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Tartaric Acid Modified Rice Hull as a Sorbent for Methylene Blue Removal

[1]Siew-Teng Ong, [2]Pei-Sin Keng, [1]Ai-Wen Chong, [3]Siew-Ling Lee and [4]Yung-Tse Hung
[1]Department of Chemical Science, Faculty of Science, University Tunku Abdul Rahman, Jalan University, Bandar Barat, 31900 Kampar, Perak, Malaysia
[2]Department of Pharmaceutical Chemistry, International Medical University, No. 126, Jalan 19/155B, Bukit Jalil, 57000 Kuala Lumpur, Malaysia
[3]Ibnu Sina Institute for Fundamental Science Studies, University Technology Malaysia, 81310 Skudai, Johor Malaysia
[4]Department of Civil and Environmental Engineering, Cleveland State University, Cleveland, Ohio USA

Abstract: Problem statement: Improper dye discharge from various industries such as textile, paper, cosmetic and plastics into receiving streams can be one of the sources towards water pollution. The release of these effluents not only causes various disruptions in the ecosystems, but also poses hazard effect as most of the dyes are highly toxic, mutagenic and carcinogenic in nature. **Approach:** To prepare an inexpensive and efficient sorbent by chemically modifying rice hull for the removal of Methylene Blue (MB) which is predominantly used in coloring acrylic fiber. Batch experiments were carried out for the removal of MB from aqueous solution by using Tartaric Acid Modified Rice Hull (TARH). Parameters studied include effect of pH, contact time, initial dye concentration and agitation rate and sorption isotherm. **Results:** From the results, the percentage uptake of MB increased with increasing contact time and agitation rate. Based on the linear regression correlation coefficient, R^2, the system under study is more appropriately described by the pseudo-second order model. Maximum sorption capacity calculated from the Langmuir model is 25.0 mg g^{-1} for MB. **Conclusion:** The study has shown the effectiveness of TARH in the removal of MB, a basic dye from synthetic solutions.

Key words: Adsorption, methylene blue, batch study, kinetics

INTRODUCTION

Chemical oxidation, chemical coagulation, biological treatment and photodegradation are some of the most commonly practiced processes for the removal of dyes from industrial wastewater. However, most of these methods suffer from some drawback such as high operational cost, generate secondary pollutants or unable to treat large quantities of wastes. Therefore, various biological and industrial by products have been investigated intensively for their ability to remove dye from aqueous solution as they can be obtained readily and are in great abundance. The utilization of these materials could also result in waste minimization.

Rice hull is generated as a waste during the first stage of rice milling, when rough rice or paddy rice is husked (husk is separated from the rest of the grain). It contains approximately 20% silica in combination with a large amount of the structural polymer, lignin. Ong *et al.* (2009) reported that modifying rice straw with ethylenediamine resulted in enhancement of Congo Red removal. Rice straw treated with citric acid showed similar sorption enhancement (Gong *et al.*, 2006). Rice hull which had a relatively low affinity for reactive dyes showed increased sorption capacity upon chemical modifications (Ong *et al.*, 2010).

Sorption of dyes onto various sorbents demonstrated that the sorption capacities are affected by operational parameters such as pH, contact time, initial dye concentration and particle size. In this study, we report the performance of tartaric acid modified rice hull under various conditions as a sorbent for Methylene Blue (MB).

MATERIALS AND METHODS

Sorbates: The cationic dye MB (Sigma-Aldrich) was used without further purification. Standard dye solution

Corresponding Author: Siew-Teng Ong, Department of Chemical Science, Faculty of Science, University Tunku Abdul Rahman, Jalan University, Bandar Barat, 31900 Kampar, Perak, Malaysia

of 1000 mg L^{-1} were prepared as stock solutions and subsequently diluted when necessary.

Sorbents: Rice hull was washed thoroughly with water to ensure the removal of dust and ash. It was then rinsed several times with distilled water and dried overnight in an oven at 50°C. The dried rice hull was then ground to pass through a 1 mm sieve and labeled as unmodified rice hull.

Modification process: About 5 g grinded rice hull was mixed with 35 m L of 1.2 M Tartaric Acid (TA). The mixture was stirred until homogenous and dried at 50°C overnight. The treated rice hull was subsequently washed with distilled water until neutral and dried overnight at 50°C. The final product was labeled as Tartaric Acid Modified Rice Hull (TARH).

Batch experiments: The batch studies were carried out at room temperature (25±2°C) by mixing 0.1 g of TARH with 20.0 mL MB solution in a centrifuge tube and shaken on an orbital shaker at 150 revolutions min^{-1} (rpm) for 5 h unless otherwise stated. The reaction mixture was then centrifuged at 3000 rpm for phase separation. All the batch experiments were carried out in duplicate and the results given are the means with a Relative Standard Deviation (RSD) of less than 5%. Control experiments without sorbent was carried out to ascertain that the sorption was by the sorbent and not the wall of the container. The percentage of dye uptake (percent uptake) was calculated using the following equation:

$$\text{Percent uptake} = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

Where:
C_o = The initial dye concentration (mg L^{-1})
C_t = The dye concentration (mg L^{-1}) at any time

To examine the effect of pH, the pH of the dye solution was adjusted to the values in the range of 3-9 using 0.1 M hydrochloric acid (HCl) and 0.1 M sodium chloride (NaOH) prior to the experiment. Effect of contact time was studied by shaking the sorption mixture at various predetermined time intervals and analyzes the dye concentration at the end of contact time. Sorption isotherms were obtained by varying the dye concentrations from 20-90 mg L^{-1}. The effect of agitation was carried out by varying the agitation rate from 50-200 rpm.

Techniques: The dye concentration was analyzed using a Perkin Elmer Lambda 35 UV-vis spectrophotometer. All measurements were made at the wavelength corresponding to maximum absorption for MB, λ_{max} = 665 nm. Dilutions were carried out when measurement exceeded the linearity of the calibration curve.

RESULTS

Figure 1 shows the comparative uptake of MB by unmodified and modified rice hull. The effect of pH on the uptake of MB by TARH is shown in Fig. 2. Time course experiments on MB sorption are shown in Fig. 3. Table 1 show the correlation coefficients based on pseudo first and second order kinetic models. Langmuir and Freundlich constant for MB sorption were included in Table 2. The variation of MB uptake with agitation rate is shown in Fig. 6.

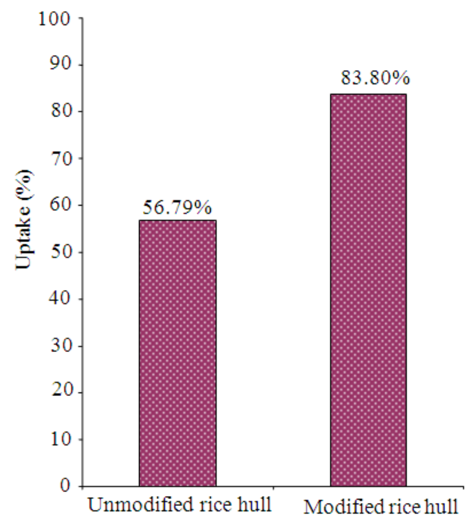

Fig. 1: Comparative studies of unmodified and modified rice hull

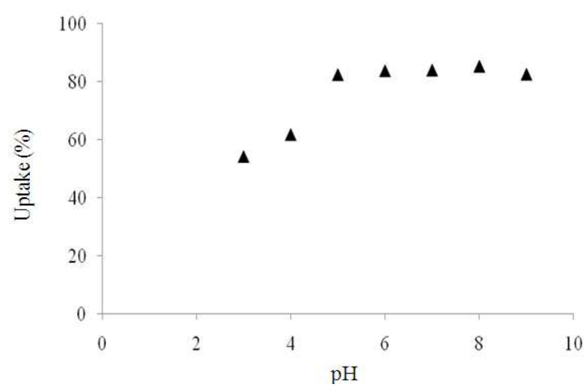

Fig. 2: Effect of pH on the sorption of MB by TARH

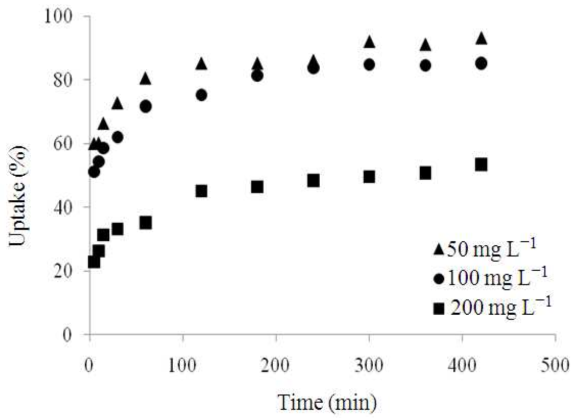

Fig. 3: Effect of initial dye concentrations and contact time on sorption of MB by TARH

Table 1: Pseudo-first and pseudo-second order kinetic correlation coefficients for different initial MB concentrations

Initial MB concentration (mg L^{-1})	Pseudo-first order kinetic (R^2)	Pseudo-first order kinetic (R^2)
50	0.9005	0.9989
100	0.8633	0.9992
200	0.6982	0.9997

Table 2: Langmuir and Freundlich isotherm model constants and correlation coefficients for sorption of MB by TARH

	Langmuir isotherm		Freundlich isotherm		
N* (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F	1 n^{-1}	R^2
24.63	0.1733	0.982	4.436	0.546	0.975

DISCUSSION

Comparison study: The comparative uptake of MB by unmodified and modified rice hull at the natural pH of the dye solutions is shown in Fig. 1. It is apparent that the sorption of MB was enhanced when TARH is being used as the sorbent. The presence of carboxyl groups in TARH is believed to be primarily responsible for the sorption of MB. Previous investigations have also postulated that the sorption of positively charged species is due to the presence of binding sites such as carboxyl and hydroxyl groups on the surface (Tang *et al*., 2003; Munaf and Zein, 1997; Wong *et al*., 2003).

Effect of pH: It is well known that pH of the solution is one of the prime factors influencing the sorption's efficiency of a system. Fig. 2 shows the MB sorption increase with increasing pH value. At low pH, the removal of MB was suppressed by H^+ ions that surrounded the surface of the sorbent hindering the approach of MB to the carboxylate groups present on the surface of TARH. The protonation of carboxylate groups would also reduce the MB sorption. With increasing pH, sorption became favorable due to the deprotonation of carboxyl groups (-COO), resulting in more sorption sites available for binding with MB. This phenomenon favors the sorption of positively charged dye due to electrostatic attraction (Namasivayam *et al*., 2001).

Effect of initial dye concentration and contact time: The rates of MB sorption at various initial concentrations (50, 100 and 200 mg L^{-1}) is shown in Fig. 3. The percentage of sorption decreased with increasing solution concentration while the amount of dye sorbed increased. The fast uptake at the beginning may be attributed to the rapid attachment of the dye molecules to the surface of the sorbent and the following slower sorption to intraparticle diffusion (Fawzi *et al*., 2003). In order to gain important insight on the reaction pathways and the sorption mechanisms, experimental data were fitted into the following equations (Langergren and Svenska, 1898; Ho and McKay, 1999; 2000):

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 (\text{pseudo} - \text{first order}) \quad (1)$$

and

$$t / q_t = 1 / h + t / q_e (\text{pseudo} - \text{second order}) \quad (2)$$

Where:

q_e = The amount of dyes sorbed at equilibrium (mg g^{-1})
q_t = The amount of dyes sorbed at time t (mg g^{-1})
k_1 = The rate constant of pseudo-first order sorption (1 min^{-1})
h ($k_2 q_e^2$) = The initial sorption rate (mg g^{-1} min^{-1})
k_2 = The rate constant of pseudo- second order kinetics (g mg^{-1} min^{-1})

It was found that application of pseudo-second order model provides better correlation of the experimental data than the pseudo-first order model for the different systems studied (Table 1). It thus appears that the system under study is more appropriately described by the pseudo- second order model which was based on the assumption that the rate limiting step may be chemical sorption or chemisorptions involving valency forces through sharing or exchange of electron between sorbent and sorbate (Ho and McKay 2000).

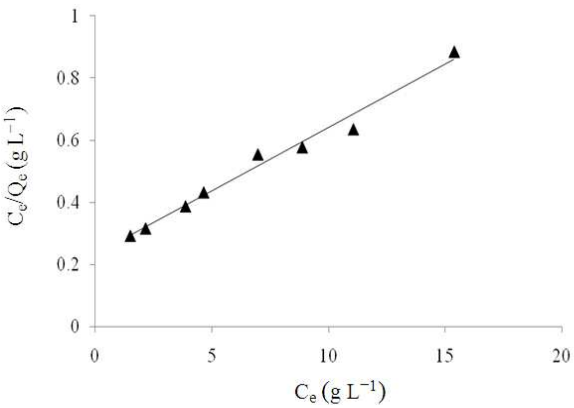

Fig. 4: Langmuir isotherm on sorption of MB by TARH

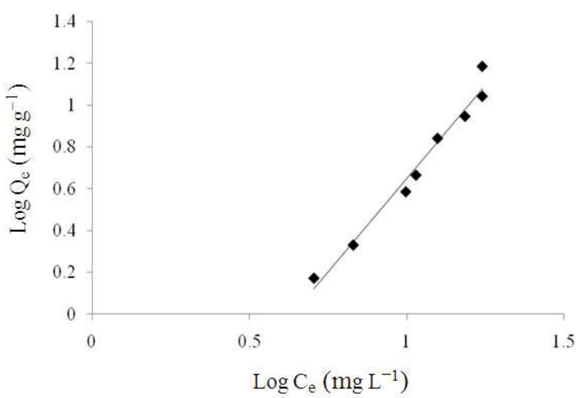

Fig. 5: Freundlich isotherm on sorption of MB by TARH

Sorption isotherm: The sorption data in the present study was fitted into Langmuir and Freundlich isotherm models. The linear plots of C_e/Q_e versus C_e and log Q_e versus log C_e are shown in Fig. 4 and 5 respectively. Table 2 gives the coefficients for the linearized forms of the isotherm models for sorption of MB on TARH. Although these two models are based on different assumptions: Langmuir model implies monolayer coverage and constant sorption energy while Freundlich model deals with physicochemical sorption on heterogeneous surfaces, both Langmuir and Freundlich models appear to provide reasonable fittings for the sorption data of MB on TARH.

Applicability of both isotherms to sorption of dyes by agricultural wastes, activated carbons prepared from wastes and treated spent bleaching earth have been reported previously (Ong *et al*., 2007; Malik, 2003; Lee *et al*., 1999).

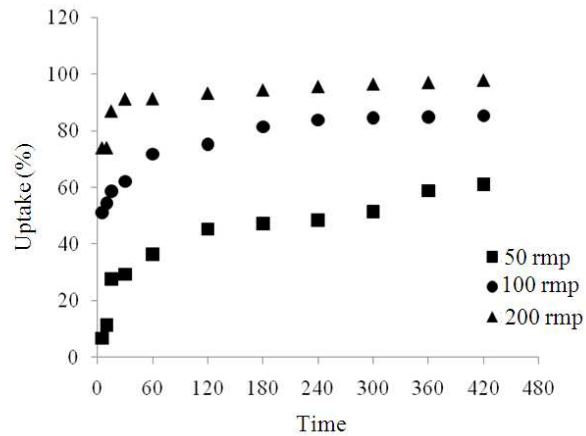

Fig. 6: Effect of agitation rate on sorption of MB by TARH

Effect of agitation rate: The experimental results obtained from a series of contact time studies for the sorption of MB onto TARH in which the degree of agitation was varied from 50-200 rpm are presented in the Fig. 6. For the first 5 min, the percentage uptake increased from 6.74-73.99% as the agitation rate increased from 50-200 rpm and gradually attained equilibrium after 3 h. The results suggests that increasing agitation rate decreases the film resistance to mass transfer surrounding the sorbent particles thus increasing sorption of dye molecules.

CONCLUSION

The study has shown the effectiveness of TARH in the removal of MB, a basic dye from synthetic solutions. The equilibrium data conform to both Langmuir and Freundlich isotherms. Analysis of data indicates that pseudo-second order kinetic model provided a better correlation of the experimental data than pseudo-first order model. As rice hull is readily available in great abundance in Malaysia, it can be considered as an attractive alternative to the more expensive technologies used in wastewater treatment containing dye.

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