was calculated by:

$$qt = \frac{(C_0 - C_t)V}{W}, \quad (2)$$

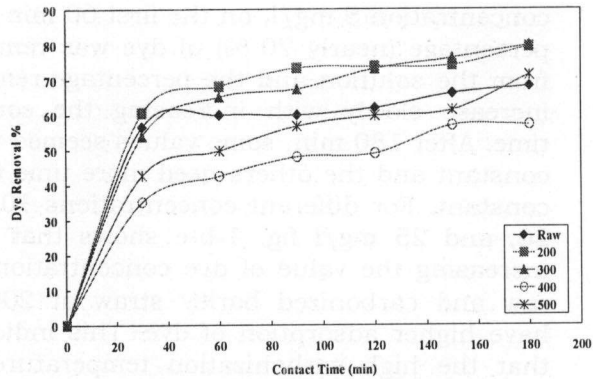
where C_0 and C_t (mg/l) is the liquid-phase concentrations of dye at any time., respectively. V is the volume of the solution (l) and W is the mass of dry sorbent used (g).

3. Results and discussion

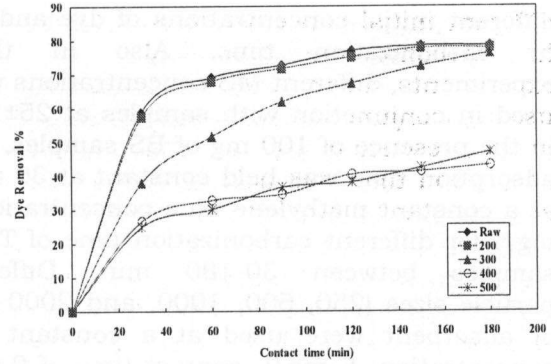
3.1. Effect of contact time on different dye concentration

Fig. 1-a shows the effect of contact time on MB adsorption onto BS and TABS with initial

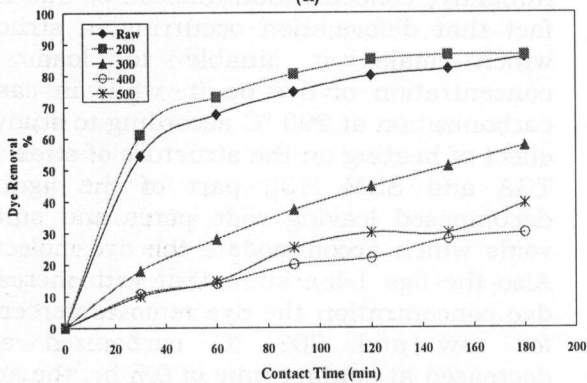
concentration 5 mg/l, on the first 60 min high percentage (nearly 70 %) of dye was removed from the solution and the percentage removal increase slowly with increasing the contact time. After 180 min, some values seemed to be constant and the others need more time to be constant. For different concentrations 10, 15, 20, and 25 mg/l fig. 1-b-e shows that with increasing the value of dye concentration the raw and carbonized barley straw at 200 °C have higher adsorption of dye. This indicates that the high carbonization temperature for straw have low affinity to work with high initial dye concentration this can be due to the fact that deformation occurring in structure which make it unable to load high concentration of dye on it, while in case of carbonization at 200 °C according to study the effect of heating on the structure of straw with TGA and SEM [13], part of the lignin is decomposed leaving wide pores and suitable voids which accommodate the dye molecules. Also the figs 1-b-e show that with increasing dye concentration the dye removal percentage for raw and 200 °C carbonized straw decreased at contact time of 0.5 hr, the actual amount of dye adsorbed per unit mass of adsorbent increased with increase of initial dye concentration in the test solution. This may be attributed to the fact that the process of dye adsorption, initially dye molecules have to first encounter the boundary layer effect and then they have to diffuse from boundary layer film onto adsorbent surface and finally, they have to diffuse into the porous structure of the adsorbent so with increasing dye concentration the pores are blocked with dye and hence the percentage removal decreases [14].



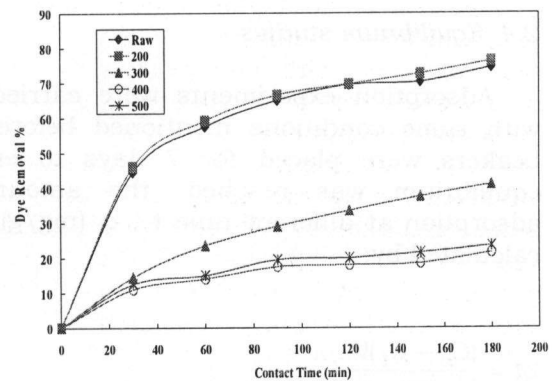
5 mg/L dye concentration
(a)



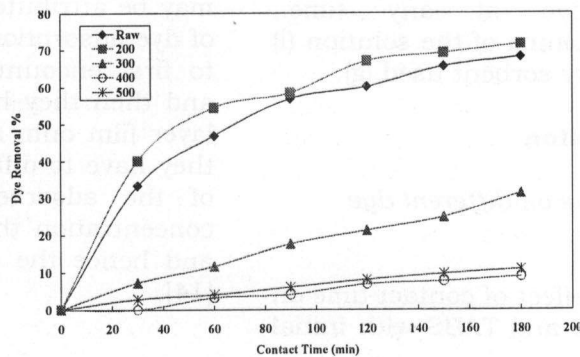
10 mg/L dye concentration
(b)



15 mg/L dye concentration
(c)



20 mg/L dye concentration
(d)



25 mg/L dye concentration
(e)

Fig. 1-a-e. The variation of amount adsorbed with adsorption time at different initial dye concentration on barley straw with different carbonization temperature.

Table 1
Isotherm parameters for removal of MB by raw and TABS

Isotherm parameters	Raw	200 °C	300 °C	400 °C	400 °C
N	0.89	0.74	0.51	-0.6	1.69
K _F	4.13	2	20.1	2.69	12.6
R ²	0.665	0.935	0.70	0.976	0.964

3.2. Effect of carbonization time and dye concentration on adsorption

The effect of carbonization time fig. 2 was studied for 0.5, 1, 2, and 3 hours of carbonization at different temperatures. Figs. 2a-e include different dye concentrations (5-25 mg/l), which show that at concentration 5 mg/l the dye removal increases for carbonization at 200 °C with increasing time of carbonization while for samples carbonized at higher temperature than 200 °C are less effective probably because of fiber destruction at high temperature. Also with increasing dye concentration the higher dye removal value maintain for carbonization at 200 °C but the removal value with increasing carbonization time seems to be constant and start to decrease. The removal of methylene blue from aqueous solutions by adsorption on carbonized straw increases with time, but at a lower rate; this may be attributed to the fact that in the beginning of the adsorption process, the methylene blue is adsorbed on the external surface of particles which increases the concentration of methylene blue on the surface and leads to formation of methylene blue aggregates. Methylene blue molecules are known to form dimmers and aggregates, depending on the conditions of solution such pH, concentration of the dye and presence of other ions [15,16]. Methylene blue aggregates can migrate from the external surface of barley straw to the inner pores, resulting in deaggregation of the methylene blue aggregates and restoring monomers. Similar results have been reported in literature for removal of dyes [17, 18]. In batch type adsorption process monolayer of adsorbate is generally formed on the surface of adsorbent [19] and removal rate of adsorbate species from aqueous solution is controlled especially by the rate of transport of the species from the outer sites to interior sites of the adsorbent particles [17].

3.3. Effect of particle size

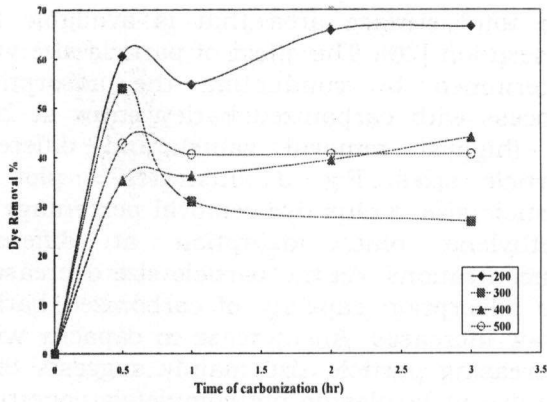
Adsorption is a surface phenomenon, so that, the extent of adsorption is proportional to specific surface area, i.e., to that portion of

the total surface area that is available for adsorption [20]. The effect of particle size was determined by conducting the adsorption process with carbonized barley straw at 200 °C (highest removal value) and different particle sizes. Fig. 3 illustrates a plot of particle size versus dye removal percentage of methylene blue adsorption at different concentrations. As the particle size decreases, the adsorption capacity of carbonized barley straw increases. An increase in capacity with decreasing particle size mainly suggests that the dye molecules do not completely penetrate the particle or partly that the dye molecules preferentially adsorb near the outer surface of the particle [21]. The effect of adsorbent particle size on the adsorption process can be explained as follows, as the particle size decreases, more surface area is available for the adsorption process. Matthews [22] ascribed the increases in adsorption capacity with decreasing the particle size to that adsorption is mainly at the external surface area of the adsorbent as the smaller particles have a larger external surface area for adsorption process. A similar trend was observed by Poots et al. [23] when peat was used to remove acid dyes from aqueous solutions.

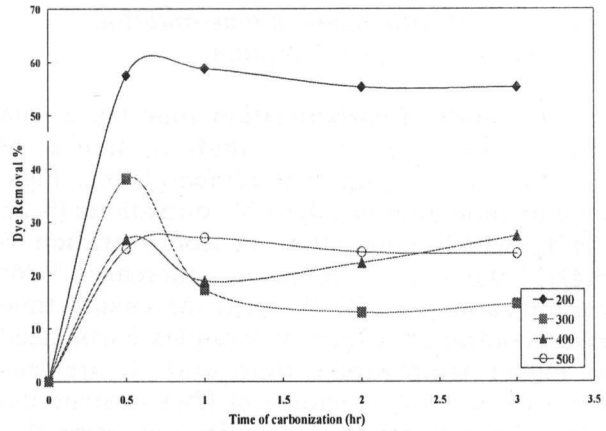
3.4. Isotherm analysis

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface [24]. The equilibrium isotherms in this study have been described in terms of, Freundlich and Temkin isotherms. The Freundlich isotherm [25] is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces and adsorption capacity is related to the concentration of MB dye at equilibrium. A linear form of the Freundlich equation is generally expressed as follows:

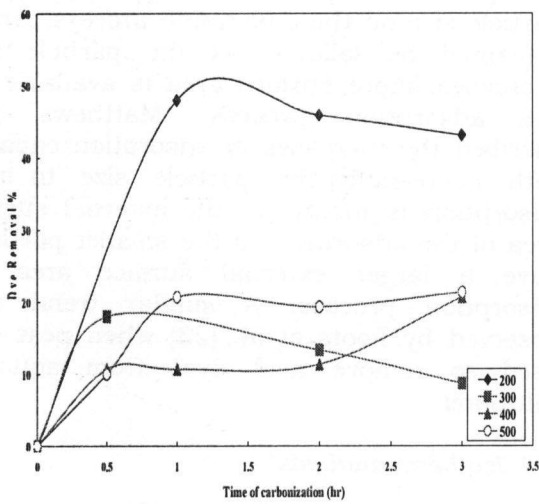
$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (3)$$



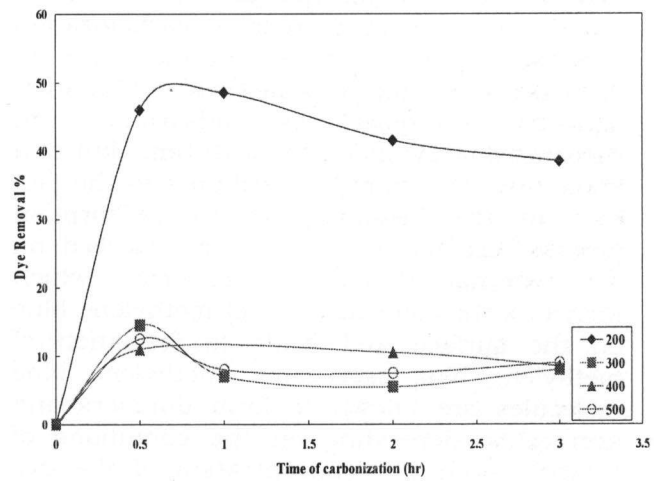
5 mg/L dye concentration
(a)



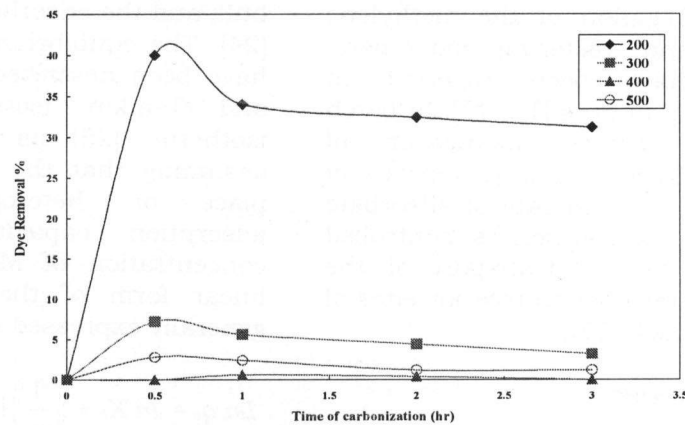
10 mg/L dye concentration
(b)



15 mg/L dye concentration
(c)



20 mg/L dye concentration
(d)



25 mg/L dye concentration
(e)

Fig. 2. Effect of carbonization time on different initial dye concentration.

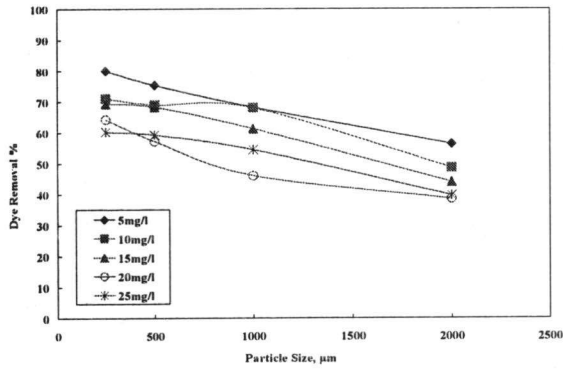


Fig. 3. Effect of adsorbent particle size on the adsorption of methylene blue with different initial concentrations.

where K_F ($\text{mg/g (l/mg)}^{1/n}$) is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. The magnitude of the exponent, $1/n$, gives an indication of the favorability of adsorption. The plot of $\ln q_e$ versus $\ln C_e$ fig. 4 is employed to evaluate the intercept K_F and the slope $1/n$ for raw barley straw and carbonized straw at different heating temperature. The values of K_F , n and the linear regression correlation (R^2) for Freundlich are given in table 1. The table shows that Freundlich isotherm fitted the carbonized straw at heating temperature 500 °C.

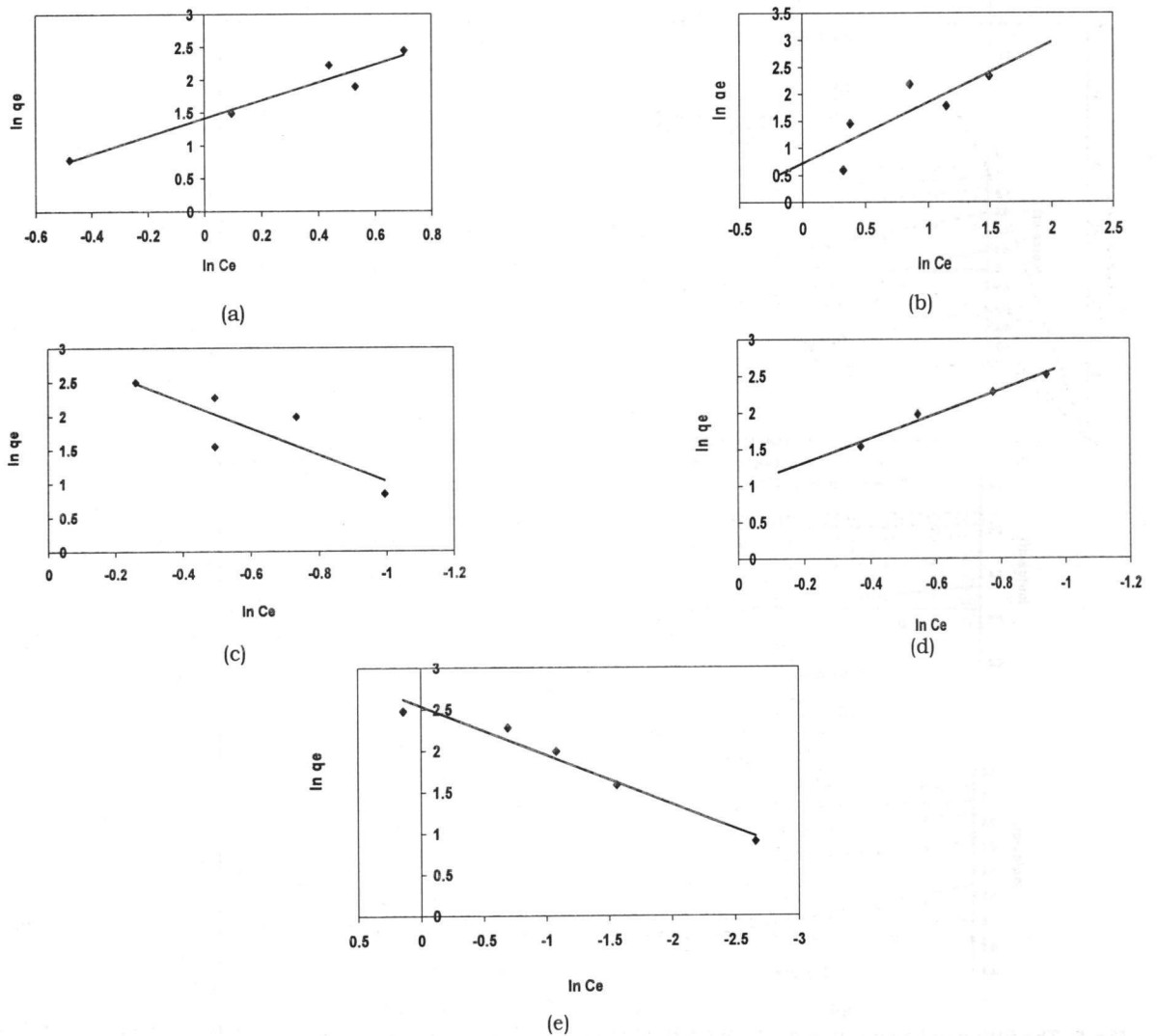


Fig. 4. Freundlich isotherm of MB adsorption onto barley straw. a- Raw BS, b- TABS at 200 °C, c- TABS at 300 °C, d- TABS at 400 °C, e- TABS at 500 °C.

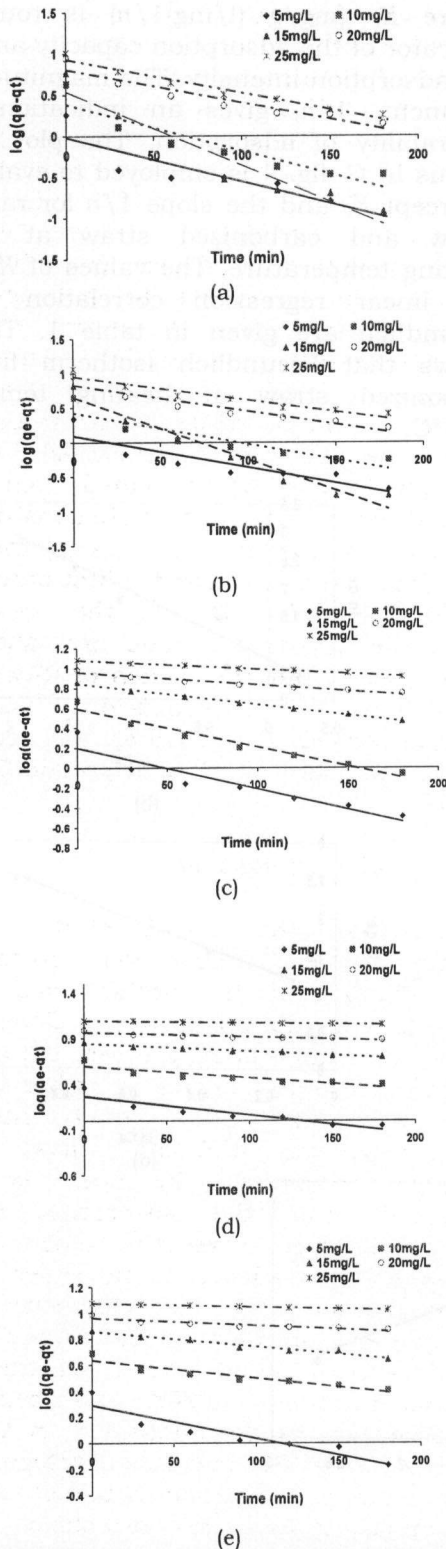


Fig. 5. The fitting of Lagergren's model for MB adsorption on barley straw at different concentrations at 25±1 °C. a- Raw BS, b- TABS at 200 °C, c- TABS at 300 °C, d- TABS at 400 °C, e- TABS at 500 °C

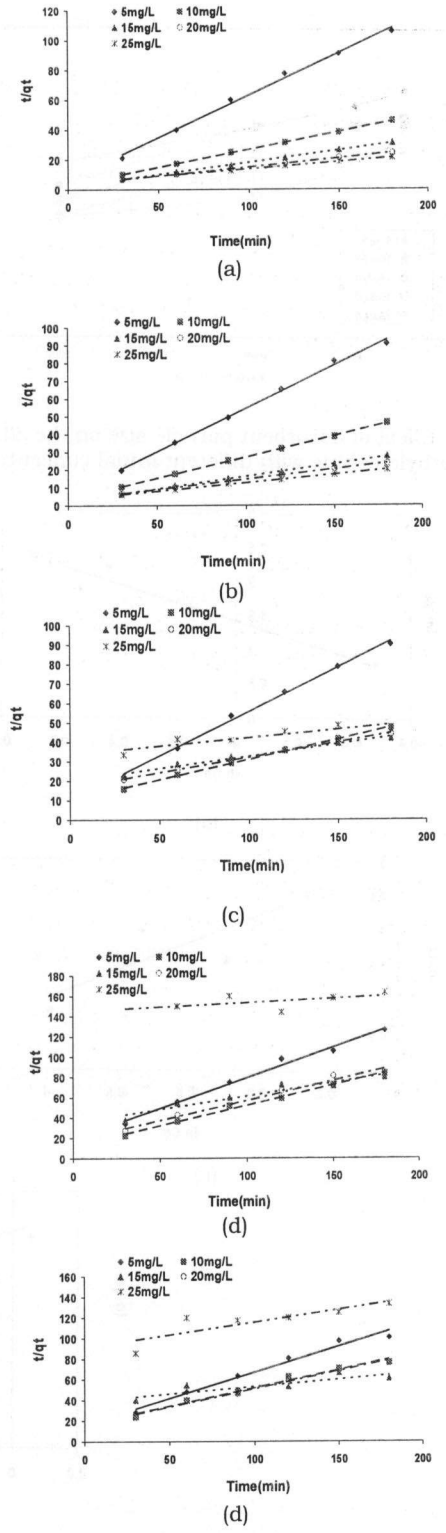


Fig. 6. The fitting of pseudo second order model for MB adsorption on barley straw at different concentrations at 25±1 °C. a- Raw BS, b- TABS at 200 °C, c- TABS at 300 °C, d- TABS at 400 °C, e- TABS at 500 °C

3.5. Kinetic study

The effect of initial methylene blue concentration on the kinetics of adsorption of the dye at neutral pH for raw and carbonized barley straw were studied and then analyzed using the Lagergren's Pseudo first order and Ho's pseudo second order models [26]. The Lagergren equation, a pseudo-first-order equation, describes the kinetics of adsorption process as follows:-

$$dq/dt = k_1(q_e - q_t) \quad (4)$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), q_t the amount of adsorbate adsorbed at time t (mg/g) and k_1 is the rate constant of pseudo-first order adsorption (min^{-1}). Since $q=0$ at $t = 0$. By integrating eq. (1) for the boundary conditions $t=0$ to $t = t$ and $q=0$ to $q_t = q_t$, gives:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

The value of the adsorption rate constant (K_1) for MB sorption by raw and carbonized barley straw at different heating temperature was determined from the plot of the $\log(q_e - q_t)$ against (t) fig. 5. The parameters of pseudo-first order model summarized in table 2

On the other hand, the pseudo second order kinetic equation of Ho based on adsorption capacity may be expressed in the form:-

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (7)$$

$$q_t = \frac{t}{(1/k_2 q_e^2) + (t/q_e)} \quad (8)$$

Which has a linear form as follow:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where k_2 is the rate constant of pseudo second order adsorption (g/mg min) which can be determined experimentally from the slope and intercept of plot t/q_t versus t fig. 6. Table 2 presents the coefficient of the pseudo-first and second -order adsorption kinetic models. For raw and TABS at 200 °C, although the correlation coefficient values at high concentration are higher than 0.8, the experimental q_e values do not agree with calculated ones obtained from the linear plots this shows that the adsorption of MB onto raw barley straw and TABS at 200 °C are not a first-order kinetic while 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, while for TABS at 300 °C the $q_{e/cal}$ values fitted the $q_{e/exp}$ for pseudo first and second order model, but the values of R^2 were more consistent for pseudo first- order model than pseudo second. For TABS at 400 and 500 °C heating temperature they fit pseudo first-order model.

3.6. Sorption mechanism

Although the kinetic studies help in identifying the adsorption process, the determination of the sorption mechanism is important for design purposes. Considering a solid-liquid adsorption process, the adsorbate transfer is characterized by either boundary layer diffusion (external mass transfer) or intra- particle 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 adsorbent external surface through the boundary layer diffusion.
 - Diffusion of the adsorbate from the external surface 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.

The kinetic results were analyzed by the intraparticle diffusion model. Since the particles are vigorously agitated during the

adsorption period, it is assumed that the rate is not limited by mass transfer from the bulk liquid to the particle external surface. The rate-limiting step may be film or intraparticle diffusion. The intraparticle diffusion model is expressed as [26]

$$q_t = K_{id}t^{0.5} + C \quad (10)$$

where C is the intercept and k_{id} is the intraparticle diffusion rate constant (mg/g min^{0.5}), which can be evaluated from the slope of the linear plot of qt versus $t^{1/2}$ fig. 7. The k_{id} values were obtained from the slope of the linear portions of the curve of different initial concentrations and are shown in table 3.

According to this model, the plot of uptake, q_t , versus the square root of time ($t^{0.5}$) 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.

Table 2
Comparison of the Pseudo first order and pseudo second order adsorption rate constants at 25 °C, and calculated and experimental q_e value for different initial dye concentration (C_0 : mg/l; q_e : mg/g; k_1 : min⁻¹; k_2 : g/mg min)

Initial concentration(mg/l)	q_e (exp) (mg/g)	Pseudo- first order kinetic model			Pseudo- second order kinetic model		
		K_1	q_e (cal)	R^2	q_e (cal)	K_2	R^2
Raw							
5	1.81	0.012	0.9957	0.8145	1.77	0.0469	0.9945
10	4.27	0.0129	2.42	0.8597	4.24	0.0177	0.9995
15	5.9	0.0207	3.48	0.9194	6.2	0.0132	0.9988
20	8.83	9.2*10 ⁻³	6.44	0.9073	8.95	3.89*10 ⁻³	0.9988
25	10.27	9.4*10 ⁻³	8.56	0.9651	10.79	2.1*10 ⁻³	0.9986
200 °C							
5	2.19	0.0106	1.25	0.8071	2.1	0.034	0.9965
10	4.45	0.0104	2.66	0.8308	4.22	0.0147	0.996
15	6.65	0.021	4.48	0.9519	7.15	9.67*10 ⁻³	0.9992
20	9.23	8.75*10 ⁻³	6.76	0.9046	8.7	3.65*10 ⁻³	0.999
25	11.49	7.8*10 ⁻³	8.95	0.9168	10.69	2.27*10 ⁻³	0.997
300 °C							
5	2.32	9.4*10 ⁻³	1.59	0.8881	2.19	0.0185	0.9962
10	4.69	8.98*10 ⁻³	3.92	0.9673	4.82	4.47*10 ⁻³	0.9982
15	7.26	4.8*10 ⁻³	7.01	0.9958	7.91	9.49*10 ⁻⁴	0.9779
20	9.69	2.99*10 ⁻³	9.12	0.9631	8.39	6.49*10 ⁻³	0.9964
25	12.1	2.07*10 ⁻³	12.02	0.9929	11.74	2.03*10 ⁻⁴	0.7972
400 °C							
5	2.31	4.8*10 ⁻³	1.86	0.8547	1.67	9.68*10 ⁻³	0.9875
10	4.66	2.99*10 ⁻³	3.95	0.8066	2.49	3.78*10 ⁻³	0.993
15	7.21	2.07*10 ⁻³	6.96	0.9716	3.81	5.47*10 ⁻³	0.9176
20	9.77	1.15*10 ⁻³	9.23	0.8314	2.55	5.94*10 ⁻⁴	0.9778
25	12.3	4.6*10 ⁻³	12.37	0.966	11.91	4.56*10 ⁻³	0.2495
500 °C							
5	2.465	5.7*10 ⁻³	1.95	0.8765	1.99	9.7*10 ⁻³	0.9751
10	4.89	3.2*10 ⁻³	4.32	0.8932	2.86	2.47*10 ⁻³	0.9785
15	7.33	2.76*10 ⁻³	7.21	0.9677	7.12	4.76*10 ⁻³	0.6895
20	9.75	1.38*10 ⁻³	9.15	0.8421	2.86	6.52*10 ⁻³	0.9854
25	11.92	6.9*10 ⁻³	11.86	0.9927	4.14	7.6*10 ⁻³	0.685

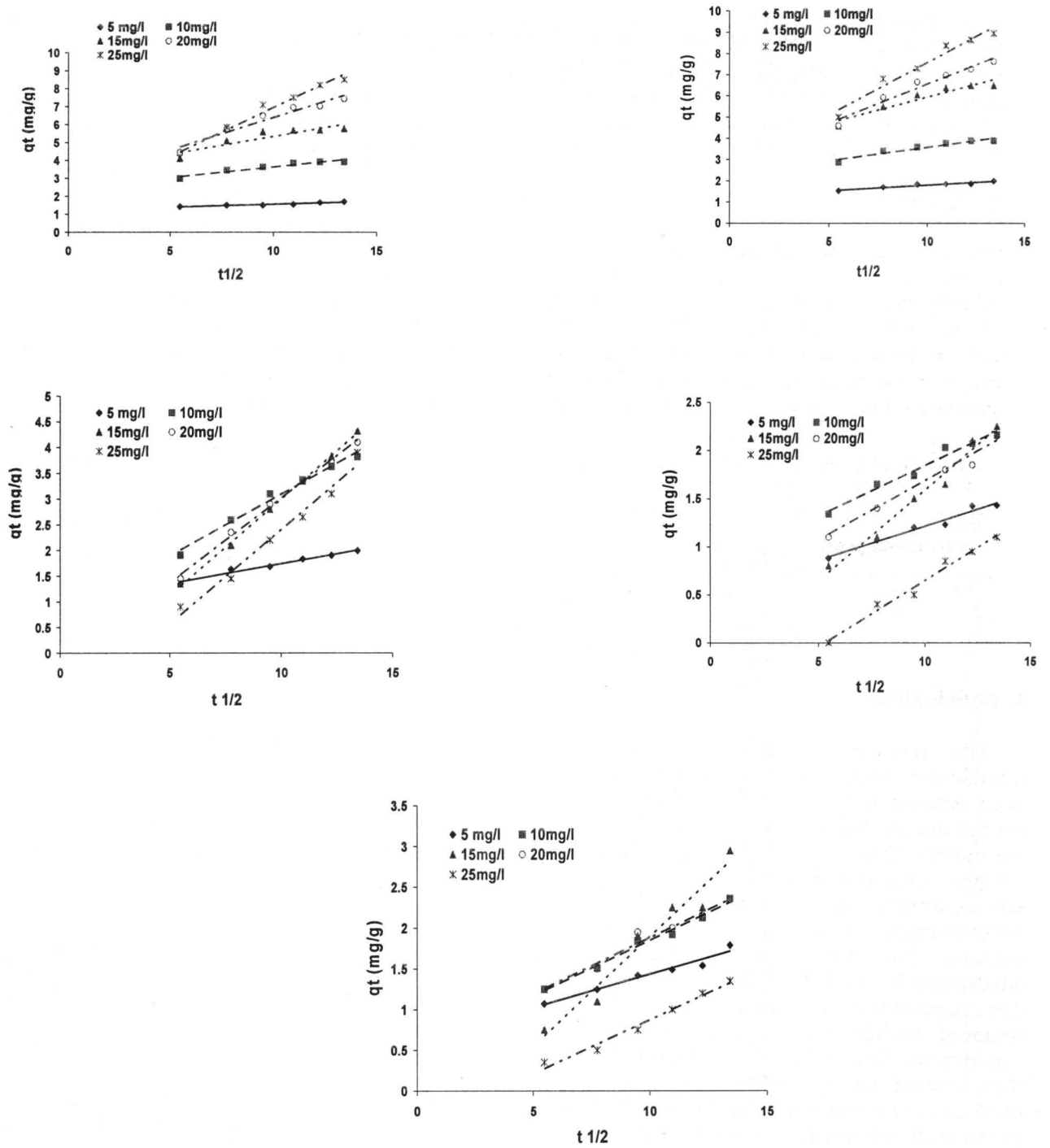


Fig. 7a-e. Intra particle diffusion plot for the adsorption at raw and different carbonization temperature with different initial MB concentration.

Table 3
Intraparticle diffusion constants for different initial MB concentrations

Initial concentration (mg/l)	K_{id} (mg/g min ⁻¹)	C	R ²
Raw			
5	0.0338	1.219	0.9119
10	0.1196	2.4507	0.9296
15	0.1994	3.3547	0.8205
20	0.362	2.7725	0.9466
25	0.5452	1.4908	0.969
200 °C			
5	0.0523	1.2718	0.927
10	0.1265	2.3167	0.9303
15	0.2428	3.5084	0.9108
20	0.3654	2.8904	0.958
25	0.4922	2.6415	0.9603
300 °C			
5	0.0776	0.9653	0.9761
10	0.2403	0.6929	0.985
15	0.3753	-0.7544	0.9989
20	0.3296	-0.2773	0.9965
25	0.3677	-1.2701	0.9788
400 °C			
5	0.0707	0.5068	0.9688
10	0.1044	0.7989	0.9704
15	0.1883	-0.2962	0.9806
20	0.1226	0.462	0.9538
25	0.1377	-0.729	0.9811
500 °C			
5	0.0824	0.612	0.9571
10	0.1364	0.486	0.9862
15	0.2696	-0.8002	0.9542
20	0.1381	0.5007	0.9691
25	0.1325	-0.4523	0.9796

4. Conclusions

The removal of methylene blue from wastewater using modified barely straw has been investigated under different experimental conditions in batch mode. The adsorption of methylene blue was dependent on adsorbent surface characteristics, adsorbent particle size, contact time and methylene blue concentration in wastewater. Initial pH of solution has no marked effect on the adsorption for this dye except in case of high dye concentration. Maximum dye was removed within the first 30 min of every experiment. The present investigation showed that treated barely straw can be effectively used as a raw material for the preparation of biosorbent. Adsorption kinetics for raw and TABS at 200 and 300 °C followed pseudo second-order kinetics model at room temperature. While at heating temperature 400 and 500 °C they followed pseudo first order-model.

References

- [1] O' Neill, C. Hawkes, F.R. Louren Co, N.D. Pinheiro and H.M. Delee, "Colour in Textile Effluents- Sources. Measurement Discharge Consents and Simulation: a Review", J. Chem. Technol. Biotechnol., Vol. 74, pp. 1009-1018 (1999).
- [2] A.K. Jain. A. Bhatnagar, "A Comparative Adsorption Study with Different Industrial Wastes as Adsorbents for Removal of Cationic Dyes from Water", Journal of Colloid and Interface Science, Vol. 281, pp. 49-55, (2005).
- [3] N. Kannan and M.M. Sudaram, "Kinetics and Mechanism of Removal of Methylene Blue by Adsorption on Various Carbons- a Comparative Study", Dyes and Pigments, Vol. 51, pp. 25-40 (2001).
- [4] K.G. Bhatt Acharyya and A. Shirma, "Kinetics and Thermodynamics of Methylene Blue Adsorption on Neem (Azadirachta Indica) Leaf Powder", Dyes and Pigments, Vol. 65, pp. 51-59 (2005).
- [5] G.M. Walker and L.R. Weatherley, "Fixed Bed Adsorption of Acid Dyes Onto

- Activated Carbon", Environmental Pollution, Vol. 99, pp. 133-136 (1998).
- [6] Z. Al Qodah, "Adsorption of Dyes Using Shale Oil Ash", Wat. Res, Vol. 34 (17), pp. 4295-4303 (2000).
- [7] K. Okada, N. Yamamoto, Y. Kameshima and A. Yasumori, "Porous Properties of Activated Carbons from Waste Newspaper by Chemical and Physical Activation", J. Colloid Interface Sci., Vol. 262, pp. 179-193 (2003).
- [8] Chern Jia- Ming and WU Chia- Yuan., "Desorption of Dye from Activated Carbon Beds: Effects of Temperature", Water Research, Vol. 35, pp. 4159-4165 (2001).
- [9] C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani and K. Ranganathan, "Removal of Dyes from Aqueous Solution by Cellulosic Waste Orange Peel", Bioresource Technology, Vol. 57, pp. 37-43 (1996).
- [10] K.R. Ramakrishna and T. Viraraghavan, "Dye Removal Using Low Cost Adsorbents", Water Science Technology, Vol. 36, pp.198-96 (1997).
- [11] M. Dogan, M. Alkan, A. Turkyilmaz and Y. Ozdemir, "Kinetics and Mechanisms Onto Perlite", Journal of Hazardous Materials, pp. 141-148, B. 109 (2004).
- [12] C. Namasivayam, D. Prabha and M. Kumutha, "Removal of Direct Red and Acid Brilliant Blue by Adsorption Onto Banana Pith", Bioresource Technology, Vol. 64, pp. 77-79 (1998).
- [13] A.A. Amer, Azza El-Maghraby, G.F. Malash and Nahla. A. Taha, "Extensive Characterization of Raw Barley Straw and Study the Effect of Steam Pretreatment", Journal of Applied Sciences Research, Vol. 3 (11), pp. 1336-1342 (2007).
- [14] V.K. Garg, Hem Lata and R.K. Gupta, "Removal of a Basic Dye from Aqueous Solution by Adsorption Using Parthenium hysterophorus: An agricultural Waste", Dye and Pigments, Vol. 74, pp. 653-658 (2007).
- [15] D. Mohan and K.P. Singh, "Single and Multi Component Adsorption of Cadmium and Zinc Using Activated Carbon Derived from Bagasse-An Agricultural Waste", Water Res, Vol. 36, pp. 2304-2318 (2004).
- [16] W.J. Weber Jr., J.C. Morris and J. Sanitary Eng. Div. Procced. "Kinetics of Adsorption on Carbon from Solution", Am. Soc. Civil Eng., Vol. 89, pp. 31-59 (1963).
- [17] Y.S. Ho and G. McKay, Can. "The Kinetics of Sorption of Basic Dyes from Aqueous Solution by Sphagnum Moss Peat", J. Chem. Eng., Vol. 76, pp. 822-827 (1998).
- [18] J.A. Medley and M.W. Andrews, "The Effect of a Surface Barrier on Uptake Rates of Dye Into Wool Fibers", Textile Resour. J., Vol. 29, pp. 398-403 (1959).
- [19] G.E. Boyd and A.W. Adamson, L.S. Myers Jr. and J. Am., "The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites, II: kinetics", Chem. Soc., Vol. 69, pp. 2836-2848 1947).
- [20] A.. Dailfullah, B. Girgis and H. Gad, "A Study of the Factors Affecting the Removal of Humic Acid by Activated Carbon Prepared from Biomass Material", Colloids Surf., 1-10, 235 (2004).
- [21] R.S. Juang, R.L. Tseng, F.C. Wu and S.H. Lee, "Adsorption Behaviour of Reactive Dyes from Aqueous Solution on Chitosan", J. Chem. Technol. Biotechnol, Vol. 70, pp. 391-399 (1997).
- [22] R. Matthews, Ph.D. Thesis, Queen's University Belfast, Belfast, UK, "Adsorption of dyes using Kudzu, Peanut Hulls and MDF Sawdust" (2003).
- [23] V.J. Poots, G. McKay and J.J. Healy, "The Removal of Acid Dye from Effluent Using Natural Adsorbent-I Peat", Wat. Res, Vol. 10, pp. 1061-1066 (1976).
- [24] J. Eastoe and J.S. Dalton, "Dynamic Surface Tension and Adsorption Mechanisms of Surfactants at the Airwater Interface", Adv. Colloid Interface Sci., Vol. 85, pp. 103-144, (2000).
- [25] H. Freundlich, "Uber Die Adsorption in l"Osungen [Adsorption in Solution]", Z. Phys. Chem., Vol. 57, pp. 384-470, (1906).
- [26] Y.S. Ho, Ph.D. Thesis, University of Birmingham, Birmingham, U.K.", Adsorption of Heavy Metals from Waste Streams by Peat" (1995).

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