J. Mater. Environ. Sci. 3 (1) (2012) 149-156
ISSN : 2028-2508
CODEN: JMESCN

Carbonized green tea dredge, a potential adsorbent for removal of remazol brilliant yellow dye

Muhammad Ahmad*[1], Misbahul Ain Khan[1], Umar Farooq[1], Makshoof Athar[2]

1-Department of chemistry, The Islamia University Of Bahawalpur, Bahawalpur 63100, Pakistan

2-Institute of chemistry, The university of Punjab, Lahore, Pakistan

Received in Aug 2011, Revised 19 Sept 2011, Accepted 19 Sept 2011.

* Corresponding author: E-mail address: ahchemist@gmail.com ;

Abstract

Carbonized spent green tea dredge was used as adsorbent for the Remazol Brilliant Yellow [RBY] dye adsorption in a batch process. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption. Experimental results show that the kinetic model of pseudo second order provided a good description of the whole experimental data more than the kinetics of Lagergreen first order. The results revealed that the spent tea dredge, being waste, have the potential to be used as a low-cost adsorbent for the removal of Remazol Brilliant Yellow from aqueous solutions.

*Key Words***:** Adsorption, Remazol Brilliant Yellow, Green tea dredge, Adsorption isotherm, kinetic model

Introduction

Textile dyeing, one of the large water consuming industries produces large volumes of wastewater in dyeing and finishing processes. Such effluents contain coloured synthetic dyes and can pose a serious problem to receiving water bodies. Moreover, dyes used in the textile industry may be toxic to aquatic organisms and can be resistant to natural biological degradation. Hence, the removal of color synthetic organic dyestuff from wastewater effluents becomes environmentally important. Remazol Brilliant Yellow is a textile dye belongs to vinyl sulfone fiber reactive dyes which are used for cotton silk and wool. In presence of alkali, these dyes chemically react with the hydroxyl group of cellulose and form firm, covalent linkages. These dyes are versatile enough to suit different dyeing methods. Due to their use in textile they can contribute to water pollution when released into the environment.

Several treatment processes are in practice for the removal of dyes from wastewater. These processes include: solar photo-Fenton degradation [1], photo catalytic degradation [2], photo-Fenton processes [3], biodegradation [4], integrated chemical–biological degradation [5], electrochemical degradation [6]and adsorption [7].

Adsorption process is one of highly promising way to remove dyes from wastewaters. Adsorption on activated carbon is the most widespread technology used in removal of dyes [8; 9], phenols [10; 11] pesticides [12], and other hazardous chemicals [13; 14] present in wastewater, but its high cost limits its commercial application. In recent years, development of alternative and economic adsorbents is in progress.

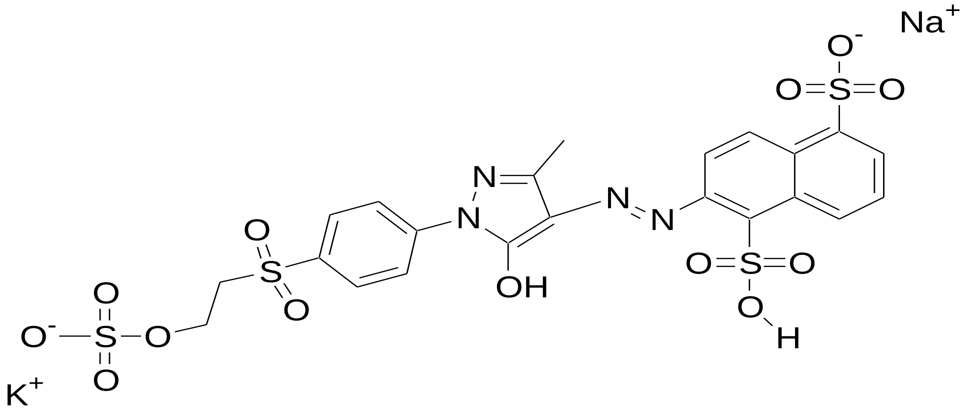
Such alternatives include palm ash [15; 16] ,chitosan ,oil palm ash composite beads [17] pomelo (Citrus grandis) peel [18], pumpkin seed hull [19], broad bean peels [20], oil palm trunk fibre [21], sodium montmorillonite clay [22], salts-treated beech sawdust [23], chitosan bead [24], biomass fly ash [25], zeolites [26] and almond shells [27].

Green tea is basically the dried and processed leaves of plant called *Camellia sinensis* [28]. It is largely consumed around the globe and is considered the second most popular beverage in the world after water. It is estimated that somewhere between 18 and 20 billion cups of tea are consumed daily on our planet. Canned or bottled tea drinks as well as instant tea drinks are produced on industrial scale by hot water extraction of tea leaves, and disposal of spent tea dredge after extraction is a problem faced by manufacturers. Hence, the utilization of such waste is most desirable. Therefore, the aim of this study was to investigate the potential of spent tea dredge an abundantly available solid waste, as a non conventional adsorbent in the removal of Remazol Brilliant Yellow from aqueous solutions.

Experimental details

Adsorbate

The dye used in this study was Remazol Brilliant yellow 3GL gran purchased from Dystar Textilfarben, GRBYH & Co. Deutschland KG Frankfurt Germany. The RBY was chosen in this study because of its known strong adsorption onto solids. The wavelength of maximum absorption for this dye was 417 nm which was determined experimently by measuring absorbance in whole visible region of electromagnetic spectrum.



Structural formula of Remazol Brilliant Yellow

Preparation of adsorbent

Spent tea dredge was obtained from commercial green tea (Tapal green tea) leaves. Beverages were first prepared according to package instructions suggested by the manufacturers.Typically, one tea bag was steeped, under gentle stirring in 125 mls of distilled water at 90 ◦C for 3 min. After this time, spent tea leaves were recovered and repeatedly washed with distilled water in order to remove soluble and coloured compounds. Then it was oven dried at 60 ◦C for 48 hr. The dried biomass was then carbonized for 2hrs at 900 ˚C in order to get adsorbent and stored in plastic bottles for further use in experiments. No other chemical or physical treatments were used prior to adsorption.

Batch experiments

The adsorption of RBY from aqueous solution onto carbonized green tea waste CGT was performed using batch equilibrium technique. The effect of contact time on the amount of dye adsorbed was investigated as a function of initial concentration of dye, pH and temperature. For equilibrium studies, fixed amount of CGT (0.20 g) was added into a number of 250 mL stoppered glass Erlenmeyers flasks containing a definite volume (50 mL in each flask) of different initial concentrations (20–250 mg/L) of dye solution without changing the solution pH at 30°C. The flasks were then placed in a thermostatic water-bath shaker keeping the working temperature constant and agitation was provided at 180 rpm till equilibrium was reached. At time t = 0 and predetermined time intervals till the equilibrium, the dye concentrations were measured using a single beam spectrophotometer (Sanyo-Japan) at wavelength corresponding to maximum absorption (417 nm). The amount of adsorption at equilibrium, q_e (mg/g), was calculated by

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

Where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V (L) is the volume of the solution and W (g) is the mass of dry sorbent used.

The dye removal percentage can be calculated as follows:

$$\text{Removal percentage} = \frac{C_0 - C_e}{C_0} \times 100$$

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

The data obtained from the adsorption tests were then used to calculate the adsorption capacity, q_e (mgg^{-1}), of the adsorbent by a mass balance relationship, which represents the amount of adsorbed dye per the amount of dry adsorbent.

Results and discussions

Effect of contact time

The effect of contact time on dye adsorption at initial concentrations (20,60,100,150,250 mg/L) was investigated as shown in Fig 1, It was observed that the rate of removal of dye was rapid initially but it gradually decreased with time until it reached equilibrium. The graph pattern was almost same of all dye concentrations. The graphs show the maximum percent removal of the dye is after about 420 minutes. The rate of removal is higher in the beginning due to larger surface area available of the adsorbent.

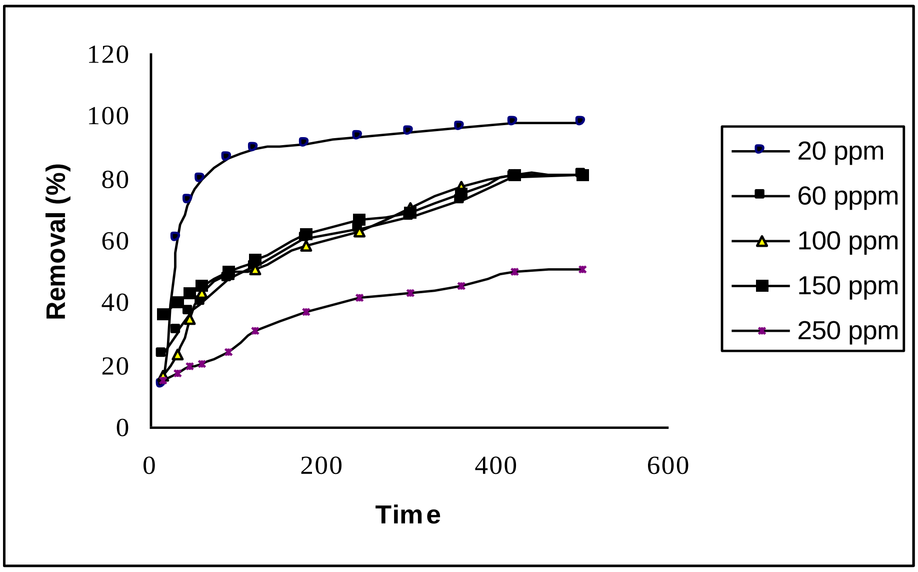


Figure 1: Effect of contact time on the removal of RBY dye .Conditions: 4g/L CGT , pH=7 , 50 mL of RBY solution, temperature 25 °C , Agitation speed 180 rpm.

Effect of solution pH on dye adsorption

The influence of solution pH on RBY adsorption was studied using 0.20 g of adsorbent, 20 mg/L dye initial concentration, pH 2–9 at 30 ◦C. The pH was adjusted with 0.01N NaOH and 0.01N HCl solutions and measurement were done using a pH meter (Cam lab DR2800).The samples were constantly agitated at 180rpm for the equilibrium time.

The dye adsorption was very slightly changed over the pH value from 2 to 9. The dye adsorption was found to be maximum at pH 9.5.The results revealed that pH has very little effect on the adsorption of RBY on CGT.

Effect of temperature

The effect of temperature was studied by carrying out experiments at four different temperatures, 30, 40, 50 and 60 ˚C. Results revealed that the adsorption decreased with increasing temperature, which shows that the removal of RBY is favourable at low temperature and hence is an exothermic process. Thus the adsorption of RBY is leading to a decrease in the residual forces on the surface of the CGT adsorbent and hence causing a decrease in the surface energy of the adsorbent.

Isotherm analysis

The equilibrium isotherms in this study were analyzed using the Langmuir and Freundlich isotherms .The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent surface [29]. A basic assumption is that sorption takes place at specific homogenous sites within the adsorbent. Once a dye molecule occupies a site, no further adsorption can take place at that site. The Langmuir adsorption isotherm has been successfully used to explain the adsorption of basic dyes from aqueous solutions [7–9].

The Langmuir isotherm is:

$q_e = q_{max}K_LC_e/ (1 + K_LC_e)$

Where q_e is the solid phase adsorbate concentration at equilibrium (mg/g), q_{max} the maximum adsorption capacity corresponding to complete monolayer adsorption (mg/g), C_e the concentration of adsorbate at equilibrium (mg/L) and K_a (L/mg) is the Langmuir isotherm constant. The linear form of the model is as under:

$C_e/q_e = 1/q_{max}K_L + C_e/q_{max}$

The constants can be evaluated from the intercepts and the slopes of the linear plots of C_e/q_e vs. C_e.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor RL that is given by Eq:

$R_L = 1/ (1 + bC_0)$

Where C_0 is the highest initial concentration of adsorbate (mg/L), and b (L/mg) is Langmuir constant. The value of RL indicates the shape of the isotherm to be either unfavorable (R_L>1), linear ($R_L = 1$), favorable ($0<R_L< 1$) or irreversible (RL = 0).

It was observed that the equilibrium adsorption data followed Langmuir's isotherm. It indicates the homogenous nature of adsorbent surface i.e. each dye molecule/CGT adsorption has equal adsorption activation energy and demonstrates the formation of monolayer coverage of dye molecule on the outer surface of CGT. The RL values for the adsorption of RBY onto adsorbent are in the range of 0.002805–0.0339, and R^2=1 indicating that the adsorption is a favorable process.

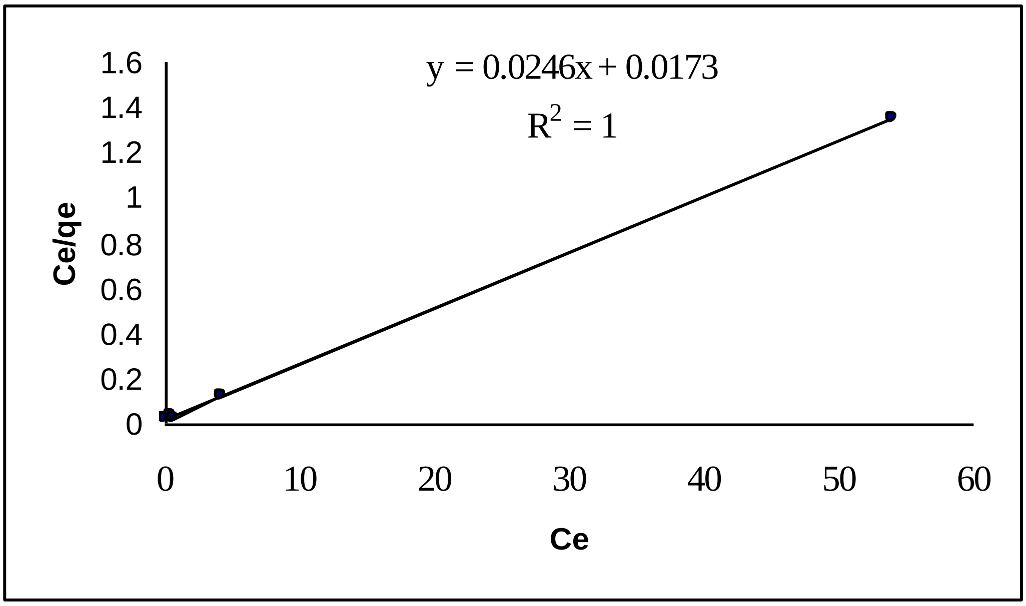


Figure 2: Langmuir plot for adsorption of RBY on CGT adsorbent.

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces and adsorption capacity is related to the concentration of adsorbate at equilibrium:

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

Where q_e is the solid phase adsorbate concentration in equilibrium (mg/g), C_e is the equilibrium liquid phase concentration (mg/L), K_F the Freundlich constant (mg/g $(L/mg)^{1/n}$) and 1/n is the heterogeneity factor. The linear form of the model is as under (Fig.3):

$$\text{Log } q_e = \text{Log } K_F + 1/n \text{ Log } C_e$$

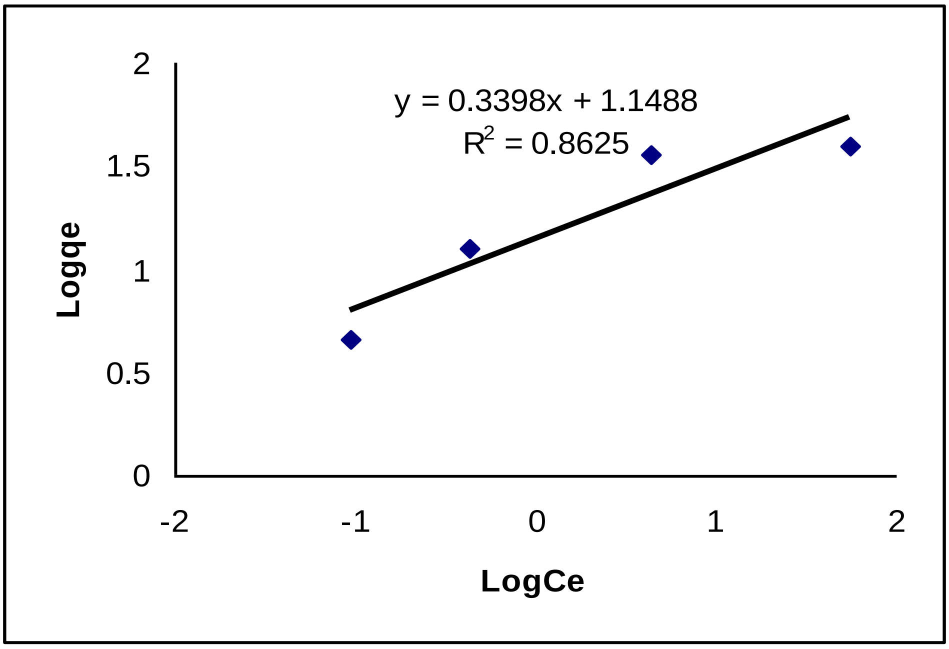


Figure 3: Freundlich plot for adsorption of RBY on CGT adsorbent

The isotherm parameters of the Freundlich isotherm n= 3.109 and R^2 =0.7767 are also indicating favourable adsorption But Langmuir model yielded a much better fit than the Freundlich model.

Table1: Isotherm parameters obtained from the two isotherm models for the adsorption of RBY onto CGT adsorbent.

Freundlich isotherm			Langmuir isotherm			
K_F ($mg^{1-n}L^ng^{-1}$)	N	R^2	q_{max}(mgg^{-1})	K_L(Lmg^{-1})	R_L	R^2
16.00357	3.109453	0.7767	40.65041	1.421965	0.002805	1

Adsorption kinetics

The modeling of the kinetics of adsorption of RBY on CGT adsorbent was investigated by the Lagergreen pseudo-first-order model and pseudo-second-order model to understand the dynamics of adsorption process.

Pseudo-first-order kinetic model

The pseudo-first-order model was described by Lagergren as:

$$\text{Log } (q_e - q_t) = \text{Log } q_e - k_1 t / 2.303$$

Where q_e (mg/g) and q_t (mg/g) are the amount of dye adsorbed at equilibrium and at any time t and k_1 (1/min) is the rate constant of pseudo-first-order adsorption. A linear plot of log ($q_e - q_t$) against time can be used to calculate the rate constant.

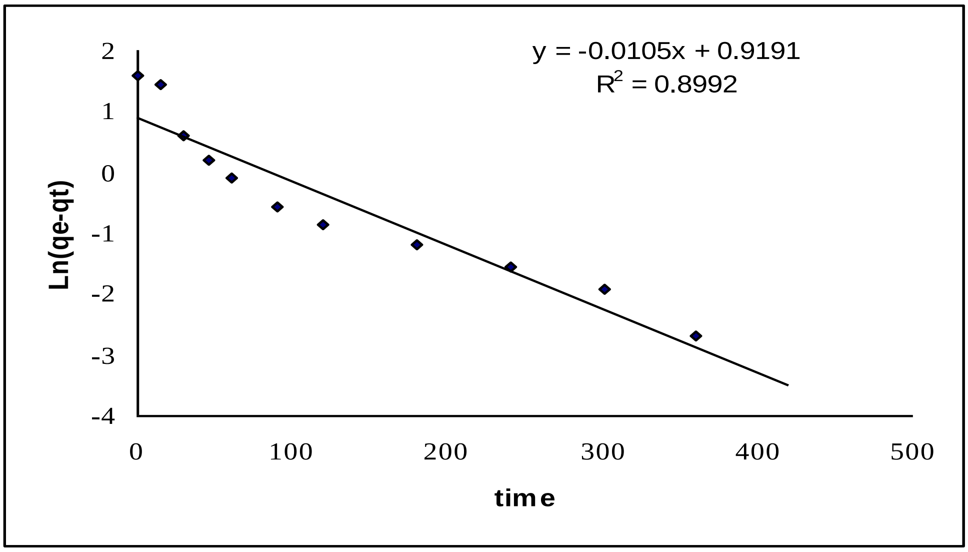


Figure 4: Pseudo first order kinetic plot for adsorption of RBY on CGT adsorbent

Pseudo second order kinetic model

The pseudo-second-order kinetics may be expressed as

$$t/q_t = 1/k_2 q_e^{\,2} + 1/q_e$$

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

From the parameters obtained in both plots it can be observed that the experimental data for the RBY adsorption better fit in second order model with better R^2 (0.9725) than that of first order (0.8992).

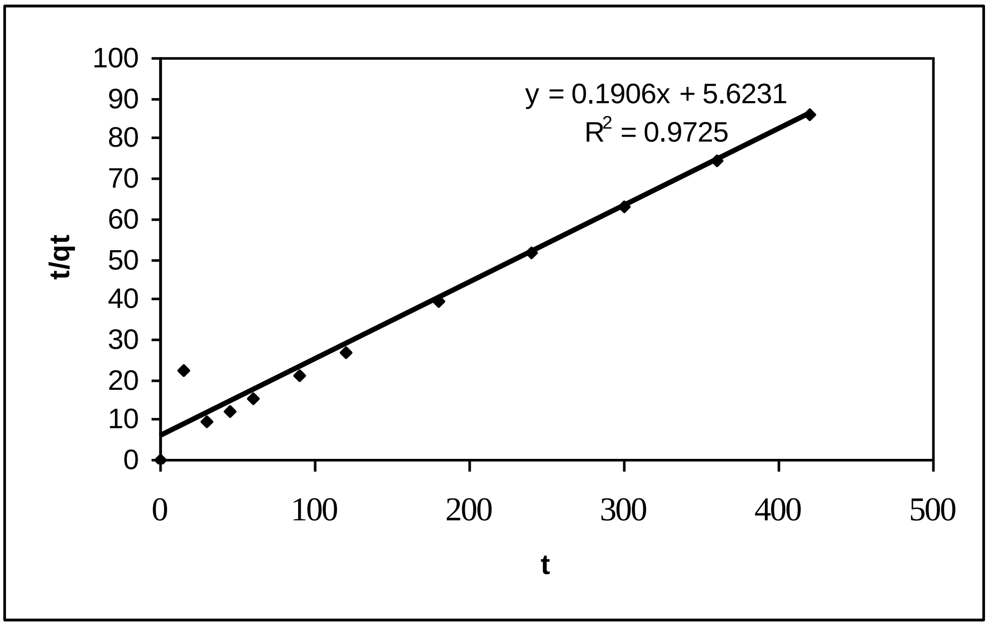


Figure 5: pseudo second order kinetic plot for adsorption of RBY on CGT adsorbent

Table2: The adsorption kinetic model rate constants for adsorption of RBY on CGT adsorbent

Pseudo first order		pseudo second order		
K_1	R^2	K_2	q_e	R^2
0.0105	0.8992	0.006461	5.24659	0.9725

Conclusion

Based upon the experimental results of this study, following conclusions can be drawn

1- The equilibrium time period for removal of RBY onto CGT adsorbent is 7 hours.

2- The maximum removal of the dye occurs at pH= 9.5

3- Isotherm study indicates the experimental data better fit in Langmuir model

4- Pseudo second order kinetics is applicable for whole range of the contact time and not the pseudo first order

5- Adsorption of RBY onto CGT adsorbent is an exothermic process.

Acknowledgements: Thanks goes to Higher education commission of Pakistan (H.E.C) for providing research facilities .

References

1-Durán, A., Monteagudo, J.M., Amores. E., *Appl. Catal. B: Environ.* 80 (2008) 42-50.
2-Sun, J., Qiao, L., Sun, S., Wang, G., *J. Hazard. Mater.* 155(2008)312-319.
3-García-Monta˜no, J. et al., *J. Hazard. Mater*. 138 (2006) 218-225.
4-Azmi, W., Sani, R.K., Banerjee, U.C., *Enzyme Microb. Technol.* 22(1998)185-191.
5-Sudarjanto, G., Keller-Lehmann, B., Keller, J., *J. Hazard. Mater.* 138(2006)160-168.
6-Fan, L., Zhou, Y., Yang, W., Chen, G., Yang, F., *Dyes Pigments*. 76(2008)440-446.
7-Hameed, B.H., Din, A.T.M. and Ahmad, A.L., *J. Hazard.Mater*. 141(2007)819-825.
8-Tan, I.A.W., Hameed, B.H., Ahmad, A.L., *Chem. Eng. J.* 127(2007)111-119.
9-Hameed, B.H., Ahmad, A.L., Latiff, K.N.A., *Dyes Pigments.* 75(2007)143-149.
10-Kumar, A., Kumar, S., Gupta, D.V., *J. Hazard. Mater*. 147 (2007) 155-166.
11-Hamdaoui, O., Naffrechoux, E., *J. Hazard. Mater*. 147(2007)401-411.
12-Daneshvar, N., Aber, S., Khani, A., Khataee, A.R., *J. Hazard. Mater*. 144 (2007) 47-51.
13-Dwivedi, C.P., Sahu, J.N., Mohanty, C.R., Mohan, B.R., Meikap, B.C., *J. Hazard. Mater*. 156 (2008) 596-603.
14-Tsai, J.H., Chiang, H.M., Huang, G.Y., Chiang, H.L., *J. Hazard. Mater*. 154(2008)1183-1191.
15-Ahmad, A.A., Hameed, B.H., Aziz, N., *J. Hazard. Mater*. 141(2007)70-76.
16-Hameed, B.H., Ahmad, A.A., Aziz, N., *Chem. Eng. J*. 133 (2007) 195-203.
17-Hasan, M., Ahmad, A.L., Hameed, B.H., *Chem. Eng. J.* 136 (2008) 164-172.
18-Hameed, B.H., Mahmoud, D.K., Ahmad, A.L., *Colloids Surf. A: Physicochem. Eng. Aspects* 316 (2008) 78-84.
19-Hameed, B.H. and El-Khaiary, M.I., *J. Hazard. Mater*. 155 (2008) 601-609.
20-Hameed, B.H. and El-Khaiary, M.I., *J. Hazard. Mater*. 154 (2008) 639-648.
21-Hameed, B.H. and El-Khaiary, M.I., *J. Hazard. Mater*. 154 (2008) 237-244.
22-Selvam, P.P. et al., *J. Hazard. Mater*. 155 (2008) 39-44.
23-Barragan, B.E., Costa, C., Carmen Marquez, M., *Dyes Pigments*. 75 (2007) 73-81.
24-Bekc¸i, Z., Özveri, C., Seki, Y. and Yurdakoc, K., *J. Hazard. Mater*. 154(2008)254-261.
25-Pengthamkeerati, P., Satapanajaru, T., Singchan, O., *J. Hazard. Mater*. 153 (2008) 1149.
26-Alpat, S.K., Ozbayrak, O., Alpat, S., Akcay, H., *J. Hazard. Mater.* 151(2008)213-220.
27-Doulatiardejani, F., Badii, K., Limaee, N.Y., Shafaei, S.Z., Mirhabibi, A.R., *J. Hazard. Mater.* 151(2008)730-737.
28-Mokgalaka, N.S., McCrindle, R.I., Botha, B.M., *J. Anal. Atomic Spectrom*. 19 (2004) 1375.
29- Langmuir.I, *J. Am. Chem. Soc*. 40 (1918) 136-403.