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Removal of Methylene blue from aqueous solution by Delonix regia (Gulmohar) tree bark

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Abstract : Removal of Methylene blue (MB) from aqueous solution under different conditions was investigated using *Delonix regia* (Gulmohar) tree bark (DRTB) as adsorbent. Batch mode experiments were conducted to study the effects of pH, contact time, adsorbent dose and initial concentration on the adsorption of Methylene blue. Maximum adsorption was found at pH 7. Freundlich and Langmuir adsorption isotherms were also applied and they showed good fits to the experimental data. The pseudo first- and second-order kinetic models were also applied to the experimental data. The data agreed very well with the pseudo second-order kinetic model. Intrapartical diffusion model revealed that the process was complex and followed both surface adsorption and particle diffusion.

Key-words : Adsorption, Methylene blue, Delonix regia, low-cost adsorbent, adsorption kinetics.

Introduction

Many industries use dyes to color their final products and discharge their effluents into natural water causes severe problems because they are toxic to aquatic life and damage the aesthetic nature of the environment. At present, more than 10,000 dyes have been effectively commercialized [1].

Methylene blue is a thiazine (cationic) dye, which is most commonly used for coloring among all other dyes of its category. Methylene blue is an important basic dye widely used for printing, dyeing cotton, dyeing leather and in purified zinc free form it is used as an antiseptic and for other medicinal purposes [2]. Although Methylene blue is not strongly hazardous, it can have various harmful effects. The dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. If swallowed, the dye causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. It may also cause methemoglobinemia, cyanosis, convulsions, tachycardia, and dyspnea, if inhaled [2]. Acute exposure to Methylene blue can causes, symptoms such as difficulties in breathing, vomiting, diarrhea and nausea, irritation to the skin can occur in humans [3]. Hence, it is necessary to remove Methylene blue from waste waters.

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Various techniques like precipitation, ion exchange, chemical oxidation and adsorption have been used for the removal of toxic pollutant from wastewater [4]. Adsorption has received considerable attention for colour removal from wastewaters as it offers the most economical and effective treatment method. Activated carbon is commonly used for dye removal [5]. However, it is expensive and the regeneration or disposal of it has several problems. Thus, the use of several low cost adsorbents has been studied by many researches. Low cost adsorbents like peanut hull, wheat bran, neem leaf powder [1-3] *Saraca indica* leaf powder, rosewood sawdust, barley straw, tea waste and *Mangifera Indica* (Mango) leaves, *Leucaena Leucocephala* (Subabul) Seed Pods [6-11] have been found to be cheap and eco-friendly.

In the present investigation attempt has been made to investigate the adsorption of Methylene Blue (MB) from aqueous solution by *Delonix regia* (Gulmohar) tree bark (DRTB). The influences of various operating parameters such as solution pH, dye concentration, contact time and adsorbent dose on the dye removal have been investigated.

Materials and Methods

Adsorbent Material:

Delonix regia (Gulmohar) tree bark (DRTB) was collected from nearby agricultural field. It was cut in to small segment and dried in sunlight until almost all the moisture evaporated. Then the material was ground using a food processor. Then it was ground to get desired particle size of 100 to 200 μm. It was then soaked 2 hours in 0.1M NaOH solution to remove the lignin content. Excess alkalinity was then removed by neutralizing with 0.1N HCl. The DRTB was then washed several times with distilled water till the washings are free from color and turbidity. The washed DRTB was oven dried at 50 ^{0}C for 24 hrs and stored for the study.

Batch Adsorption Studies:

The adsorption experiments were carried out in a batch process. The influence of pH on dye adsorption was studied by shaking 50 ml, 20 mg/l dye solution with 2 g/l of adsorbent in 100 ml conical flask for 60 minute over a range of pH values from 2 to 10. The pH was adjusted using 0.1N HCl and 0.1N NaOH with digital pH meter Equiptronics model-EQ 610. The supernent was separated by centrifugation and the concentration of dye was determined from the respective standard curve by measuring the absorbance with UV-VIS spectrophotometer (Systronics-118) at λ_{max} = 665 nm. The effect of contact time and initial concentration were studied by shaking 50 ml, 10, 30, 50, 70 and 100 mg/l dye solution with 2 and 4 g/l adsorbent at optimum pH 7. The effect of adsorbent dose was studied by shaking different amount of adsorbent (0.5 to 6 g/l) with 100 mg/l MB.

Discussion of Results:

Effect of pH:

The solution pH is one of the most important factors that control the sorption of dyes on adsorbent material. Figure-1 shows the effect of pH on dye removal. It is observed that the removal of MB by DRTB increases from 9 to 78.25 % when the solution pH increased from 2 to 7. In the pH range 7 to 10, the effect of pH is not significant. The acidic pH influences sorption because the proton concentration decreases when the initial pH increases, and then the dye molecules have more chance to react with the active sites on the surface of ABPP because of a lower proton competition [12]. The optimum pH 7 was selected for further experiments.

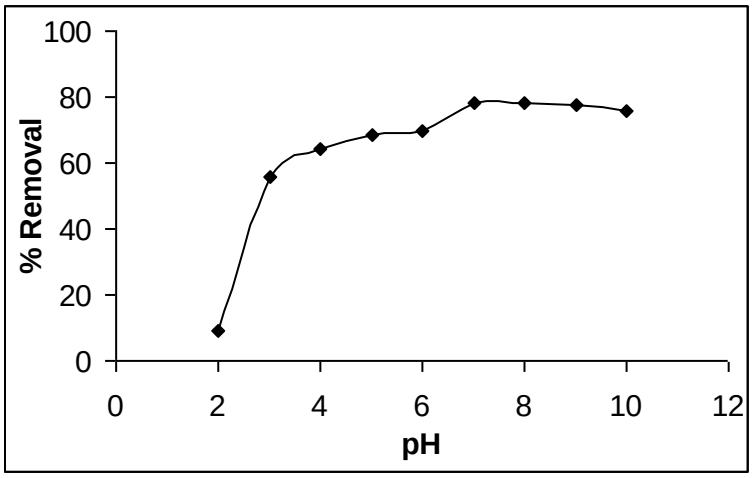

Fig. 1: Effect of pH on percent removal of MB by DRTB.
(MB conc.: 20 mg/l, adsorbent: 2 g/l, agitation time: 60 min)

Effect of Contact Time:

The experimental results of sorption of MB by DRTB at various initial concentrations (10, 30, 50, 70 and 100 mg/l) with contact time are shown in figure-2. Percent adsorption decreased from 82.5 to 69.1 and 92 to 85.5 with increase in initial MB concentration from 10 to 100 mg/l using 2 and 4 g/l DRTB, respectively. But the amount of MB adsorbed per unit mass of DRTB increased from 4.125 to 34.55 mg/g and 2.3 to 21.375 mg/g with increase in dye concentration from 10 to 100 mg/l using 2 and 4 g/l DRTB, respectively. The result indicates that the adsorption of MB is fast at the initial stage and then it becomes slower near the equilibrium. It would be due to a large number of vacant surface sites are available for adsorption at initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between MB dye adsorbed on the surface of DRTB and solution phase [13].

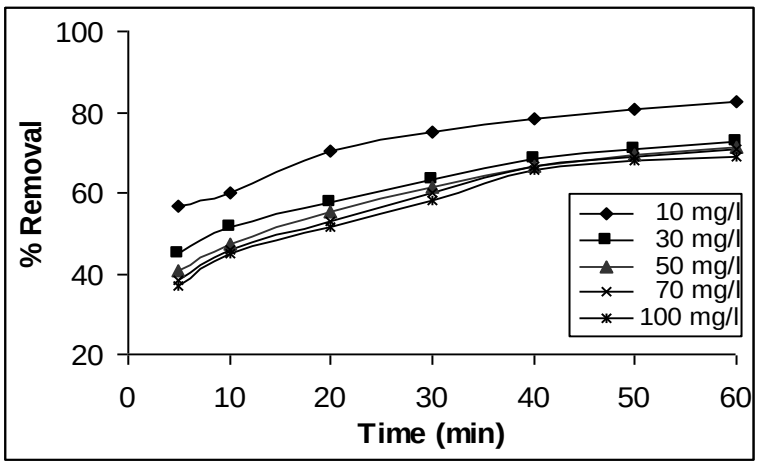

Fig. 2: Effect of contact time on percent removal of MB by DRTB.
(MB conc.: 10, 30, 50, 70 and 100 mg/l, adsorbent: 2 g/l, pH: 7)

Effect of Adsorbent Dose:

The adsorption experiments were carried out with 0.5 to 6 g/l DRTB dosages at initial MB concentration of 100 mg/l and contact time 60 minutes. Figure-3 shows the effect of adsorbent dosage on percent removal of MB. The sorption of MB increased from 32 to 90 % with an increase in adsorbent dose from 0.5 to 6 g/l. This may be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase dose of the adsorbent and consequently leads to a better adsorption [14].

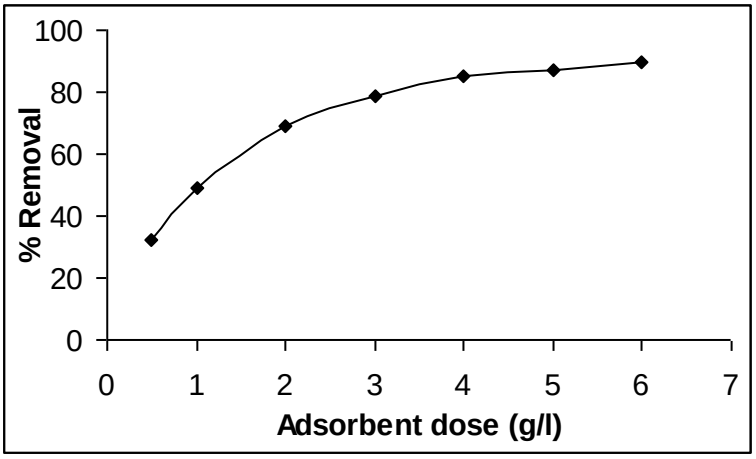

Fig. 3: Effect of adsorbent dose on percent removal of MB by DRTB.

(MB conc.: 100 mg/l, pH: 7, agitation time: 60 min)

Adsorption Isotherm:

Adsorption isotherm describes the relationship between the equilibrium amounts of solute adsorbed on adsorbent and the amount of remaining solute. Langmuir and Freundlich isotherm models are commonly used for description of adsorption process.

The isotherm derived by Langmuir for adsorption of dye from aqueous solution given by equation-1.

$$Ce / (X/M) = 1/ bVm + Ce /Vm \quad \text{..... (1)}$$

Where,

$q_e = X/M$ = Amount of adsorbate adsorbed per unit weight of adsorbent (mg/g).

Ce = Equilibrium concentration of adsorbate in aqueous solution (mg/l).

Vm and b = Langmuir constants related to the adsorption capacity (mg/g) and energy of adsorption (l/mg), respectively.

The linear plot of $Ce/(X/M)$ against Ce shows that the adsorption obeys Langmuir isotherm model. The values V_m and b were determined from the intercept and slope of the linear plot are summarized in table-1. The model good fit for the experimental data and the correlation coefficients R^2 higher than 0.9285 indicates the applicability of Langmuir isotherm model.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L is shown in equation-2.

$$R_L = 1 / (1 + b\ Co) \quad \text{..... (2)}$$

Where, Co is initial solute concentration (mg/l) and b is Langmuir adsorption constant (l/mg).

The R_L Value found to be 0.0133 are greater than zero and less than unity showing favorable adsorption of MB onto DRTB under conditions used in this study [15].

The sorption data of MB sorption onto DRTB was also fitted to Freundlich isotherm, in the linear form of equation-3.

$$log\ (X/M) = log\ K_f + (\ 1/n\ ) log\ Ce \quad \text{..... (3)}$$

Where,

X/M = Amount of adsorbate adsorbed per unit adsorbent (mg/g).

Ce = Equilibrium concentration of adsorbate in aqueous solution (mg/l).

K_f = Freundlich constant related to adsorption capacity (mg/g).

$1/n$ = Heterogeneity factor.

Straight lines were obtained by plotting *log* (*X/M*) against *log Ce* (Fig.4), which show that sorption of MB obeys Freundlich isotherm well. The K_f and *1/n* values were calculated from intercept and slop of the plot respectively and presented in table-1. The high value of correlation coefficient and *1/n* is lower than 1, indicating that adsorption of MB on DRTB follows Freundlich isotherm. The adsorption data obeyed both Freundlich and Langmuir models exhibiting heterogeneous surface conditions and monolayer adsorption [16].

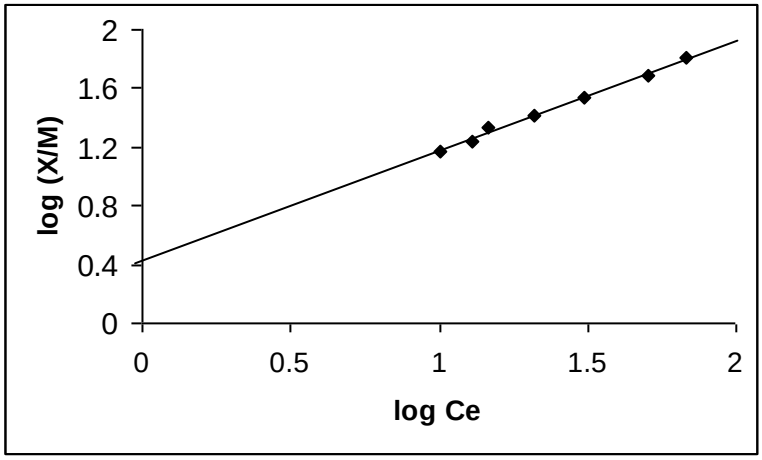

Fig. 4: Freundlich plot for adsorption of MB by DRTB.

(MB ions concentration: 100 mg/l, pH: 7, agitation time: 60 min)

Table 1: Langmuir and Freundlich isotherm parameters for MB uptake by DRTB.

Langmuir constants			**Freundlich constants**		
***Vm* (mg/g)**	***b* (l/mg)**	R^2	K_f	*1/n*	R^2
157.90	9.5954×10^{-2}	0.9285	2.692	0.7407	0.9953

Adsorption Kinetics:

A study of the adsorption kinetics is desirable because it provides information regarding the mechanism of adsorption, which is important for the assessment of efficiency of the process. Pseudo first and second order kinetic models and intra-particle diffusion model were used to investigate the mechanism of adsorption and the potential rate controlling step.

Pseudo First-order Model:

The sorption kinetics can be defined by a pseudo first- order equation-4.

$$log\ (q_e - q_t) = log\ (q_e) - K_1 t / 2.303 \quad \text{.....} \quad (4)$$

Where,

q_e = Amount of adsorbate adsorbed at equilibrium per unit mass of adsorbent (mg/g)

q_t = Amount of adsorbate adsorbed at time t (mg/g)

K_1 = Rate constant of pseudo first-order adsorption (min^{-1})

t = Time (min^{-1})

The plots of log (q_e-q_t) against t (Fig.5) give linear relationship from which K_1 and q_e, can be determined from the slope and intercept respectively. The experimental q_e values do not agree with the calculated ones, obtained from the linear plots (Table 2). This shows that the adsorption of MB on DRTB is not a first-order reaction [10].

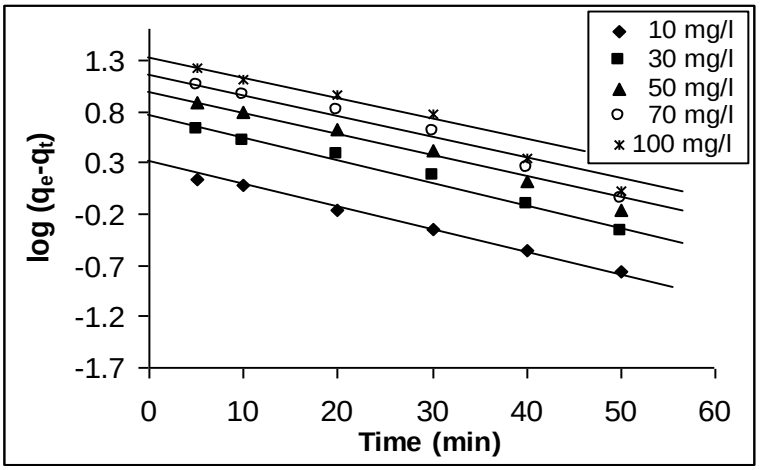

Fig. 5: Lagergren plots for the adsorption of MB by DRTB.
(MB conc.: 10, 30, 50, 70 and 100 mg/l, adsorbent: 2 g/l, pH: 7)

Pseudo Second-order Model:

The pseudo second-order rate model can be written as equation-5.

$$t / q_t = 1/ K_2 q_e^2 + t / q_e \quad \text{..... (5)}$$

The plot of t/q_t versus t of the equation gives linear relationship (Fig.6). Values of K_2 and q_e were calculated from the intercept and slope of the plots respectively. The values of the calculated q_e, K_2, h and correlation coefficients R^2 are presented in table-2. The calculated q_e values give good agreement with experimental q_e values. This shows that the model can be applied for the adsorption process and confirms that the sorption of MB onto DRTB follows the pseudo second-order kinetic model [17].

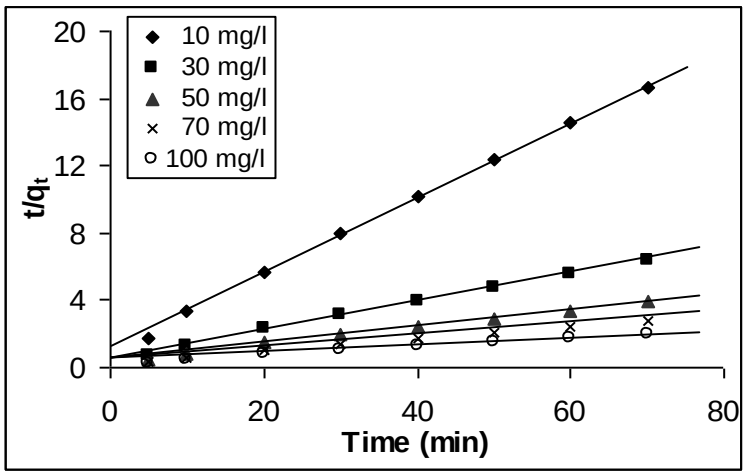

Fig. 6: Pseudo second-order plots.
(MB conc.: 10, 30, 50, 70 and 100 mg/l, adsorbent: 2 g/l, pH: 7)

Table 2: Comparison of first-order and second-order adsorption rate constants, calculated and experimental q_e values for different initial MB concentrations and adsorbent dose.

MB conc. (mg/l)	$q_{e(exp)}$ (mg/g)	First-order kinetic model			Second-order kinetic model			
		K_1 (min^{-1})	$q_{e(cal)}$ (mg/g)	R^2	K_2 (g/mg·min)	$q_{e(cal)}$ (mg/g)	h (mg/g min)	R^2
2 g/l Gulmohar bark								
10	4.2	4.60×10^{-2}	1.77	0.9879	4.93×10^{-2}	4.50	1.0002	0.9985
30	11.02	4.37×10^{-2}	5.37	0.9848	1.65×10^{-2}	11.71	2.2716	0.9964
50	18	4.29×10^{-2}	9.12	0.9884	0.77×10^{-2}	19.75	2.9412	0.9973
70	25	4.07×10^{-2}	13.18	0.9748	0.33×10^{-2}	27.77	3.8458	0.9942
100	35.15	3.76×10^{-2}	18.62	0.9616	0.49×10^{-2}	37.59	4.9992	0.9935
4 g/l Gulmohar bark								
10	2.31	4.29×10^{-2}	0.52	0.9213	22.28×10^{-2}	2.36	1.2500	0.9994
30	6.85	4.14×10^{-2}	1.41	0.9759	7.01×10^{-2}	6.89	3.3350	0.9997
50	11.25	3.89×10^{-2}	2.69	0.9758	2.87×10^{-2}	12.03	4.1662	0.9996
70	15.43	3.79×10^{-2}	9.54	0.9774	1.89×10^{-2}	16.25	5.0000	0.9996
100	21.75	3.45×10^{-2}	4.89	0.9719	0.18×10^{-2}	22.06	7.1424	0.9997

Intra-particle Diffusion:

Weber and Morris suggested the kinetic equation-6 to investigate the adsorption is intra-particle diffusion or not.

$$q_t = K_{id}\, t^{0.5} + C \quad \text{..... (6)}$$

Where, C is the intercept gives an idea about boundary layer thickness (mg/g), q_t is the amount of solute adsorbed (mg/g) at time t and K_{id} is the intra-particle diffusion rate constant (mg/g·$min^{0.5}$).

A plot of q_t versus $t^{0.5}$ is given in the figure-7. The intra-particle diffusion rate constant calculated from the slope of the linear portion of curves (Table 3). The initial curve portions are shown to the boundary layer diffusion and the final linear portions shown to the intra-particle diffusion effect [18]. The linear portions of the curves did not pass through the origin. This indicates that the mechanism of removal of MB by DRTB is complex and both the surface adsorption as well as intra-particle diffusion contributes to the rate-determining step.

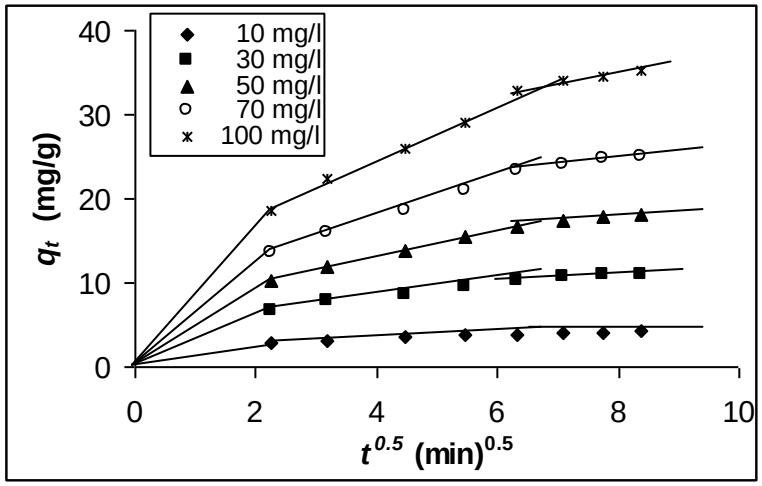

Fig. 7: Intra-particle diffusion plots for MB.
(MB conc.: 10, 30, 50, 70 and 100 mg/l, adsorbent: 2 g/l, pH: 7)

Table 3: Intra-particle diffusion rate parameters for adsorption of Methylene blue.

Methylene blue concentration (mg/l)	Intra-particle rate constants ($mg/g \cdot min^{0.5}$)		
	K_{id1}	K_{id2}	K_{id3}
2 g/l Gulmohar bark			
10	1.2857	0.7327	0.3454
30	6.3090	1.9293	0.6580
50	11.1860	3.6464	0.8773
70	13.0503	5.5930	1.7272
100	19.4869	7.9558	1.8029
4 g/l Gulmohar bark			
10	1.9191	0.4386	0.1212
30	5.5272	0.9212	0.3489
50	8.4443	2.3030	0.6141
70	11.1311	2.0020	0.8966
100	15.3533	4.6060	1.3160

Conclusions

Adsorption of MB from its dilute solution is observed with the DRTB. The following conclusions were drown based on above study,

- The maximum adsorption was found at pH 7.
- Maximum 92 % adsorption take place when 2 g/l DRTB adsorbent dose used for 10 mg/l MB and contact time 60 minutes
- The sorption of MB increases with increase in adsorbent dose.
- The high value of correlation coefficient 0.9953 and *1/n* is lower than 1, indicating that adsorption of MB on DRTB follows Freundlich isotherm.
- Adsorption of methylene blue follows pseudo-second order kinetics
- Intrapartical diffusion model revealed that the process was complex and followed both surface adsorption and particle diffusion.

The results suggest that *Delonix regia* (Gulmohar) tree bark could be used as effective, low-cost, natural adsorbent for the removal of Methylene blue.

References:

1. Gong R., Li M., Yang C., Sun Y. and Chen J., Removal of cationic dyes from aqueous solution by adsorption on peanut hull, Journal of Hazard. Mater., 2005, 121, 247-250 .
2. Hamdaoui O. and Chiha M., Removal of methylene blue from aqueous solutions by wheat bran, Acta Chim. Slov., 2007, 54, 407-418.
3. Bhattacharya K.G. and Sharma A., Kinetics and thermodynamics of methylene blue adsorption on neem (*Azadirachta indica*) leaf powder, Dyes Pigments, 2005, 65, 51-59.
4. Atef S. and Lzaydien A., Adsorption of methylene blue from aqueous solution onto a low-cost natural *Jordanian Tripoli*, Am. Journal of Environ. Science, 2009, 5(3), 197-208.
5. Chern Jia-Ming and Wu Chia-Yuan, Desorption of dye from activated carbon beds: effects of temperature, pH and alcohol, Water Research, 2001, 35, 4159-4165.
6. Goyal P., Sharma P., Srivastava S. and Srivastava M. M., *Saraca indica* leaf powder for decontamination of Pb: removal, recovery, adsorbent characterization and equilibrium modeling, Int. J. Environ. Sci. Tech., 2008, 5(1), 27-34.
7. Garg V.K., Amita M., Kumar R. and Gupta R., Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian rosewood sawdust: a timber industry waste, Dyes and Pigments, 2004, 63, 243-250.

8. Husseien M., Amer A.A., Azza EI- Maghraby and Nahla A. Taha, Utilization of straw as a source of a activated carbon for removal of methylene blue from aqueous solution, J. of Applied Sci. Res., 2007, 3(11), 1352-1358.
9. Uddin Md. T., Islam Md. A., Mahmud S. and Rukanuzzaman Md., Adsorptive removal of methylene blue by tea waste, J. Hazard. Mater., 2009, 164, 53-60.
10. Murugan T., Ganapathi A. and Valliappan R., Removal of dyes from aqueous solution by adsorption on biomass of Mango (*Mangifera Indica*) leaves, E-Journal of Chemistry, 2010, 7(3), 669-676.
11. Patil A. K. and Shrivastava V. S., Removal of Cu(II) Ions by *Leucaena Leucocephala* (Subabul) Seed Pods from Aqueous Solutions, E-Journal of Chemistry, 2010, 7(S1), S377-S385.
12. Ansari R. and Mosayebzadeh Z., Removal of basic dye methylene blue from aqueous solutions using sawdust and sawdust coated with polypyrrole, 2010, J. Iran. Chem. Soc., 7(2), 339-350.
13. Hameed B.H., Din A.T.M. and Ahmed, A.L., Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies, 2007, J. Hazard. Mater., 141, 819-825.
14. Jain R. and Sikarwar S., Removal of hazardous dye congo red from waste material, J. Hazard. Mater., 2008, 152, 942-948.
15. Aksu Z., Biosorption of reactive dyes by dried activated sludge: Equilibrium and kinetic Model, Biochem. Eng. J., 2001, (7), 79-84.
16. Xuejiang W., Ling C., Siqing X., Jianfu Z., Chovelon J.M. and Renault N.J., Biosorption of Cu (II) and Pb (II) from aqueous solutions by dried activated sludge, Mineral Eng., 2006, 19, 968-971.
17. Ho Y.S. and McKay G., The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res., 2000, 34(3), 735-742.
18. Karunakaran K. and Thamilarasu P., Removal of Fe(III) from aqueous solutions using *ricinus communis* seed shell and polypyrrole coated *Ricinus Communis* seed shell activated carbons, Int. J. of ChemTech Research, 2010, 2 (1), 26-35.

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