Research Article
Kinetic for Adsorption of Dye Methyl Orange by the Modified Activated Carbon from Rice Husk

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Abstract: In this study, the modified activated carbon from rice husk is used as the low cost material to absorb dye Methyl Orange in aqueous solution. The effects of different process parameters like pH, initial dye concentration and contact time on the adsorption of dye are investigated. The kinetic data of adsorption studies are discussed by the pseudo first-order, pseudo second-order and intraparticle diffusion. The results were shown that the adsorption process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent.

Keywords: Dye methyl orange, kinetic, rice husk

INTRODUCTION

Environmental pollution through industrial effluents has been a serious concern in developing countries. To protect our environment from pollutants, it can be achieved either by minimizing the introduction of pollutants into the environment or by their removal from contaminated media (Safa and Bhatti, 2011). Dyes are common constituents of effluents discharged by various industries, such as paper, textile, plastic, food and textile (Moghaddam *et al*., 2010). The presence of small amounts of dye in water is highly visible and undesirable. Dyeing wastewater discharged into aqueous screams may make them unacceptable for public consumption (Gao *et al*., 2007). Moreover, the discharging of untreated industrial effluents containing dyes decreases the penetration of sunlight into the water (Qiu *et al*., 2010) and the photosynthetic activity is affected significantly (Qiu *et al*., 2009). Due to carcinogenic, mutagenic, toxic and allergenic nature of dyes, their occurrence in the aquatic system is highly dangerous (Weng *et al*., 2013). Thus, it is desirable to remove dyes from industrial effluents.

Various researches have been performed to develop effective treatment technologies for wastewaters containing dyes, such as electro-coagulation, membrane filtration, electrochemical destruction, ion exchange, irradiation, advanced oxidation, ozonation, precipitation and adsorption involving the use of activated carbon (Laszlo, 1996; Gemea *et al*., 2003; López-Grimau and Gutiérrez, 2006).

The adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available. This process is becoming an attractive and promising technology because of its simplicity, ease of operation and handling, sludge free operation and regeneration capacity.

Activated carbon is the most popular adsorbent, which has been used with great success. However, activated carbon is expensive and its regeneration and reuse make it more costly. Consequently, many researchers have studied the feasibility of using low cost substances for the removal of various dyes and pollutants from wastewaters (Lakshmi *et al*., 2009; Othman *et al*., 2006; Prado *et al*., 2004; Srivastava *et al*., 2007).

Milling of rice crop produced rice husk as agriculture waste material having no commercial significance. Rice husks are commonly used as a low value energy resource, burned in the field, or discarded, which are unfavorable to the environment (Chen *et al*., 2011). In China, the annual rice husks production is approximately 40 million tons and much of this amount is not utilized because of the poor protein and high ash content of rice husks (Qu *et al*., 2010). Rice husk primarily consists of ash and organic matter, which comprises cellulose, hemicellulose and lignin (Liou and Wu, 2009). It also have a silica content of about 20%, which makes them valuable feed stock for the production of silica based materials that can be applied in separation, adsorption, catalysis and thermal insulation (Lin *et al*., 2013).

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In this study, the modified activated carbon from rice husk is used as the low cost material to absorb dye in aqueous solution. The effects of different process parameters like pH, initial dye concentration and contact time on the adsorption of dye are investigated. The kinetic data of adsorption studies are processed to understand the mechanism of Methyl Orange dye onto the modified activated carbon.

MATERIALS AND METHODS

Preparation of the adsorbents: The rice husk was obtained from a rice mill near Yancheng in Jiangsu Province of P.R. China. It was washed several times with distilled water to remove dust and other foreign particles. The cleaned rice husk was dried at 338 K for 12 h in order to achieve constant weight. Then they were grounded and sieved into a uniform size of 200 meshes. The 50 g of the rice husk was soaked stilly with 100 mL 5 mol/L $ZnCl_2$ and 0.4 mol/L $CuCl_2$ solution in 250 mL Erlenmeyer flasks for 24 h at room temperature. Then, it was dried again at 338 K for 12 h to constant weight and was carbonized at 873 K with N_2 in a muffle furnace for 120 min. The product of 200 mesh modified activated carbon from rice husk was thus obtained and then stored for later adsorption experiments.

Adsorption experiments: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 1.0 g of modified activated carbon and 100 mL of Methyl Orange dye with various initial concentrations (100, 200, 300, 400 and 500 mg/L) in aqueous solution. The flasks were placed in a shaker at a constant temperature of 308 K and 200 rpm. The samples were then filtered and the residual concentration of dye Methyl Orange was analyzed using a UV-1600 spectrophotometer at a wavelength corresponding to the maximum absorbance for dye Methyl Orange.

Analytical methods: The textural characteristics of modified activated carbon from rice husk including surface area, pore volume, pore size distribution were determined using standard N_2-adsorption techniques.

The surface physical morphology of modified activated carbon from rice husk 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 Methyl Orange was measured with a UV-1600 spectrophotometer at 465 nm.

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

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

where,

C_0 and C_t (mg/L)	= The initial and equilibrium liquid-phase concentrations of dye Methyl Orange, respectively
V(L)	= The solution volume
m(g)	= 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 error estimates given in the text and error bars in figures are standard deviation of means (mean±SD). All statistical significance was noted at $\alpha = 0.05$ unless otherwise noted.

RESULTS AND DISCUSSION

Characterization of modified activated carbon from rice husk: The scanning electron micrograph photograph of the modified activated carbon from rice husk is shown as Fig. 1. It shows uniform pore size distribution within the entire mesopore range.

Average particle size of the modified activated carbon from rice husk is 5 nm. The BET surface area is 1915 m^2/g. The total pore volume is 1.426 cm^3/g. This result can be attributed to the adsorption of dye in aqueous solution.

Effect of contact time: The contact time needed to reach adsorption equilibrium is necessary in studying the adsorption equilibrium and adsorption kinetics of the modified activated carbon from rice husk under simulated conditions.

Figure 2 shows the effect of contact time on the adsorption of dye Methyl Orange by the modified activated carbon from rice husk at a constant temperature of 308 K, 200 rpm, pH value of 6.0 and 200 mg/L of initial dye Methyl Orange concentration.

From Fig. 2, it showed that the adsorption of dye Methyl Orange increased with an increase in agitation time. This increase was fast in the beginning and then slow removal was observed till equilibrium. The equilibrium was established after 50 min.
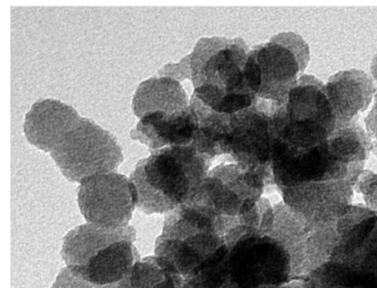

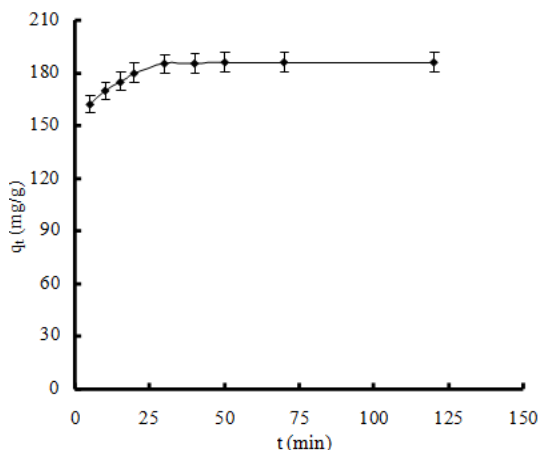Fig. 1: SEM image of the modified activated carbon from rice husk

Fig. 2: Effect of contact time on the adsorption of dye methyl orange by the modified activated carbon from rice husk

In the start, the adsorption rate was rapid due to adsorption of dye molecules on the upper surface of the adsorbent. Then it became slow due to slow passing of ye molecules into the inner structure of the adsorbent (Ahmad *et al*., 2007; Vadivelan and Kumar, 2005).

Effect of pH: The pH of the solution influences the properties of the modified activated carbon from rice husk, affects the adsorption mechanisms and dissociation of the dye molecules. The effects of pH on the adsorption of dye Methyl Orange on the modified

activated carbon from rice husk were studied in the pH ranging from 2 to 10 at a constant temperature of 308 K, 200 rpm, contact time of 50 min and 200 mg/L of initial dye Methyl Orange concentration. The experiment result was shown in Fig. 3.

From Fig. 3, it was shown that the adsorption capacity decreased with the increased pH value of solution.

Effect of initial dye concentration: The effect of initial dye Methyl Orange concentration on the adsorption capacity of the modified activated carbon from rice husk was determined in the initial dye concentration ranging from 100 to 500 mg/L at a constant temperature of 308 K, 200 rpm, contact time of 50 min and pH value of 6.0. The results were shown as Fig. 4.

From Fig. 4, it can be concluded that the adsorption capacity increased with the increased dye concentration. It may be the reasons that in the start, the dye molecules were adsorbed externally and adsorption rate increased rapidly. When the external surface became saturated, the dye molecules were adsorbed into the porous structure of the adsorbent (Safa and Bhatti, 2011; Çolak *et al*., 2009). The initial concentration of the dyes provides an important driving force to overcome the mass transfer resistance of all molecules between the aqueous and solid phases (Bulut *et al*., 2007).
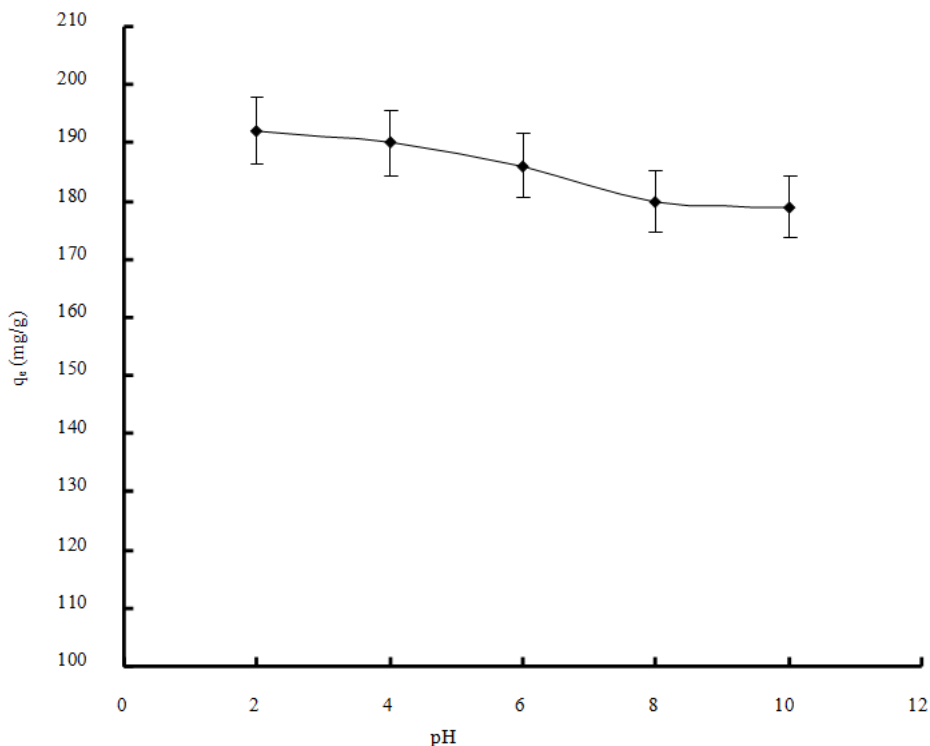

Fig. 3: Effect of pH in solution on the adsorption of dye methyl orange by the modified activated carbon from rice husk
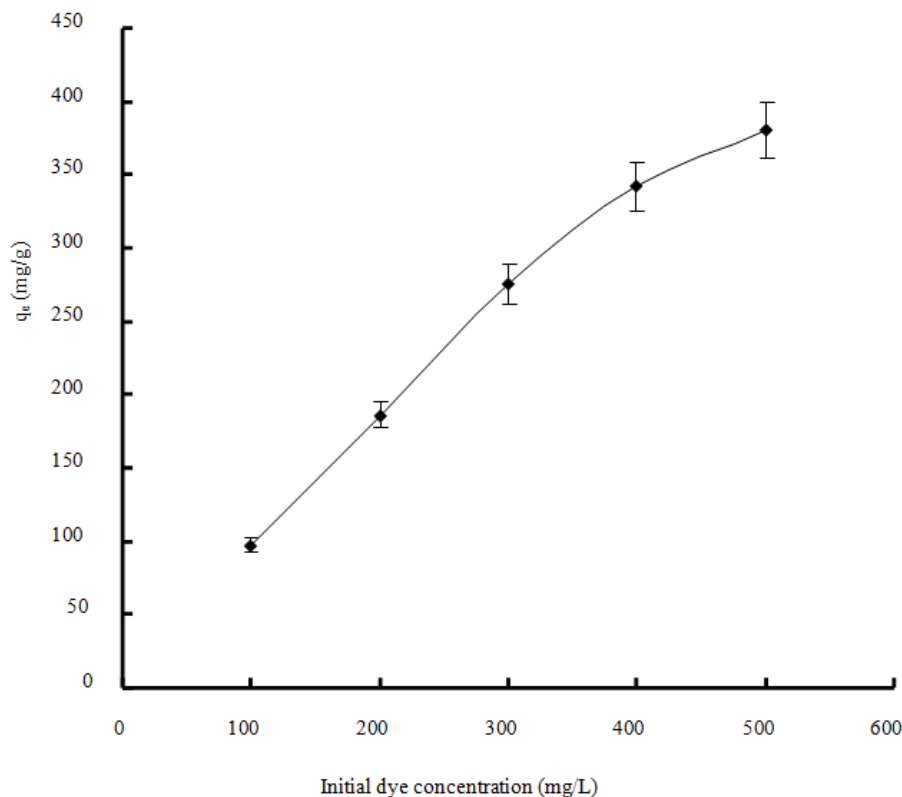
Fig. 4: Effect of initial dye concentration on the adsorption of dye methyl orange by the modified activated carbon from rice husk

Table 1: The kinetic parameters for the adsorption of dye methyl orange on the modified activated carbon from rice husk

Pseudo first-order		Pseudo second-order		Intra-particle diffusion	
k_1 (min^{-1})	R^2	k_2 (g/mg/min)	R^2	k_p (mg/g/min$^{0.5}$)	R^2
0.0635	0.9269	0.00916	0.9962	5.6102	0.8326

Adsorption kinetic models: Kinetic studies are necessary to optimize different operating conditions for the absorption. The adsorption kinetics of dye Methyl Orange on the modified activated carbon from rice husk were investigated by three different models, such as the pseudo first-order, pseudo second-order and intra-particle diffusion. The linear pseudo first-order model of Lagergren is given as follows (Bouhamed *et al.*, 2012):

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1 \times t}{2.303} \qquad (2)$$

where, Q_e and Q_t are the amounts of dye Methyl Orange absorbed onto the adsorbent at equilibrium and at t, respectively (mg/g). k_1 is the rate constant of first order adsorption (min^{-1}).

The pseudo second-order kinetic model can be expressed as follows (Ho and McKay, 1998):

$$\frac{t}{Q_t} = \frac{1}{k_2 \times Q_e^2} + \frac{t}{Q_e} \qquad (3)$$

where, k_2 is the rate constant of second-order adsorption (g/mg/min).

The intra-particle diffusion equation is written as follows (Weber and Morris, 1963):

$$Q_t = k_p \times t^{0.5} + C \qquad (4)$$

where, k_p (mg/g/min$^{0.5}$) is the intra-particle diffusion rate constant and C (mg/g) is a constant characterizing boundary layer thickness.

According to Eq. (2) to (4), the kinetic parameters of pseudo first-order kinetic model, pseudo-second-order kinetic model and the intra-particle diffusion kinetic model for adsorption of dye Methyl Orange on the modified activated carbon from rice husk were calculated. The experiment data came from Fig. 2. Table 1 is the kinetic parameters for adsorption of dye Methyl Orange on the modified activated carbon from rice husk.

From Table 1, it can be confirmed that the adsorption of Methyl Orange on the modified activated carbon from rice husk 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.

CONCLUSION

Adsorption studies for the removal of dye Methyl Orange from aqueous solutions have been carried out using the modified activated carbon prepared from rice husk. The experiment result shows that the modified activated carbon from rice husk is an effective adsorbent for the removal of dye Methyl Orange from aqueous solution. The adsorption rate is affected by the pH value of solution, contact time and initial dye Methyl Orange concentration. Moreover, the adsorption process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent.

ACKNOWLEDGMENT

REFERENCES

Ahmad, A.A., B.H. Hameed and N. Aziz, 2007. Adsorption of direct dye on palm ash: Kinetic and equilibrium modeling. J. Hazard. Mater., 141: 70-76.

Bouhamed, F., Z. Elouear and J. Bouzid, 2012. Adsorptive removal of copper(II) from aqueous solutions on activated carbon prepared from Tunisian date stones: Equilibrium, kinetics and thermodynamics. J. Taiwan Inst. Chem. E., 43: 741-749.

Bulut, Y., N. Gozubenli and H. Aydin, 2007. Equilibrium and kinetics studies for adsorption of directblue71 from aqueous solution by wheat shells. J. Hazard. Mater., 144: 300-306.

Chen, Y., Y.C. Zhu, Z.C. Wang, Y. Li, L.L. Wang, L.L. Ding, X.Y. Gao, Y.J. Ma and Y.P. Guo, 2011. Application studies of activated carbon derived from rice husks produced by chemical thermal process: A review. Adv. Colloid Interfac, 163: 39-52.

Çolak, F., N. Atar and A. Olgun, 2009. Biosorption of acidic dyes from aqueous solution by *Paenibacillus macerans*: Kinetic, thermodynamic and equilibrium studies. Chem. Eng. J., 150: 122-130.

Gao, B.Y., Y. Wang, Q.Y. Yue, J.C. Wei and Q. Li, 2007. Color removal from simulated dye water and actual textile wastewater using a composite coagulant prepared by polyferric chloride and polydimethyldially ammonium chloride. Sep. Purif. Technol., 54: 157-163.

Gemea, A.H., I.A. Mansour., R.G. El-Sharkawy and A.B. Zaki, 2003. Kinetics and mechanism of the heterogeneous catalyzed oxidative degradation of indigo carmine. J. Mol. Catal. A-Chem., 193: 109-120.

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

Lakshmi, U.R., V.C. Srivastava, I.D. Mall and D.H. Lataye, 2009. Rice husk ash as an effective adsorbent: Evaluation of adsorptive characteristics for Indigo Carmine dye. J. Environ. Manage., 90: 710-720.

Laszlo, J.A., 1996. Preparing an ion exchange resin from sugarcane bagasse to remove reactive dye from waste water. Text. Chem. Color., 28(5): 13-17.

Lin, L., S.R. Zhai, Z.Y. Xiao, Y. Song, Q.D. An and X.W. Song, 2013. Dye adsorption of mesoporous activated carbons produced form NaOH-pretreated rice husks. Bioresource Technol., 136: 437-443.

Liou, T.H. and S.J. Wu, 2009. Characteristics of microporous/mesoporous carbons prepared from rice husk under base and acid-treated conditions. J. Hazard. Mater., 171: 693-703.

López-Grimau, V. and M.C. Gutiérrez, 2006. Decolourisation of simulated reactive dye bath effluents by electrochemical oxidation assisted by UV light. Chemosphere, 62: 106-112.

Moghaddam, S.S., M.R.A. Moghaddam and M. Arami, 2010. Coagulation/flocculation process for dye removal using sludge from water treatment plant: Optimization through response surface methodology. J. Hazard. Mater., 175: 651-657.

Othman, I., R.M. Mohamed, I.A. Ibrahim and M.M. Mohamed, 2006. Synthesis and modification of ZSM-5 with manganese and lanthanum and their effects on decolorization of indigo carmine dye. Appl. Catal. A-Gen., 299: 95-102.

Prado, A.G.S., J.D. Torres, E.A. Faria and S.C.L. Dias, 2004. Comparative adsorption studies of indigo carmine dye on chitin and chitosan. J. Colloid Interf. Sci., 277(1): 43-47.

Qiu, M.Q., Q.L. Jian, D.L. Yu and K. Feng, 2010. Removal of methylene blue using acid and heat treatment of clinoptilolite. Desalin. Water Treat., 24: 61-66.

Qiu, M.Q., C. Qian, J. Xu, J.M. Wu and G.X. Wang, 2009. Studies on the adsorption of dyes into clinoptilolite. Desalination, 243: 286-292.

Qu, Y.N., Y.M. Tian, B. Zou, J. Zhang, Y.H. Zheng, L.L. Wang, Y. Li, C.G. Rong and Z.C. Wang, 2010. A novel mesoporous lignin/silica hybrid from rice husk produced by a sol-gel method. Bioresource Technol., 101: 8402-8405.

Safa, Y. and H.N. Bhatti, 2011. Kinetic and thermodynamic modeling for the removal of direct

red-31 and direct orange-26 dyes from aqueous solutions by rice husk. Desalination, 272: 313-322.

Srivastava, V.C., I.D. Mall and I.M. Mishra, 2007. Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash and rice husk ash. Chem. Eng. J., 132(1-3): 267-278.

Vadivelan, V. and K.V. Kumar, 2005. Equilibrium, kinetics, mechanism and process design for the sorption of methylene blue onto rice husk. J. Colloid Interf. Sci., 286: 90-100.

Weber, W.J. and J.C. Morris, 1963. Kinetics of adsorption on carbon from solution. J. Sanit. Eng. Div. Am. Soc. Civ. Eng., 89: 31-59.

Weng, C.H., Y.T. Lin, C.K. Chang and N. Liu, 2013. Decolourization of direct blue 15 by Fenton/ultrasonic process using a zero-valent iron aggregate catalyst. Ultrason. Sonochem., 20: 970-977.