Iraqi Journal of Chemical and Petroleum Engineering
Vol.15 No.1 (March 2014) 65- 72
ISSN: 1997-4884

University of Baghdad
College of Engineering

Adsorption of Methyl Green Dye onto Bamboo in Batch and Continuous System

Ahmed Adnan Atshan
Chemical Engineering Department- College of Engineering- Al-Nahrain University

Abstract

Adsorption techniques are widely used to remove certain classes of pollutants from waters, especially those that are not easily biodegradable. Dyes represent one of the problematic groups. The removal of methyl green from waste water using bamboo was studied in batch and continuous system. In batch system equilibrium time and adsorption isotherm was studied at different concentrations (5, 10, 15, 20, 25 and 30 ppm) and 50 mg weight of adsorbent.

Langmuir and Freundlich equations were applied for adsorption isotherm data. Langmiur equation was fitted better than Freundlich equation (R^2=0.984 for Langmuir equation).The maximum percentage dye removal obtained 79.4% and adsorption capacity was 15.5 mg/g. For continuous system the breakthrough curve was studied at different bed depths (1, 2 and 4 cm), different concentrations (5 and 10 ppm), and different flow rates (5 and 10 ml/min).

Keywords: Adsorption Isotherm, Methyl green, Bamboo, Fixed bed column.

Introduction

The waste water disposed by textile industries is causing major hazards to the environment and drinking water due to presence of large number of contaminants like acids, bases, toxic,organic, inorganic,dissolved solids and colour.In effect,the discharge of contaminents such as dyes in the environment is worring for both toxicological and esthetical reasons as damage the qualityof the receiving streams and is toxic to food chain organisms.These colored compounds are not only aestheyically displeasing but also inhibiting sunlight into the stream and reducing the photosynthesis reaction.Since many organic dyes are harmful to human beings,the removal of colourfrom process or waste effluents becomes environmentally important [1].

Various physical and chemical methods have been employed for the removal of such colored effluent from water.These include coagulation [2], reverseosmosis [3], photo-degradation [4], electrochemical oxidation [5], ozonation [6] and adsorption, etc. Adsorption is ,however,more popular among all these methods because of its low cost ,simple design, easy operation and the possibility of adsorbent recycling [7]. Most commercial systems currently use activated carbon as sorbent to remove dyes in wastewater,which is an expensive material.

Adsorption of dyes on various materials have been extensively investigated,and activated carbon has proved the most effective because of its high specific surface area,high adsorption capacity and low selectivity for both ionic and non ionic dyes [8].

Recently, in order to decrease the cost of treatment,attempts have been made to find inexpensive alternative adsorbents. Many non –conventional low-cost adsorbents,including natural materials, biosorbents, and waste materials from industry and agriculture,have been proposed by several workers. These materials could be used as sorbents for the removal of dyes from solution. Some of the reported sorbents include clay materials [9], zeolites [11], siliceous material [10] agricultural wastes [12], industrial waste products [13], biosorbents [14] and other [15].

The aim of this work is to evaluate the adsorption capacity of bamboo in removing methyl green from aqueous solutions in batch and continuous system.In batch system study the effect of equilibrium time, initial concentration and adsorption isotherm. For continuous adsorption study the breakthrough curve at different bed depth,initial concentration and flowrate.

Expermental

1. Adsorbate

Methyl green dye was used simulated waste water as adsorbate,the chemical formula $C_{26}H_{33}N_3Cl_2$, molecular weight = 458.5g/mol, λ_{max} =203 nm (measured by UV), the chemical structure of Methyl green is shown as in figure 1.

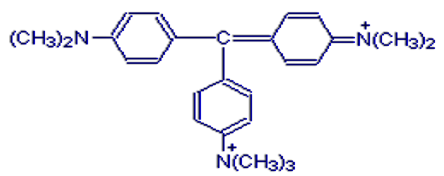

Fig. 1, Chemical structure of Methyl green dye

Stock solution (100ppm) was prepared by dissolving a certain amount of methyl green (0.1 gram) in distilled water (1 liter), and then dilutes the stock solution to give the appropriate concentrations.

2. Adsorbent

The main constituents of bamboo culms are holocellulose (60-70%), pentosans (20-25%), hemicellulose and lignin (each amounted to about 20-30%) and minor constituents like resins, tannins, waxes and inorganic salts [16]. The moisture content of bamboo 50-60% depending on the felling season, area of growth and species.

Ash content (1-3%). Bulk density was measured 0.231g/ml. Surface area was calculated 79.652 m^2/g.

Bamboo was used as adsorbent because of its high abundance, availability and can be obtained from the river. The adsorbent washing with distilled water, grinding with mill, sieving with 200µm, then washing and drying in oven at temperature 45 ˚C for 2 hours.

3. Experimental Procedure

3.1. Batch System

Bamboo was washed in distilled water repeatedly until cleaned then filtered with filter paper. Batch experiments were carried out in a shaker using 6 flasks containing 50 ml of dye solution at different initial concentration (5, 10, 15, 20, 25 and 30 ppm). The adsorbent (50 mg) was added to each flask and closed it .The shaker was operating at 100 rpm and withdrawal the sample after different intervals time then separating the adsorbent from the solution by centrifuge device then dye concentration was measured by UV. The wave length was measured at λ_{max} =203 nm.

The adsorption capacity of dyes (mg/g), (qt), on bamboo was calculated from the mass balance equation as follows:

$$q_{t=(C_0-C_e)}\frac{v}{w} \qquad \ldots(1)$$

where C_0 and C_e are the initial and equilibrium concentrations of dye solution (mg/L), respectively; V the volume of dye solution (L); and W the mass of bamboo (g).

The percentage of dye removal (%DR) was calculated as follows:

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

3.2. Continuous System

A fixed bed column used with 10 cm high and 2 cm inner diameter. Bamboo was placed inside the fixed bed column at different bed depth (1, 2 and 4 cm) respectively then the column washed with distilled water to rid from impurities and air bubbles. The solution was pumped at different flow rate into the fixed bed column at different concentrations then the sample was measured by UV device before the experiment and at different intervals time as illustrated in figure 2. These experiments were carried out at room temp. 298K.

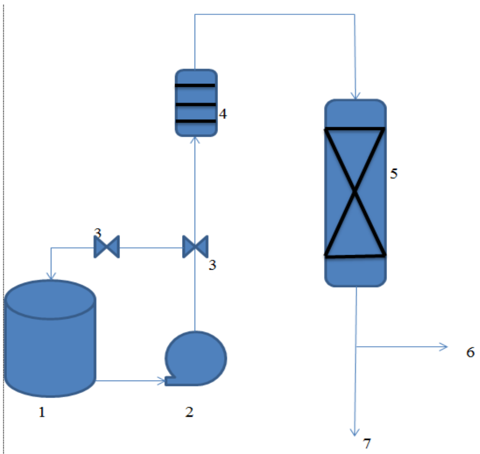

Fig. 2, Experimental rig of continuous adsorption: 1-feed tank, 2-pump, 3-valve, 4-flowmeter, 5-fixed bed column, 6-sample test, 7-drain

Results and Discussion

1. Batch System

1.1. Effect of Initial Concentration and Time

The uptake of MG onto bamboo as a function of dye concentration is shown in Figure 3. It can be seen that the amount of MG adsorbed per unit mass of adsorbent increased with increasing dye concentration, although percentage dye removal decreased with increase in initial dye concentration.

This may be attributed to an increase in the driving force of the concentration gradient with the increase in the initial dye concentration [17].

As shown in figure 3, when the adsorption time increases, the adsorption capacity of bamboo increases significantly in the first 120 min due to rapid attachment of dye to the surface of the adsorbent, and keeps increasing gradually until the equilibrium is reached and remains constants [18]. The amount of adsorbed dyes did not show significant change after 140 min, these results are agree with gregorio Crini [18].

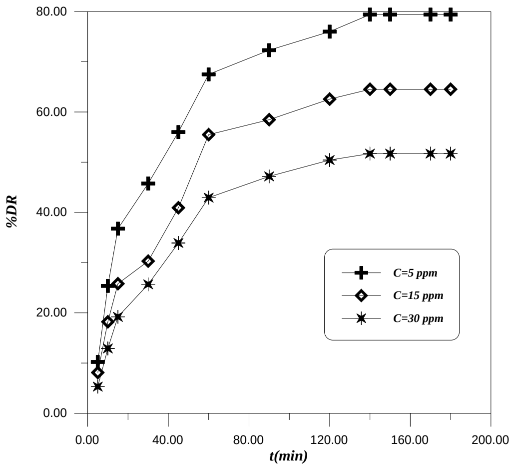

Fig. 3, Effect of initial dye concentration and time on adsorption

1.2. Adsorption Isotherm

Isotherms studies have described the adsorption mechanisms, surface properties and the affinity of adsorbent towards adsorbate [19]. The distribution of adsorption molecule between the adsorbate (liquid phase) and the adsorbent (solid phase) is constant at equilibrium due to the amount of adsorbate being adsorbed is equal to the amount of adsorbate being desorbed from the adsorbent [20]. Thus, it is important to fit the adsorption experimental data into an appropriate isotherm model. Therefore, Langmuir and Freundlich isotherms were used to evaluate the relationship between the amount of dye adsorbed at equilibrium (adsorption capacity) and the concentrations of dye (5, 10, 15, 20, 25 and 30 ppm) at equilibrium state.as shown in figures 4, 5, 6.

The Langmuir isotherm is represented as follow:

$$\frac{C_e}{q_e} = \frac{1}{q_0\, K_L} + \frac{1}{q_0} C_e \qquad \ldots(3)$$

where q_0 (mg/g) is the maximum amount of the dyes per unit weight of adsorbent to form a complete monolayer on the surface bound and K_L (L/mg) is a constant related to the affinity of the binding sites [21]. The Langmuir constants q_0 and KL were determined from the slope and intercept of the plot and their values are listed in table 1.

The Freundlich expression is based on an exponential relationship and is generally applicable to a heterogeneous surface energy distribution. The equation is shown:

$$\log q_e = logK_F + \frac{1}{n} logC_e \qquad \ldots(4)$$

Where K_F and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity. The plot of log qe versus log Ce gives straight lines with slope, 1/n and intercept, K_F, respectively.

From figures 5, 6 and table 1 it is observed that the experimental data of MG adsorption was followed by Langmuir isotherm with correlation coefficient 0.984. The monolayer adsorption capacity for the adsorption of MG was found to be 20.41 mg/g. The value of 1/n was in between 0.1 and 1.0 confirmed the heterogeneity of the adsorbent, indicating that the bonding of MG and bamboo is strong [22].

Table 1, Regression Parameters of adsorption isotherm

Model	Constants	R-Squared
Langmuir	qm=20.41 mg/g	0.984
	K_L=0.213 L/mg	
Freundlich	K_F=126.5 mg/g	0.9004
	1/n=0.84	

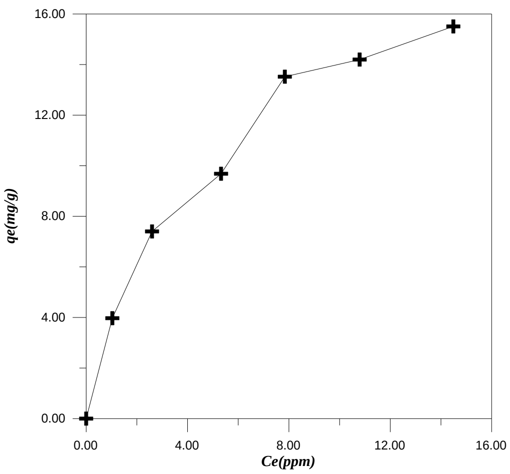

Fig. 4, Adsorption isotherm of experimental data

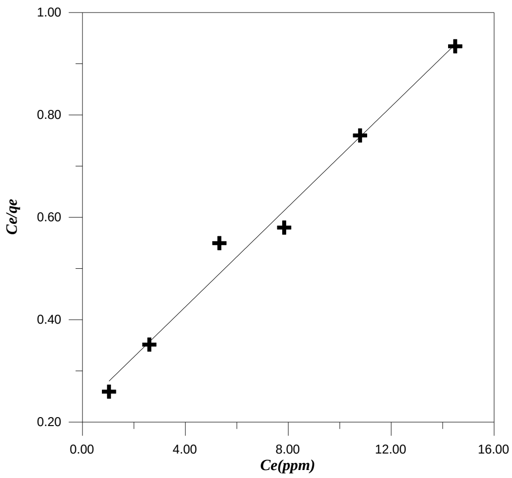

Fig. 5, Langmuir model of adsorption isotherm

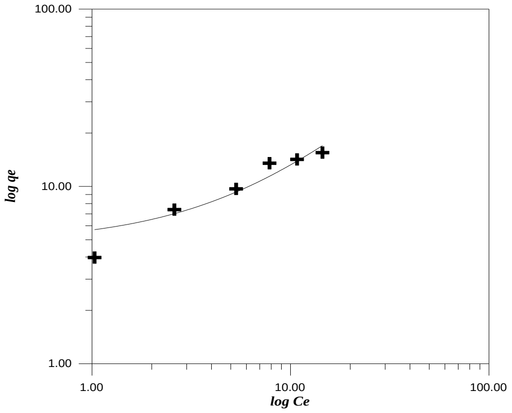

Fig. 6, Freundlich model of adsorption isotherm

2. Continuous System

2.1. Effect of Bed Depth

The adsorption of methyl green in the packed bed column is largely dependent on the bed depth, which is directly proportional to the quantity of bamboo in the column. the effect of bed depth was studied at concentration 10 ppm, flow rate 5ml/min and 298K. from figure 7 we noticed that when the bed depth increased the breakthrough time was increased. The mass transfer zone in a fixed bed travels from the entrance of the bed and progresses towards the exit.Hence, for the same influent MG concentration and fixed bed conditions,an increase in the bed depth results in alonger distance for the mass transfer zone to reach the exit and therefore an increase in the breakthrough time [23]. These results are similar to Tan [24] and Min-Yu [25].

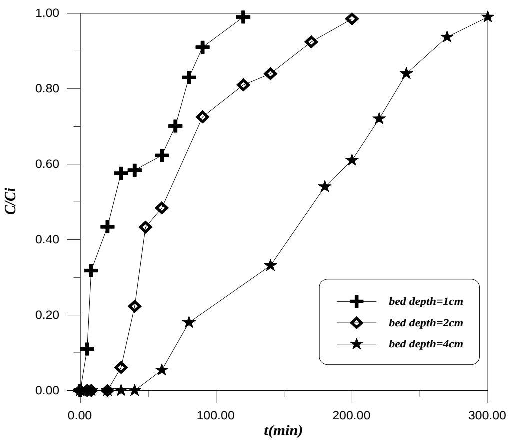

Fig. 7, Effect of bed depth on breakthrough curve

2.2. Effect of Initial Dye Concentration

The effect of initial dye concentration on the adsorption process with 10 and 20 ppm at a constant flow rate 5 mL/min and fixed bed depth 4cm is shown in Figure 8. It can be deduced that, at a lower inlet concentrations, a slower breakthrough curve and the highest treated volume are obtained. The breakthrough point for 10 ppm and 20 ppm of MG inlet concentrations occurred after 60 min and 15 min respectively. The slow transport of dyes onto adsorbent due to the lower concentration gradient and resulted in a slower breakthrough curve [26], conversely, a higher Concentration of MG has been shown lead to a higher driving force of MG to overcome the mass transfer resistance in the liquid phase. Consequently, the time required to reach saturation decreased with increasing the inlet solute concentration. These results are similar to Tan [24] and Min-Yu [25].

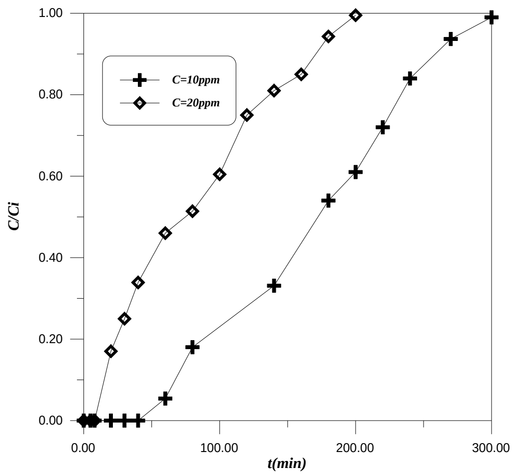

Fig. 8, Effect of initial concentration on breakthrough curve

2.3. Effect of Flow Rate

The effect of flow rate on adsorption was studied at different flow rate 5 and 10 ml/min at constant concentration 10ppm, bed depth 4cm. From Figure 9 it is observed that at higher flow rate, the rate of reaching the breakthrough time is faster whereas in lower flow rate the rate of reaching the breakthrough time is slower. This is due to the residence time distribution of influent concentration to the adsorbent is greater in lower flow rate [27, 26].

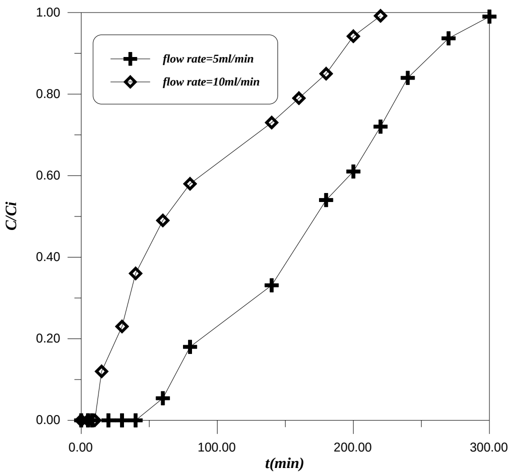

Fig. 9, Effect of flow rate on breakthrough curve

Conclusions

Bamboo shows a good adsorbent for removal methyl green from waste water. In batch system the maximum percentage dye removal reached to79.4% and adsorption capacity was 15.5 mg/g. It's found that adsorption was highly dependent on initial dye concentration, contact time (the adsorption capacity increasing with increase concentration and contact time). Adsorption isotherm was studied with langmuir and Freundlich models. The experimental data was fitted well with lagmuir model (R^2=0.984). For continuous system the breakthrough curve analysis reveals that the slower breakthrough time reached for lesser initial concentration, slower flow rate, and higher bed depth.

Nomenclature

DR% =percentage dye removal

MG=methyl green

C_0 = initial concentration of dye solution (mg/L)

$C_{e=}$ equilibrium concentration of dye solution (mg/L)

q_t =amount of dye adsorbed on bamboo at time t (mg/g)

q_e= amount of dye adsorbed on bamboo at (mg/g) equilibrium

C=effluent concentration at time t (mg/L)

Ci= initial concentration of dye solution (mg/L)

References

1- A.Bennani Karim, B.Mounir, M.Hachkar, and M.Bakasse, A.Yaacoubi, (2011), "Adsorption of malachite green dye onto raw Moroccan clay in batch and dynamic system", Canadian journal on environmental, construction and civil engineering, No.2, Vol.2, 5-13.

2- O.Tunay,Water Sci. Technol. 34 (1996), 9-16.

3- E.Fotgacs, CTibor and O.Gyula, Environ. Int. 30 (2004), 953-971.

4- K.Wu, Y.Xie, J.Zhao and H.Hidaka, J.Mol.Catal. A: Chem.144 (1999), 77-84.

5- E.Kusvuran,O.Gulnaz,S.Irmak and O.M. Atanur,H.I.Yavuz, O.Erbatur, J.Hazard. Mater. 109 (2004), 85-93.

6- T.Robinson, G.McMullan and R.Marchant, P.Nigam,Bioresour. Technol.77 (2001), 247-255.

7- Muhammad Aslam Malan,Sana Ijaz and Muhammad Naeem Ashiq, (2010), "Removal of various dyes from aqueous media onto polymeric gels by adsorption process:their kinetics and thermodynamics, Desalination 263, 249-257

8- S. Őzcan, B. Erdem and A. Őzcan, (2004), "Adsorption of acid Blue 193 from aqueous solutions onto Nabentonite and DTMA-bentonite", J. Coll. Interf. Sci., 280, 44–54.

9- L.T. Teng, E. Khor, T.K. Tan, L.Y. Lim and S.C. Tan, (2001), "Concurrent production of chitin from shrimp shells and fugi." Carbohydrase Res., 332, 305–316.

10- A. Shukla, Y.H. Zhang, P. Dubey, J.L. Margrave and S.S.

Shukla, (2002), "The role of sawdust in the removal of unwanted materials from water" J. Haz. Mat. B, 95, 137–152.

11- S.J. Allen, G. McKay and J.F. Porter, (2004), "Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems", J. Coll. Internat. Sci., 280, 322–333.

12- Z. Aksu, (2005),"Application of biosorption for the removal of organic pollutants": a review. Proc. Biochem., 40, 997–1026.

13- C.Namasivayam and Sumithra, (2005), "Removal of direct red 12B and methylene blue from water by adsorption onto Fe (III)/Cr (III) hydroxide,an industrial solid waste.j. Environ.Manage, 74, 207-215.

14- S. Wang, Y. Boyjoo, A. Choueib and Z.H. Zhu, (2005), " Removal of dyes from aqueous solution using fly ash and red mud", Water Res., 39, 129–138.

15- S. Wang, Z.H. Zhu, A. Coomes, F. Haghseresht and G.Q. Lu, (2005)," The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater". J. Coll. Interf. Sci., 284, 440–446.

16- Tomalang, F.N., A.R. Lopez, J.A. Semara, R.F. Casin, and Z.B. Espiloy. 1980. "Properties and utilization of Philippine erect bamboo". In International Seminar on Bamboo Research in Asia held in Singapore, Research Center and the International Union of Forestry Research Organization, 266-275.

17- Hameed, B.H., D.K. Mahmoud and A.L. Ahmad, (2008), "Sorption of basic dye from aqueous solution by pomelo (*Citrus grandis*) peel in a batch system". Colloid. Surface. A, 316(1-3), 78-84

18- Gregorio Crini,(2008), "Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer" ,J Dyes and pigments, 77, 415-426

19- Y.S., Ho, C.T., Huang, W.H., Huang, (2002) "Equilibrium sorption isotherm for metal ions on the tree fern", *Process Biochemistry*, 37, 1421-1430.

20- G.O., El-Sayed, (2011), "Removal of methylene blue and crystal violet from aqueous solutions by palm kernel fiber", *Desalination*, 272 (1-3), 225-232.

21- C. K. Lee, K. S. Low, and P. Y. Gan. (1999), "Removal of some organic dyes by acid-treated spent bleaching earth", Environmental Technology, vol. 20, 99-104,

22- V.O., Arief, K., Trilestari, J., Sunarso, N., Indraswati, S., Ismadji, (2008), "Recent progress on biosorption of heavy metals from liquids using low cost biosorbent: characterization, biosorption parameters and mechanisms studies", *Clean*, 36(12), 937-962.

23- Aik Chong Lua, Qipeng, 2009“Adsorption of phenol by oil-palm-shell activated carbons in a fixed bed”, *Chemical EngineeringJournal* 141, 3, 713–718.

24- Tan I.A.W,Ahmad A.L,Hameed B.H."Adsorption of basic dye using activated carbon prepared from oil palm shell:batch and fixed bed studies" 2008, Desalination, 225, 13-28.

25- Min-Yu Teng, Su-Hsia Lin."Removal of methyle orange dye from water onto raw and acid activated montmorillonite in fixed bed", 2006, Desalination, 201, 71-81.

26- S. Sugashini and K. M. Meera Sheriffa Begum, “Optimization using central composite design (CCD) for the biosorption of Cr (VI) ions by cross linked chitosan carbonized rice husk (CCACR)," Clean Technologies and Environmental Policy, In press.

27- R. Han, Y. Wang, W. Yu, W. Zou, J. Shi, and H. Liu, "Biosorption of methylene blue from aqueous solution by rice husk in a fixed bed Column" , 2007 *Journal of Hazardous Materials*, 141, 3,713–718.