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Original Research Paper

Adsorption of Methylene Blue by Activated Carbon from Capsicum Straw

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ABSTRACT

Dyes are known to be toxic, carcinogenic and mutagenic. Their release into the environment can cause aesthetic pollution, and moreover, they are not degraded by conventional aerobic wastewater treatment due to their recalcitrance. Therefore, it is necessary to reduce dye concentration in the wastewater. Activated carbon was obtained from capsicum straw by chemical activation using KOH as an activator. Then it was used as an adsorbent for the removal of dye methylene blue. The adsorption of dye methylene blue by activated carbon was carried out in detail. Kinetic adsorption data were analysed by the pseudo-first-order kinetic model, the pseudo-second-order model and the intraparticle diffusion model. The experimental data were analysed by the Langmuir and Freundlich models of adsorption. The thermodynamics parameters were also calculated.

INTRODUCTION

Dyes have been extensively used in many industries, such as textile, leather, tanning, paper production, food technology, hair colouring, etc. (Njoku et al. 2014). The dyes are known to be toxic, carcinogenic and mutagenic. Their release into the environment can cause aesthetic pollution, and moreover, they are not degraded by conventional aerobic wastewater treatment due to their recalcitrance (Yu & Luo 2014). The presence of these coloured compounds in wastewater is not only aesthetically displeasing, but also they impede light penetration in the treatment plants, thus upsetting the biological treatment processes within the treatment plant. They also increase the biochemical oxygen demand (BOD) and cause lack of dissolved oxygen to sustain aquatic life. In addition, many dyes are toxic to some microorganisms, and may cause direct destruction or inhibition of their catalytic capabilities (Luna et al. 2013, Salima et al. 2012). Therefore, it is necessary to reduce dye concentration in the wastewater before their biological treatment processes.

Many treatment methods have been adopted to remove dyes from wastewater, which can be divided into physical, chemical and biological methods (Ribeiro et al. 2012). Although chemical and biological methods are effective for removing dyes, they require specialized equipment and are usually quite energy intensive. In addition, large amounts of by-products are often generated (Vargas et al. 2012).

Generally, physical methods which include adsorption, ion exchange, and membrane filtration are effective for removing reactive dyes without producing unwanted by-products (Li et al. 2011). Adsorption has been used extensively in industrial processes for many purposes of separation and purification. The removal of coloured and colourless organic pollutants from industrial wastewater is considered as an important application of adsorption processes using suitable adsorbent. At present, there is growing interest in using low cost, commercially available materials for the adsorption of dyes. A wide variety of materials, such as fly ash, peat, wood, palm-fruit bunch particles, activated carbon from fertilizer waste and activated slag, are being used (Li et al. 2013, Muthiulan et al. 2013, Nabil et al. 2014, Ghaedi & Mosallanejad 2014).

Activated carbons are materials having complex porous structures with associated energetic as well as chemical inhomogeneities. Their structural heterogeneity is a result of the existence of micropores, mesopores and macropores of different sizes and shapes (Chen et al. 2013). Activated carbon is one of the most important adsorbents from an industrial view of point. The main application of this adsorbent is for separation and purification of gaseous and liquid phase mixtures (Nuithitikul et al. 2010, Wang et al. 2014, Kaušpėdienė et al. 2010). However, appropriate properties and cost of adsorbent materials are the key aspects for practical applications when dealing with dye wastewater. One of the ways to decrease the cost of adsorbent production is the use of inexpensive precursors such as agricultural by-products and wastes (Liu et al. 2011, Ranjithkumar et al. 2014, Mahmoodi et al. 2011). It was demonstrated that agricul-

tural by-products and various biosorbent materials have promising capacities to remove a variety of pollutants (Thinakaran et al. 2008, Ho & Mckay 1998, Niu et al. 2007).

The aim of this work is to study the ability of the activated carbon obtained from capsicum straw by chemical activation using KOH as an activator to remove dye from aqueous solutions. The equilibrium and kinetic studies have been performed. The importance of obtaining isotherms and kinetics curve lies in developing a model which accurately represents the results obtained and could be used for design purposes.

MATERIALS AND METHODS

Materials: The capsicum straw was obtained from Shaoxing city in Zhejiang province of P.R. China. The capsicum straw was dried at 105°C for 12 h, to achieve constant weight, then comminuted and sieved into a uniform size of 120 mesh. The 50 g of the capsicum straw was soaked stilly with 100mL 10% KOH solution in 250 mL Erlenmeyer flasks for 24 h at room temperature. Then, it was dried again at 105°C for 12h to constant weight and was carbonized at 700°C in a muffle furnace for 60 min. The product of 120 mesh activated carbon was thus obtained and then stored for later adsorption experiments.

The methylene blue dye with commercial purity was used without further purification. The chemical structure is shown in Fig. 1.

Adsorption experiments: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.10g of activated carbon and 100 mL of dye solution with various initial concentrations (20mg/L, 30mg/L, 40mg/L and 50mg/L). The initial pH was adjusted to 5.0 with 1 mol/L HCl. The flasks were placed in a shaker at a constant temperature (293, 303 and 313K) and 100 rpm. The samples were then filtered and the residual concentration of dye methylene blue was analysed using a UV-1600 spectrophotometer at a wavelength corresponding to the maximum absorbance for dye methylene blue.

Analytical methods: The textural characteristics of activated carbon including surface area, pore volume, pore size distribution were determined using standard N_2-adsorption techniques. The surface physical morphology of activated carbon was observed by a scanning electron microscope.

The value of pH was measured with a pH probe according to APHA Standard Method. The concentration of dye methylene blue was measured with a UV-1600 spectrophotometer at 665 nm.

The amount of adsorbed dye q_t (mg/g) at different times, was calculated as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad ...(1)$$

where C_o and C_t (mg/L) are the initial and equilibrium liquid-phase concentrations of dye methylene blue respectively. V (L) is the solution volume and m (g) is the mass of adsorbent used.

Statistical analyses of data: All experiments were repeated in duplicate and the data of results were the mean and the standard deviation (SD). The value of the SD was calculated by Excel Software. All the data were analysed by the Langmuir and Freundlich adsorption models to test the effects of temperature and initial dye methylene blue concentration. The kinetic adsorption data were discussed using the pseudo-first-order model and pseudo-second-order model. All error estimates given in the text and error bars in the figures are the standard deviation of means (mean ± SD). All statistical significance was noted at $\alpha = 0.05$ unless otherwise noted.

RESULTS AND DISCUSSION

Characterization of activated carbon: The surface of the activated carbon was observed using scanning electron microscopy as shown in Fig. 2. It can be seen from the micrograph that the activated carbon contains porous structure and presents an adequate morphology for dye methylene blue adsorption.

The characteristics of activated carbon are obtained from the standard N_2-adsorption techniques. The BET surface area is 676 m^2/g, the total pore volume is 0.72 cm^3/g and the nominal pore size is 1.21 nm. In addition, the content of C, N and H in activated carbon were 86.24%, 1.13% and 0.25% respectively. It shows that activated carbon has a large specific surface area.

Adsorption isotherms: The capacity of an adsorbent can be described by its equilibrium sorption isotherm. The Langmuir and Freundlich adsorption models are commonly adopted to investigate the adsorption behaviour of materials and the correlation among adsorption parameters. Accordingly, equilibrium data were simulated by the Langmuir (Langmuir 1916) and Freundlich models (Freundlich 1906).

The Langmuir isotherm equation is represented by the following eq. (2):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad ...(2)$$

Where C_e is the equilibrium concentration of dye methylene blue (mg/L), q_e is the amount of dye methylene blue adsorbed (mg/g), q_m is the maximum adsorption capacity of dye methylene blue (mg/g), and K_L is the Langmuir ad-

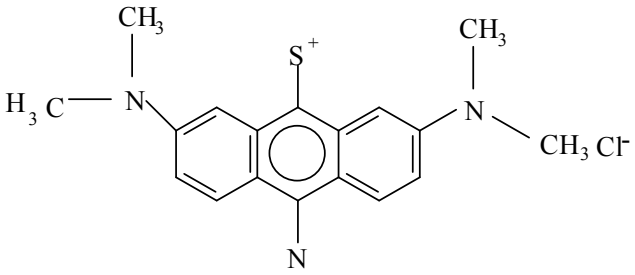

Fig.1: Chemical structures of methylene blue.

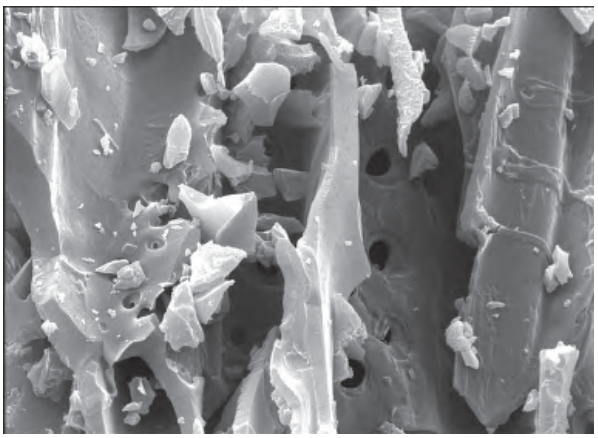

Fig.2: SEM image of activated carbon.

sorption equilibrium constant (L/mg) related to the affinity of the binding sites.

The Freundlich isotherm equation is described by the following eq. (3):

$$q_e = K_F C_e^{\frac{1}{n}} \quad ...(3)$$

where K_F and n are the Freundlich adsorption isotherm constants, which are indicators of adsorption capacity and adsorption intensity respectively.

The corresponding values of Langmuir and Freundlich isotherms for dye methylene blue adsorption on activated carbon are listed in Table 1. The results indicate that the Langmuir isotherm fits better than the Freundlich isotherm. The value of R_L is between 0 and 1, which indicate heterogeneity of the adsorbents and favourable adsorption (Machado et al. 2011). The maximum adsorption capacity obtained from the Langmuir isotherm is 34.12 mg/g.

Adsorption kinetics: The influence of contact time on the removal of dye methylene blue in a solution by activated carbon is shown in Fig. 3.

It can be concluded that adsorption rate of dye methylene blue increased sharply at a short contact time and slowed down gradually as equilibrium was approached. It may be

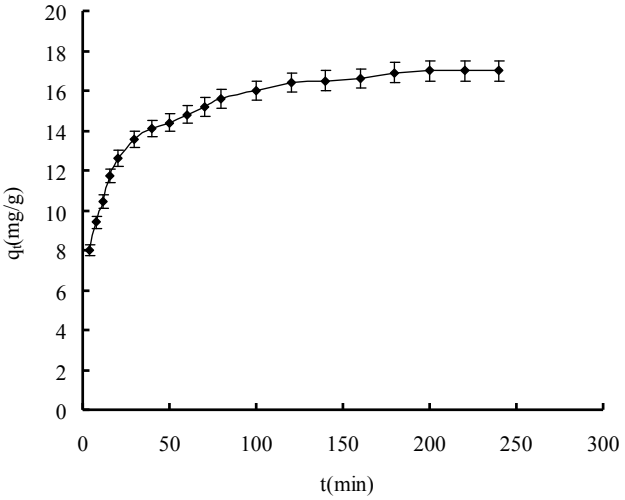

Fig.3: Effect of contact time on adsorption of dye methylene blue in solution onto activated carbon. Experimental conditions: 0.10 g of activated carbon, 20mg/L of initial dye methylene blue concentration, 120 meshes of particle size, 293 K, 100 rpm and pH 5.0.

due to the availability of an initial large number of vacant surface active sites for adsorption and adsorption rate was very fast. As equilibrium was approached, the filling of vacant sites becomes difficult due to repulsive forces between dye methylene blue adsorbed on solid surface and dye methylene blue from solution.

In order to investigate the mechanism of dye methylene blue sorption, three models were used in this study.

The linear pseudo-first-order model of Lagergren is given as follows (Thinakaran et al. 2008):

$$\ln(q_e - q_t) = \ln q_e - k_1 \times t \quad ...(4)$$

where q_e and q_t are the amounts of dye methylene blue absorbed onto the adsorbent (mg/g) at equilibrium and at t respectively. k_1 is the rate constant of first-order adsorption (min^{-1}).

The pseudo-second-order kinetic model developed by Ho and McKay (Ho & Mckay 1998) is based on the experimental information of solid-phase sorption. The linear pseudo-second-order model can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad ...(5)$$

Table 1: Equilibrium model parameters for the adsorption of dye methylene blue onto activated carbon. Experimental conditions: 0.10 g of activated carbon, 120 meshes of particle size, contact time of 200 min, 293 K, 100 rpm and pH 5.0.

Langmuir model			Freundlich model		
q_m (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	n	R^2
34.12	0.34	0.9938	0.021	0.505	0.9754

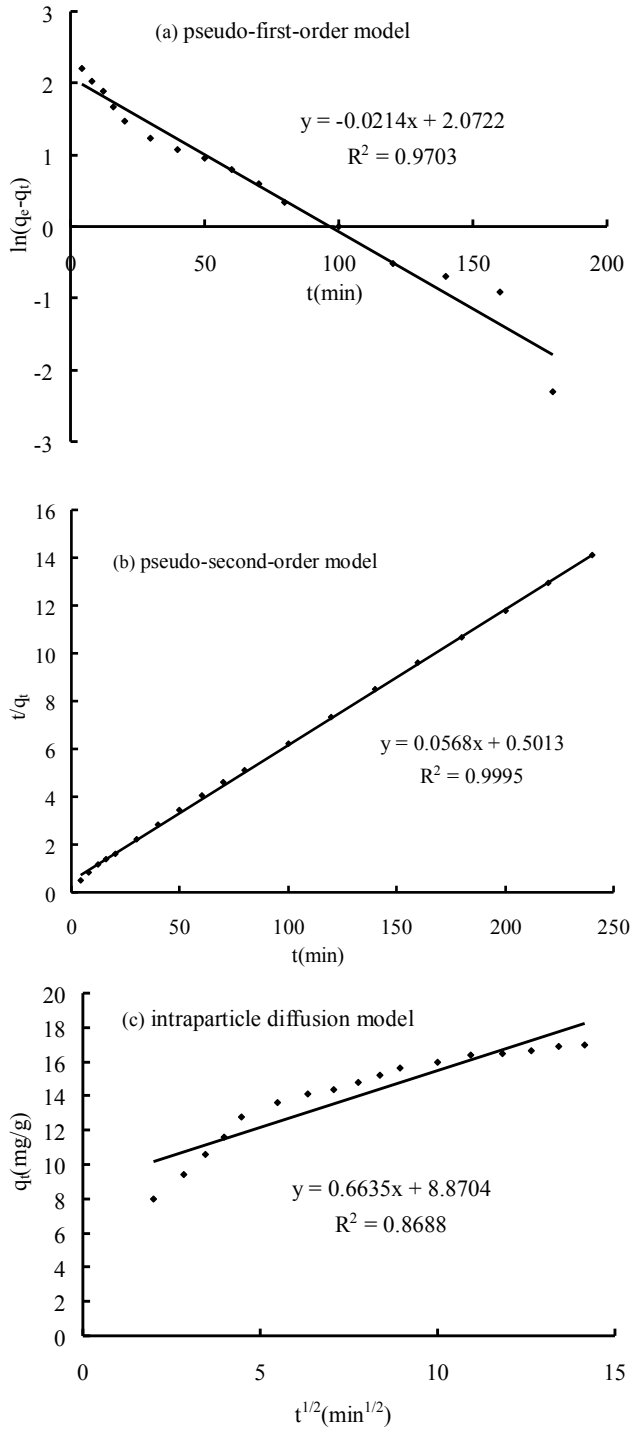

Fig. 4: (a) pseudo-first-order model for adsorption of dye methylene blue onto activated carbon at 293 K. (b) pseudo-second-order model for adsorption of dye methylene blue onto activated carbon at 293 K. (c) intraparticle diffusion model for adsorption of dye methylene blue onto activated carbon at 293K. Experimental conditions: 0.10 g of activated carbon, 20mg/L of initial dye methylene blue concentration, 120 meshes of particle size, 293 K, 100 rpm and pH 5.0.

where k_2 is the rate constant of second-order adsorption ($g \cdot mg^{-1} \cdot min^{-1}$).

The intraparticle diffusion model can be expressed as follows:

$$q_t = k_i t^{\frac{1}{2}} \quad ...(6)$$

where k_i is the constant of intraparticle diffusion rate. It is obtained from the slope of the straight line of q_t versus $t^{\frac{1}{2}}$.

The adsorption kinetic models are shown in Fig. 4. The rate constant (k_1 k_2 and k_i), correlation coefficient R^2, and equilibrium adsorption density of q_e could be derived from this line.

The validity of the exploited models is verified by the correlation coefficient (R^2). R^2 values of the pseudo-first-order model, the pseudo-second-order model and the intraparticle diffusion model for adsorption of dye methylene blue onto activated carbon were 0.9703, 0.9995 and 0.8688 respectively. This result confirmed that the adsorption of dye methylene blue onto activated carbon better fits to pseudo-second order kinetic model. It implies that the predominant process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent (Niu et al. 2007, Arulkumar et al. 2011).

Effect of temperature and thermodynamics parameters: The effect of temperature is shown in Fig. 5. It was found that the adsorption rate of dye methylene blue increased with increasing solution temperature from 293K to 313K. It also indicate that the adsorption is an endothermic process. The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle diffusion of adsorbate molecules into the pores of the activated carbons at higher temperatures (Wang et al. 2010).

The thermodynamic parameters of free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were used to describe thermodynamic behaviour of the adsorption of dye methylene blue onto the activated carbon. These parameters were calculated from the following equations (Duan et al. 2012).

$$\Delta G^0 = -RT \ln K_a \quad ...(7)$$

$$\ln K_a = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad ...(8)$$

$$K_a = \frac{q_e}{C_e} \quad ...(9)$$

Where T is the solution temperature (K), K_a is the adsorption equilibrium constant, R is the gas constant (8.314 $J.mol^{-1}$

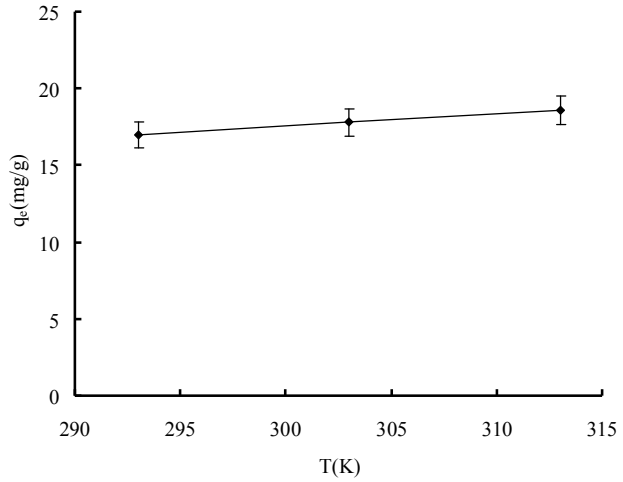

Fig. 5: Effect of temperature on adsorption of dye methylene blue onto activated carbon. Experimental conditions: 0.10 g of activated carbon, 20mg/L of initial dye methylene blue concentration, 120 meshes of particle size, contact time of 200 min, 100 rpm and pH 5.0.

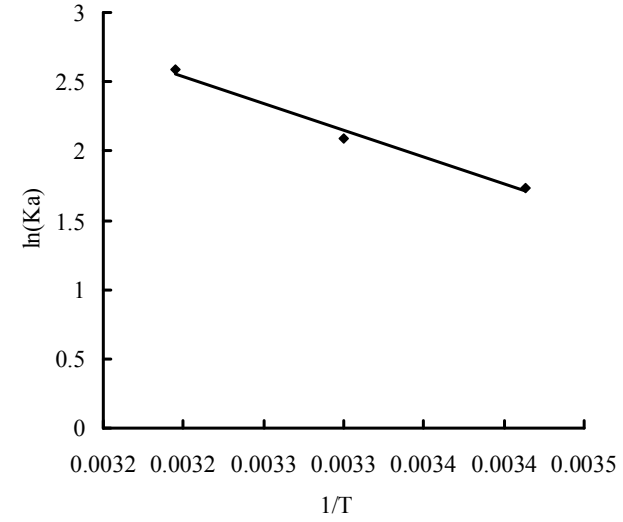

Fig.6: Determination thermodynamic parameters for adsorption of dye methylene blue onto activated carbon. Experimental conditions: 0.10 g of activated carbon, 20mg/L of initial dye methylene blue concentration, 120 meshes of particle size, contact time of 200 min, 100 rpm and pH 5.0.

$.K^{-1}$), q_e is the amount of adsorbate adsorbed per unit mass of adsorbate at equilibrium (mg/g) and C_e is the equilibrium concentration of the adsorbate (mg/L).

Thermodynamic parameters (ΔH^0, ΔS^0 and ΔG^0) for dye methylene blue adsorption were evaluated using eqs. (7)-(9). The values of ΔH^0 and ΔS^0 were determined from the slope and intercept of the plot of $\ln K_a$ versus 1/T (Fig. 6).

The values of (ΔH^0, ΔS^0 and ΔG^0) are listed in Table 2. As the temperature increases, and the value of ΔG^0 decreases. It indicates less driving force and hence resulting in lesser adsorption capacity at higher temperatures. Above 303K, the

Table 2: Thermodynamic parameters for the adsorption of dye methylene blue onto activated carbon.

Temperature (K)	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (KJ/mol)
293	-4.23	32.41	0.13
303	-5.27	32.41	0.13
313	-6.73	32.41	0.13

negative values of ΔG^0 indicates the adsorption of dye methylene blue onto activated carbon is spontaneous and thermodynamically favourable. The positive value of ΔH^0 indicates that the sorption process was endothermic in nature. The positive value of ΔS^0 showed the increasing randomness at solid/solution interface with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbent.

CONCLUSIONS

Activated carbon was obtained from capsicum straw by chemical activation process. The adsorption studies for the removal of dye methylene blue from aqueous solutions were carried out. The activated carbon contains porous structure and presents an adequate morphology for dye methylene blue adsorption. The adsorption isotherm studies showed that Langmuir isotherm fits better than the Freundlich isotherm. The pseudo-second order kinetic model better described the sorption data. The maximum adsorption capacity obtained from the Langmuir isotherm is 34.12 mg/g. The thermodynamic parameters showed a spontaneous, thermodynamically favourable and endothermic adsorption.

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REFERENCES

Arulkumar, M., Sathishkumar, P. and Palvannan, T. 2011. Optimization of Orange G dye adsorption by activated carbon of *Thespesia populnea* pods using response surface methodology. J. Hazard. Mater., 186: 827-834.

Chen, Y., Zhai, S.R., Liu, N., Song, Y., An, Q.D. and Song, X.W. 2013. Dye removal of activated carbons prepared from NaOH-pretreated rice husks by low-tmperature solution-processed carbonization and H_3PO_4 activation. Biores. Technol., 144: 401-409.

Duan, X.H., Srinivasakannan, C., Qu, W.W., Wang, X., Peng, J.H. and Zhang, L.B. 2012. Regeneration of microwave assisted spent activated carbon: process optimization, adsorption isotherms and kinetics. Chem. Eng. Process., 252: 5353-5362.

Freundlich, H.M.F. 1906. Uber die adsorption in losungen (adsorption in solution). Z. Phys. Chem., 57: 384-470.

Ghaedi, M. and Mosallanejad, N. 2014. Study of competitive adsorption

of malachite green and sunset yellow dyes on cadmium hydroxide nanowires loaded on activated carbon. J. Ind. Eng. Chem., 20: 1085-1096.

Ho, Y.S. and Mckay, G. 1998. Kinetic models for the sorption of dye from aqueous solution by wood. Trans. Inst. Chem. Eng., 76(2): 183-191.

Kaušpėdienė, D., Kazlauskienė, E., Gefenienė, A. and Binkienė, R. 2010. Comparison of the efficiency of activated carbon and neutral polymeric adsorbent in removal of chromium complex dye from aqueous solutions. J. Hazard. Mater., 179: 933-939.

Langmuir, I. 1916. The constitution and fundamental properties of solids and liquids. J. Am. Chem. Soc., 38: 2221-2295.

Li, W.H., Yue, Q.Y., Gao, B.Y., Ma, Z.H., Li, Y.J. and Zhao, H.X. 2011. Preparation and utilization of sludge-based activated carbon for the adsorption of dyes from aqueous solutions. Chem. Eng. J., 171: 320-327.

Li, Y.H., Liu, T.H., Peng, X.J., Wang, J.J., Sun, J.K., Wang, Y.H., Wu, S.L., Wang, Z.H., Xia, Y.Z. and Xia, L.H. 2013. Comparative study of methylene blue adsorption onto activated carbon, grapheme oxide, and carbon nanotubes. Chem. Eng. Res. Design, 91: 361-368.

Liu, W.H., Yue, Q.Y., Tu, P., Ma, Z.H., Gao, B.Y., Li, J.Z. and Xu, X. 2011. Adsorption characteristics of dyes in columns of activated carbon prepared from paper mill sewage sludge. Chem. Eng. J., 178: 197-203.

Luna, M.D.G., Flores, E.D., Genuino, D.A.D., Futalan, C.M. and Wan, M.W. 2013. Adsorption of Eriochrome black T (EBT) dye using activated carbon prepared from waste rice hulls-optimization, isotherm and kinetic studies. J. Taiwan Inst. Chem. Eng., 44: 646-653.

Machado, F.M., Bergmann, C.P., Fernandes, T.H.M., Lima, E.C., Royer, B., Calvete, T. and Fagan, S.B. 2011. Adsorption of reactive red M-2BE dye from water solutions by multi-walled carbon nanotubes and activated carbon. J. Hazard. Mater., 192: 1122-1131.

Muthiulan, P., Meenakshisundararam, M. and Kannan, N. 2013. Beneficial role of ZnO photocatalyst supported with porous activated carbon for the mineralization of alizarin cyanin green dye in aqueous solution. J. Adv. Res., 4: 479-484.

Nabil, G.M., Mallah, N.M.E. and Mahmoud, M.E. 2014. Enhanced decolorization of reactive black 5 dye by active carbon sorbent-immobilized-cationic surfactant (AC-CS). J. Ind. Eng. Chem., 20: 994-1002.

Niu, C., Wu, W., Wang, Z., Li, S. and Wang, J. 2007. Adsorption of heavy metal ions from aqueous solution by crosslinked carboxymethyl konjac glucomannan. J. Hazard. Mater., 141: 209-214.

Njoku, V.O., Foo, K.Y., Asif, M. and Hameed, B.H. 2014. Preparation of activated carbons from rambutan (*Nephelium lappaceum*) peel by microwave-induced KOH activation for acid yellow 17 dye adsorption. Chem. Eng. J., 250: 198-204.

Nuithitikul, K., Srikhun, S. and Hirunpraditkoon, S. 2010. Kinetics and equilibrium adsorption of basic green 4 dye on activated carbon derived from durian peel: effects of pyrolysis and post-treatment conditions. J. Taiwan Inst. Chem. Eng., 41: 591-598.

Ranjithkumar, V., Sangeetha, S. and Vairam, S. 2014. Synthesis of magnetic activated carbon/α-Fe_2O_3 nanocomposite and its application in the removal of acid yellow 17 dye from water. J. Hazard. Mater., 273: 127-135.

Ribeiro, R.S., Fathy, N.A., Attia, A.A., Silva, A.M.T., Faria, J.L. and Gomes, H.T. 2012. Activated carbon xerogels for the removal of the anionic azo dyes orange II and chromotrope 2R by adsorption and catalytic wet peroxide oxidation. Chem. Eng. J., 195-196: 112-121.

Salima, A., Benaouda, B., Noureddine, B. and Duclaux, L. 2012. Application of ulva lactuca and systoceira stricta algae-based activated carbons to hazardous cationic dyes removal from industrial effluents. Water Res., 47: 3375-3388.

Thinakaran, N., Panneerselvam, P., Baskaralingam, P., Elango, D. and Sivanesan, S. 2008. Equilibrium and kinetic studies on the removal of acid red 114 from aqueous solutions using activated carbons prepared from seed shells. J. Hazard. Mater., 158: 142-150.

Vargas, A.M.M., Martins, A.C. and Almeida, V.C. 2012. Ternary adsorption of acid dyes onto activated carbon from flamboyant pods (*Delonix regia*): analysis by derivative spectrophotometry and response surface methodology. Chem. Eng. J., 195-196: 173-179.

Wang, L., Yao, Y.Y., Sun, L.J., Mao, Y.J., Lu, W.Y., Huang, S.Q. and Chen, W.X. 2014. Rapid removal of dyes under visible irradiation over activated carbon fibers supported Fe(III)-citrate at neutral pH. Sep. Purif. Technol., 122: 449-455.

Wang, L., Zhang, J., Zhao, R., Li, C., Li, Y. and Zhang, C.L. 2010. Adsorption of basic dyes on activated carbon prepared from *Polygonum orientale* Linn: equilibrium, kinetic and thermodynamic studies. Desalination, 254: 68-74.

Yu, L. and Luo, Y.M. 2014. The adsorption mechanism of anionic and cationic dyes by Jerusalem artichoke stalk-based mesoporous activated carbon. J. Environ. Chem. Eng., 2: 220-229.