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Study of malachite green adsorption onto natural zeolite in a fixed-bed column

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ABSTRACT

Natural zeolite was used as adsorbent for adsorption of malachite green (MG) from an aqueous solution in a fixed-bed column. The effect of different conditions, such as coexistent salt, flow rate, bed depth and influent dye concentration were studied. The results showed that coexistent salt did not favor adsorption. Adsorption reached saturation faster with increasing the flow rate and influent MG concentration while it was the advantage of column adsorption with the increase in the zeolite bed. The data were fitted to the Thomas model and Yan model by nonlinear regressive analysis. When the flow rate was 9 ml·min^{-1} and the influent concentration of MG was 50 mg·L^{-1}, the maximum adsorption quantity reached 23.55 mg·g^{-1} according to the Thomas model. The Yan model was better than the Thomas model to predict the column adsorption process. Zeolite can be used to remove cationic dye from solution.

Keywords: Natural zoelite; Malachite green; Column adsorption; Yan model

1. Introduction

Many industries use dyes to color their products and also consume substantial volumes of water. Dyes are common constituents of effluents discharged by various industries, particularly the textile industries. Dyes are important pollutants, causing environmental and health problems to human beings and aquatic animals. Removal of dyes from wastewater can be achieved by several techniques, such as precipitation, flocculation, adsorption, ion exchange, and membrane separation [1]. Adsorption techniques are proved to be an effective and attractive process for removal of non-biodegradable pollutants (including dyes) from wastewater [2–5]. Many researchers have studied dye adsorption by different low-cost adsorbents such as agricultural byproduct, industrial waste, bottom ash, natural and modified clays [6–14].

Malachite green (MG), a basic dye, is widely used for the dyeing cotton, jute, silk, wool, leather and it is also extensively used all over the world in the fish farming industry as fungicide and disinfectant. Natural zeolite is an abundant resource of aluminosilicate available all over the world. Natural zeolite has been used as an effective adsorbent for removal of various heavy metals and dyes [15–18]. The MG adsorption onto natural zeolite has been reported [17]. However, few investigations on dye adsorption by zeolite column have been published [19].

The aim of the present work is to explore the possibility of utilizing natural zeolite for the adsorptive removal of MG from wastewater. The effect of such factors as co-salt existence, flow rate, influent dye concentration and bed depth on MG adsorption by zeolite bed column was investigated. Thomas model and Yan model were used to predict the performance.

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2. Materials and methods

The stock solutions of MG (salt of chloride) were prepared in distilled water (500 mg·L^{-1}). All working solutions were prepared by diluting the stock solution with distilled water to the desired concentration. The values of dye solution pH are near 4.5. From batch experiment, the adsorption quantity of MG by zeolite changes insignificantly within pH 4–6, so the pH of MG solution was not adjusted.

The natural zeolite used in the present study was obtained from Xinyang city in China. Before use, the zeolite were treated according to a previously published work [19]: crushed and sieved through mesh screens, and a fraction of the particles of average size (20–40 mesh) was soaked in tap water for 24 h, rinsed with distilled water in order to remove possible impurities that might induce clogging during the exchange in the column. After drying at 373 K in an oven, the sample was stored. Some of the characterization of this natural zeolite was as follows [20]. The analysis of XRD showed that the main composite of zeolite is clinoptilolite. The surface of zeolite is rough and it is composed of some elements, such as silicon, oxygen, aluminum and potassium, etc. The FT–IR spectra of zeolite composed of the peaks of sorbed water, vibration of framework and Si–O and Al–O.

Column adsorption experiments were carried out using zeolite packed into a glass column (1.0 cm inner diameter and 25 cm in height) with a bed depth of 8 cm (4 g), 10 cm (5 g), 12 cm (6 g), respectively. The experiments were conducted by pumping an MG solution in down flow mode through the fixed-bed with a peristaltic pump at a specified flow rate (Fig. 1). The temperatures of all experiments were 293 K. Samples were collected at regular intervals and in all the adsorptive processes. The concentration of MG in the effluent was analyzed using a UV spectrophotometer (Shimadzu Brand UV−3000) by monitoring the absorbance changes at a wavelength of maximum absorbance (622 nm). The experimental data was analyzed by software of Origin 6.0.

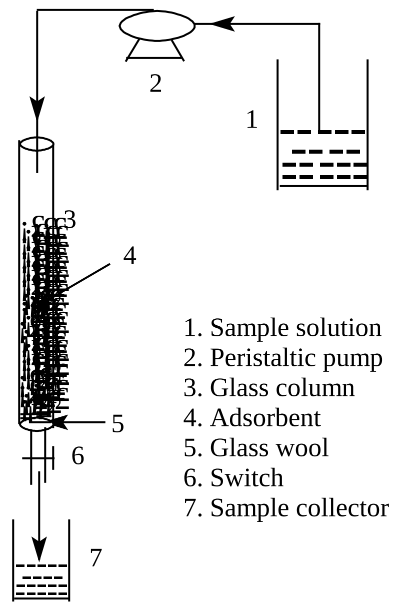

Fig. 1. Schematic flow sheet of fixed-bed column setup.

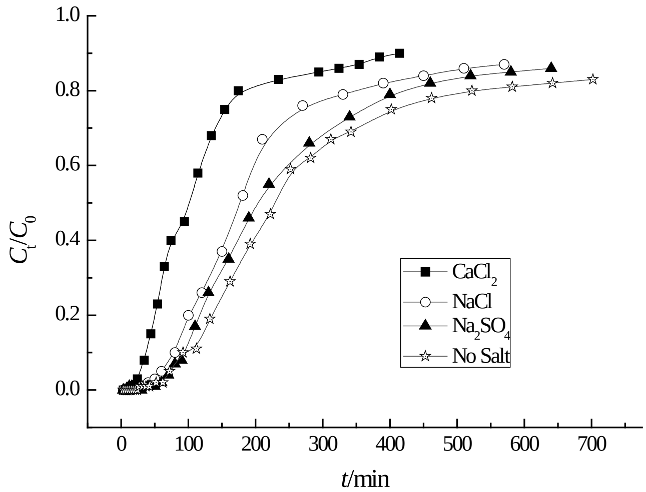

Fig. 2. Effect of salt existence on breakthrough curves (C_0 = 50 mg·L^{-1}, v = 9 ml·min^{-1}, Z = 10 cm).

3. Results and discussion

3.1. *The effect of coexistent salt in solution on breakthrough curve*

To investigate the effect of salt concentration on MG adsorption, the influent MG concentration was held constant at 50 mg·L^{-1}, the flow rate was 9 ml·min^{-1} and bed depth 10 cm. The concentration of coexistent salt was 0.02 mol·L^{-1}. The breakthrough curves are shown in Fig. 2.

As shown in Fig. 2, the existence of other salt in the solution resulted in the breakthrough curve from right to left and lower MG removal capacity. In other words, the coexistent salt in the solution resulted in a steeper slope and smaller breakthrough time, furthermore, the effect of $CaCl_2$ is more serious than the same mole concentration of NaCl and Na_2SO_4.

The reason could be attributed to the competitive effect between MG ions and metal cations from the salt for the sites available for the sorption process. Another reason is that the increase in salt concentration results in ionic strength increase and relative active coefficient becomes smaller. So the activity (effective concentration) of MG and the active sites decrease and the adsorptive capacity of MG decreases [21]. As Ca^{2+} has more contribution to ionic strength and more positive charge than Na^+, the effect of Ca^{2+} on adsorption is more serious than that of Na^+.

But for anion dye, such as Congo red, the coexistent salt is favorable for adsorption. The reason is that the electrolytes in the solution reduced the repulsive forces between the dye and the functional groups on the surface of the adsorbent due to screening effect of the superficial charge [22,23]. The comparison showed that the effect of common salt on cation dye and anion dye is different.

3.2. The effect of flow rate on breakthrough curve

The breakthrough curves at various flow rates are shown in Fig. 3.

It is shown that breakthrough generally occurred faster with a higher flow rate. Breakthrough time reaching saturation was increased with a decrease in the flow rate. At a lower rate of influent, MG had more time to contact with zeolite and this resulted in higher removal of MG in the column. The amount of dye adsorbed onto the unit bed height (mass transfer zone) increased with increasing the flow rate leading to a faster saturation at a higher flow rate.

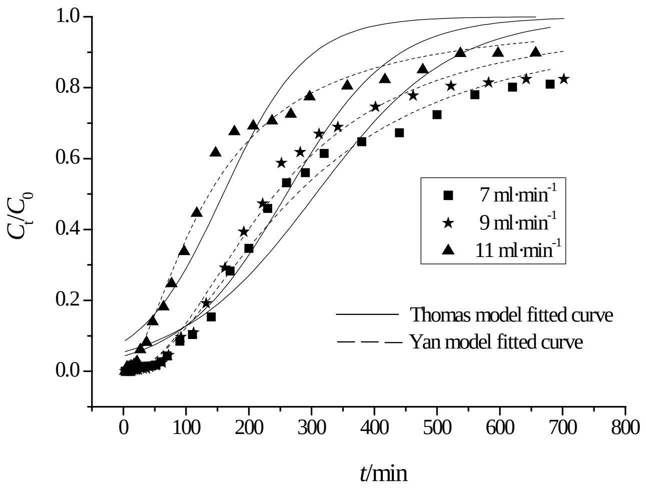

Fig. 3. Effect of flow rate on breakthrough curves (C_0 = 50 mg·L^{-1}, Z = 10 cm).

3.3. Effect of influent MG concentration on breakthrough curve

The breakthrough curves at various initial MG concentrations are shown in Fig. 4.

It is illustrated that the breakthrough time decreased with increasing the influent MG concentration. At lower influent MG concentrations, breakthrough curves were dispersed and the breakthrough occurred slower. As the influent concentration increased, sharper breakthrough curves were obtained [24–26]. These results demonstrated that the change of the concentration gradient affected the saturation rate and breakthrough time [26]. This can be explained by the fact that more adsorption sites are being covered with the increase in MG concentration. The larger the influent concentration, the steeper the slope of the breakthrough curve and smaller the breakthrough time.

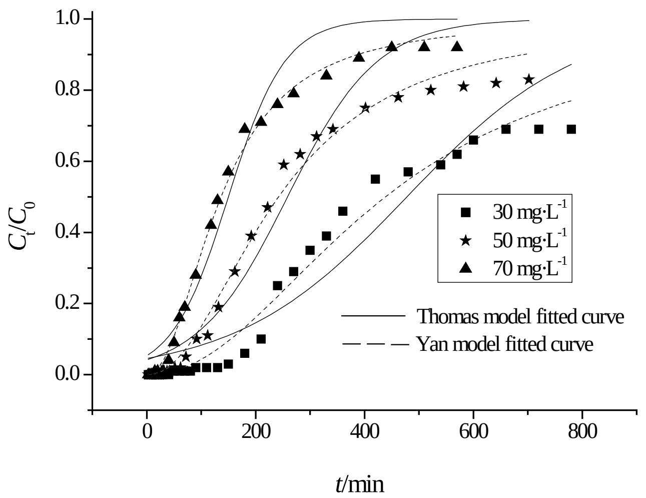

Fig. 4. Effect of influent concentration of dye on breakthrough curves (v = 9 ml·min^{-1}, Z = 10 cm).

3.4. Effect of bed depth on breakthrough curve

The breakthrough curves at different bed depths are shown in Fig. 5.

From Fig. 5, as the bed height increased, MG had more time to contact with zeolite that resulted in higher removal efficiency. So the higher bed column resulted in a decrease in the solute concentration in the effluent at the same time. The slope of the breakthrough curve decreased with increasing the bed height, which resulted in a broadened mass transfer zone.

The maximum column capacity, q_{total} (mg), for a given feed concentration and flow rate is equal to the area under the plot of the adsorbed MG concentration C_{ad} ($C_{\text{ad}} = C_0 - C_t$) (mg·L^{-1}) vs. time t (min) and is calculated from Eq. (1):

$$q_{\text{total}} = \frac{vA}{1000} = \frac{v}{1000}\int_{t=0}^{t=t_{total}} C_{\text{ad}}\,dt \tag{1}$$

where t_{total}, v and A are the total flow time (min) , volumetric flow rate (ml·min^{-1}) and the area under the breakthrough curve, respectively.

The uptake quantity (q_{ad}), the weight of MG adsorbed per unit dry weight of adsorbent (mg·g^{-1}) in the column, is calculated as follows:

$$q_{\text{ad}} = q_{\text{total}} / X \tag{2}$$

where X is the total dry weight of zeolite in the column (g).

The values of q_{ad} at different conditions were calculated and are listed in Table 1. From Table 1, the zeolite is not a good absorbent for MG according to values of q_{ad} in Table 1. However, since zeolite is a natural and cheap substance, it can be concluded that zeolite can be useful and acceptable even with these results.

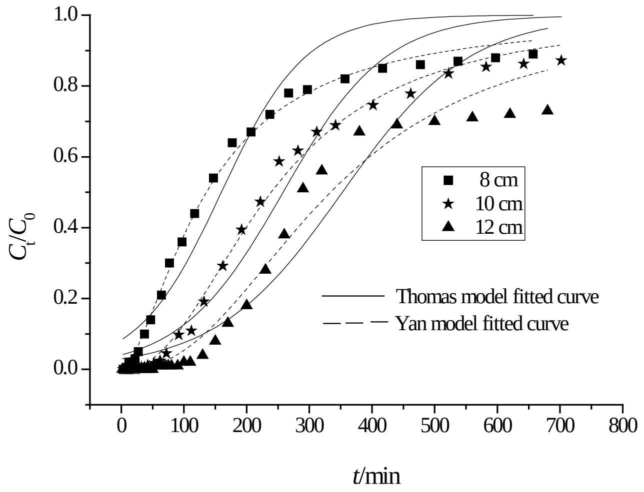

Fig. 5. Effect of bed depth on breakthrough curves (C_0 = 50 mg·L^{-1}, v = 9 ml·min^{-1}).

3.5. Application of the Thomas model

The Thomas model is one of the most general and widely used models in the column performance theory. The expression by Thomas for an adsorption column is given as follows [27]:

$$\frac{C_t}{C_0} = \frac{1}{1+\exp\left(k_{Th} q_0 X / v - k_{Th} C_0 t\right)} \quad (3)$$

where k_{Th} is the Thomas rate constant (ml·min^{-1}·mg^{-1}); q_0 is the maximum MG uptake per g of the adsorbent (mg·g^{-1}); X is the amount of the adsorbent in the column (g); C_0 is the influent MG concentration (mg·L^{-1}); C_t is the effluent concentration at time t (mg·L^{-1}); v is the flow rate (ml·min^{-1}). The value of C_t/C_0 is the ratio of the effluent and influent MG concentrations. The value of t is the flow time (min, $t = V_{eff}/v$, V_{eff} is the effluent volume at time t).

A nonlinear regression analysis with the least sum of square of errors (SSE) was used on each set of data to determine the Thomas model parameters of q_0, k_{Th}, the determined coefficients (R^2) and the SSE according to Eq. (3). The results are listed in Table 1. From Table 1, they were all fitted with determined coefficients (R^2) ranging from 0.905 to 0.960, but SSE was less than 0.01. So the Thomas model was reasonable to fit the data.

With the flow rate and initial concentration increasing, the values of k_{Th} became bigger, while the q_0 became smaller for the flow rate. With the bed depth increasing, the values of k_{Th} became smaller while the value of q_0 increased. From Table 1, all values of q_0 from the Thomas model are bigger than those from the experiments, respectively. The Thomas model is overestimating the values of q_0 [28].

3.6. Application of the Yan model

The Yan model [28] is also used to describe the column adsorption data. Use of this model can minimize the error resulting from the use of the Thomas model, especially at lower or higher time periods of the breakthrough curve. The expression is given as:

$$\frac{C_t}{C_0} = 1 - \frac{1}{1+\left(\frac{vt}{b}\right)^a} \quad (4)$$

where a and b are the constants of the Yan model, respectively.

From value of b, the value of q_0 can be estimated using following equation [28]:

$$q_0 = \frac{bC_0}{X} \quad (5)$$

The model constants (a and b) and values of q_0 are given in Table 2 using nonlinear regressive analysis. From Table 2, they were all fitted with higher determined coefficients (R^2) ranging from 0.976 to 0.997 and lower values of SSE (less than 0.002). The values of q_0 in Table 2 are smaller than those in Table 1. The breakthrough curves predicted by the Thomas model and the Yan model are also shown in Figs. 3–5. At all conditions examined, the predicted breakthrough curves from the Yan model showed reasonably better agreement with the experi-

Table 1
Thomas parameters at different conditions

C_0 (mg·L^{-1})	v (ml·min^{-1})	Z (cm)	q_{ad} (mg·g^{-1})	q_0 (mg·g^{-1})	k_{Th} (ml·min^{-1}·mg^{-1})	R^2	SSE
50	9	8	16.09	17.94±2.02	0.301±0.035	0.936	0.00840
50	9	10	16.50	23.22±2.14	0.245±0.023	0.952	0.00586
50	9	12	14.73	26.38±2.26	0.199±0.019	0.905	0.00669
50	7	10	13.57	21.45±1.96	0.186±0.019	0.923	0.00742
50	11	10	15.47	17.48±2.11	0.302±0.038	0.926	0.00983
30	9	10	12.12	25.81±2.12	0.212±0.018	0.914	0.00645
70	9	10	17.49	18.92±1.90	0.275±0.029	0.960	0.00575

Table 2
Yan parameters at different conditions

C_0 (mg·L^{-1})	v (ml·min^{-1})	Z (cm)	a	b (ml)	q_0 (mg·g^{-1})	R^2	SSE
50	9	8	1.62±0.04	1221±20	15.26±0.25	0.997	0.00039
50	9	10	2.12±0.08	2179±44	21.79±0.44	0.992	0.00099
50	9	12	2.38±0.13	3005±73	25.04±0.61	0.976	0.0017
50	7	10	1.94±0.07	1933±36	19.33±0.36	0.992	0.00075
50	11	10	1.65±0.07	1504±40	15.04±0.40	0.992	0.00102
30	9	10	2.10±0.11	3926±85	23.56±0.51	0.982	0.00135
70	9	10	2.11±0.06	1228±17	17.19±0.24	0.997	0.00037

mental curves than the Thomas model. At the lower and high time of breakthrough curves, the fitted curves of the Thomas model were far from experimental points. So the Yan model was better to predict the MG column adsorption than the Thomas model. The trend of values of q_0 and b in Table 2 is similar to values of q_0 in Table 1 with the change of experimental conditions. Several researchers studied the metal removal by adsorption in the column mode, and found that that the column kinetics could be described more adequately by the Yan model than by the Thomas model [28–30]. Our study on dye removal in column adsorption had similar results.

4. Conclusion

Natural zeolite exhibits effective adsorption for MG in aqueous solution. The adsorption of MG was dependent on the flow rate, the inlet MG concentration and bed depth. Yan model is better used to predict the breakthrough curves than Thomas model. Zeolite as adsorbent can be used to removal MG from solution.

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References

[1] T. Robinson, G. McMullan, R. Marchant and P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresour. Technol., 77 (2001) 247–255.
[2] G. Crini, Non-conventional low-cost adsorbents for dye removal: A review, Bioresour. Technol., 97 (2006) 1061–1085.
[3] V.K. Gupta, A. Mittal, V. Gaibe and J. Mittal, Adsorption of basic fuchsin using waste materials-bottom ash and deoiled soya as adsorbents, J. Colloid Interface Sci., 319 (2008) 30–39.
[4] W.H. Zou, P. Han, Y.L. Li, X. Liu, X.T. He and R.P. Han, Equilibrium, kinetic and mechanism study for the adsorption of neutral red onto rice husk, Desal. Wat. Treat., 12 (2009) 210–218.
[5] V.K. Gupta and Suhas, Application of low cost adsorbents for dye removal — A review, J. Environ. Manage., 90 (2009) 2313–2342.
[6] R.P. Han, Y. Wang, X. Zhao, Y.F. Wang, F.L. Xie, J.M. Cheng and M.S. Tang, Adsorption of methylene blue by phoenix tree leaf powder in a fixed-bed column: experiments and prediction of breakthrough curves, Desalination, 245 (2009) 284–297.
[7] M.M. Abd El-Latif and A.M. Ibrahim, Adsorption, kinetic and equilibrium studies on removal of basic dye from aqueous solutions using hydrolyzed oak sawdust, Desal. Wat. Treat., 6 (2009)252–268.
[8] V. K. Gupta, A. Mittal, D. Kaur, A. Malviya and J. Mittal, Adsorption studies on the removal of colouring agent phenol red from wastewater using waste materials as adsorbents, J. Colloid Interface Sci., 337 (2009) 345–354.
[9] D.A. Fungaro, M. Bruno and L.C. Grosche, Adsorption and kinetic studies of methylene blue on zeolite synthesized from fly ash, Desal. Wat.Treat., 2 (2009) 231–239.
[10] V.K. Gupta, R. Jain and S. Varshney, Removal of Reactofix golden yellow 3 RFN from aqueous solution using wheat husk-An agricultural waste, J. Hazard. Mater., 142 (2007) 443–448.
[11] V.K. Gupta and I. Ali, Removal of endosulfan and methoxychlor from water on carbon slurry, Environ. Sci. Technol., 42 (2008) 766–770.
[12] V.K. Gupta, C.K. Jain, I. Ali, S. Chandra and S. Agarwal, Removal of lindane and malathion from wastewater using bagasse fly ash-a sugar industry waste, Water Res., 36 (2002) 2483–2490.
[13] Y.J. Wu, L.J. Zhang, C.L. Gao, J.Y. Ma, X.H. Ma and R.P. Han, Adsorption of copper ions and methylene blue in single and binary system on wheat straw, J. Chem. Eng. Data, 54 (2009) 3229–3234.
[14] J.X. Lin and L. Wang, Adsorption of dyes using magnesium hydroxide-modified diatomite, Desal. Wat. Treat., 8 (2009) 263–271.
[15] J. Peric, M. Trgo and N. Vukojevic Medvidovic, Removal of zinc, copper and lead by natural zeolite — A comparison of adsorption isotherms, Water Res., 38 (2004) 1893–1899.
[16] R.P. Han, J.J. Zhang, P. Han, Y.F. Wang, Z.H. Zhao and M.S. Tang, Study of equilibrium, kinetic and thermodynamic parameters about methylene blue adsorption onto natural zeolite, Chem. Eng. J., 145 (2009) 496–504.
[17] S.B. Wang and E. Ariyanto, Competitive adsorption of malachite green and Pb ions on natural zeolite, J. Colloid Interface Sci., 314 (2007) 25–31.
[18] M.Q. Qiu, C. Qian, J. Xu, J.M. Wu and G.X. Wang, Studies on the adsorption of dyes into clinoptilolite, Desalination, 243 (2009) 286–292.
[19] R.P. Han, Y. Wang, W.H. Zou, Y.F. Wang and J. Shi, Comparison of linear and nonlinear analysis in estimating the Thomas model parameters for methylene blue adsorption onto natural zeolite in fixed-bed column, J. Hazard. Mater., 145 (2007) 331–335.
[20] R.P. Han, L.N. Zou, X. Zhao, Y.F. Xu, Y.F. Li, Y.L. Li and Y. Wang, Characterization and properties of iron oxide-coated zeolite as adsorbent for removal of copper (II) from solution in fixed bed

column, Chem. Eng. J., 149 (2009) 123–131.
[21] J.O.M. Bockris, A.K.N. Reddy and M.E. Gamboa-Aldeco, Modern Electrochemistry, Kluwer Academic–Plenum Publishers, Dordrecht, 2001.
[22] R.P. Han , D.D. Ding, Y.F. Xu, W.H. Zou, Y.F. Wang, Y.F. Li and L.N. Zou, Use of rice husk for the adsorption of Congo red from aqueous solution in column mode, Bioresour. Technol., 99 (2008) 2938–2946.
[23] Y.S. Al-Deg, M.I. El-Barghouthi, A.H. El-Sheikh and G.M. Walker, Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon, Dyes Pigments, 77 (2008) 16–23.
[24] R.P. Han, J.H. Zhang, W.H. Zou, H.J. Xiao, J. Shi and H.M. Liu, Biosorption of copper(II) and lead(II) from aqueous solution by chaff in a fixed-bed column, J. Hazard. Mater., 133 (2006) 262–268.
[25] R.P. Han, Y.F. Wang, W.H. Yu, W.H. Zou, J. Shi and H.M. Liu, Biosorption of methylene blue from aqueous solution by rice husk in a fixed–bed column, J. Hazard. Mater., 141 (2007) 713–718.
[26] Z. Aksu and F. Gonen, Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves, Process Biochem., 39 (2004) 599–613.
[27] H.C. Thomas, Heterogeneous ion exchange in a flowing system, J. Am. Chem. Soc., 66 (1944) 1664–1666.
[28] G. Yan, T. Viraraghavan and M. Chen, A new model for heavy metal removal in a biosorption column, Adsorpt. Sci. Technol., 19 (2001) 25–43.
[29] K. Vijayaraghavan and D. Prabu, Potential of *Sargassum wightii* biomass for copper(II) removal from aqueous solutions: Application of different mathematical models to batch and continuous biosorption data, J. Hazard. Mater., 137 (2006) 558–564.
[30] P. Lodeiro, R. Herrero and M.E. Sastre de Vicente, The use of protonated Sargassum muticum as biosorbent for cadmium removal in a fixed-bed column, J. Hazard. Mater., 137 (2006) 244–253.

Appendix

Malachite green is a basic dye of triphenylmethane type (C.I. No. 42,000, FW = 364.9, λ_{max} = 622 nm). The structure of MG is the following: