I.A.U. Karaj Branch

Journal of Applied Chemical Research, 8, 4, 75-83 (2014)

Journal of Applied Chemical Research
www.jacr.kiau.ac.ir

Rice Bran as a Sorbent for Malonic Acid From Aqueous Solution

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Received 11 Jun 2014; Final version received 17 Sep. 2014

Abstract

The adsorption of malonic acid on the rice bran was studied under various conditions such as temperature, contact time, adsorbent dose and concentration of adsorbate. Batch adsorption experiments were conducted and the result showed that the adsorption was dependent on all these parameters. The adsorption process obeys the Langmuir and Freundlich adsorption isotherms. The adsorption capacity was found to be 1.24 mg/g. The Sorption of malonic acid on the rice bran was rapid during the first 20 minutes and the equilibrium was found to be attained within 50 minutes. Negative values of Gibb́ s free energy change (ΔG°), show that the adsorption was feasible and spontaneous and negative values of enthalpy change (ΔH°), confirm exothermic adsorption. Adsorption of malonic acid on the rice bran was characterized by Fourier transform infrared (FT-IR) spectroscopy.

Keywords: *Rice bran, Adsorption isotherms, Thermodynamics, Kinetics, FT-IR.*

Introduction

Through the physical and chemical processes of sorption, it is possible to remove a significant portion of the total substance concentration, thus lowering the effluent concentration to a level that will be less detrimental to public health and environmental quality [1, 2]. Several workers have reported on the potential use of agricultural by–products as good substrates for the removal of harmful substances from aqueous solutions and wastewaters. This process attempts to put into use the principle of using waste to treat waste and become even more efficient because these agricultural by–products are readily available and often pose waste disposal problems. Hence, they are

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available at little or no cost, since they are waste products. This makes the process of treating wastewaters with agricultural by–product adsorbents more cost effective than the use of conventional adsorbents like activated carbon. In addition, there is no need for complicated regeneration process when using agricultural by–products for wastewater treatment [3-12].

Rice bran is one of the important agricultural wastes. The outer coating of a rice grain is the rice bran. It is the brown layer between the hull and the white rice. The hull and bran layer is the discarded by product during the milling process to make white rice. The rice bran is a beneficial source of lots of lignin, cellulose and silica with adequate adsorptive capacity that can be use as a sorbent [13]. Dicarboxylic acids are important compounds in biochemistry, nature and industry. Malonic acid is one of the derivatives of dicarboxylic acids by m.p of 136^{o}C and density of 1.619 g.cm^{-3}. It is used as a chelating agent [14] and potential ragent in decontamination processes for Ni-rich alloy surface [15]. Malonic acid accumulates in the pigments of some flowers [16] and fruits [17] and can be regarded as a reliable indicator of orange fruit senses [18]. Removal methods of organic compounds in industrial discharges may be traditionally divided into three main categories: physical, chemical, and biological processes. Among them, physical adsorption is generally considered to be the most efficient method for quickly lowering the concentration of dissolved organic compounds in the solution. Thus, the main objectives of this work were to characterize the physical properties of rice bran to examine its adsorption behaviors of removing malonic acid from aqueous solution. Batch experiments were conducted to investigate the effects of adsorbent dosage, absorbate concentration, contact time and temperature on the adsorption of malonic acid on the rice bran. Lngmuir and Freundlich isotherm models were used to illustrate the experimental isotherms models and isotherms constants.

Experimental

Materials

Malonic acid, sodium hydroxide and phenolphthalein were purchased from Merck. Rice bran was obtained from the Iranian rice called Hashemi in Roudsar city of Gilan.

Preparation of Adsorbent

Before the process of adsorption characterization the rice bran must be prepared. Thus, the amounts which are needed was mixed with distilled water by stirrer-magnet for 1 hr. Then it was washed with distilled water until a pH of 7.0 was attained, dried in an oven at 50^{o}C for 24 hr and stored in the desiccator. It was further crushed, grained and sieved to mesh number 35 (average particle diameter <0.5 mm) in accordance with the American Society for Testing and Materials (ASTM).

Adsorption Studies

All experiments were carried out by the samples containing 50 cc of different initial concentration (0.01- 0.05 M) of Malonic acid in the range of 28-60°C temperature. 4 g of the adsorbent was transferred into various 250 ml Erlenmeyer flask and malonic acid solution by fixed concentration was added and mixed using a stirrer- magnet for 1 hr. Then the solution was filtered its concentration was determined by titration with 0.04 M solution of NaOH. The amount of equilibrium adsorption, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C0 and Ce (mg/l) are the liquid-phase concentrations of malonic acid at initial and equilibrium, respectively. V (l) is the volume of the solution and W (g) is the the mass of dry adsorbent used [19].

Results and Discussion

The mentioned process was controlled by several operational parameters. In order to enhance the process performances, the in fluencies of these parameters were studied as follows:

Effect of Adsorbate Concentration

Several stock solutions with concentration (0.01-0.05 M) were prepared. Each solution was added to 4.0 g of the adsorbent in different 250 ml flasks and agitated using a mechanical agitator for 1 hr each. At the end of the time, the contents of the flasks were filtered and analyzed. The results are shown in figure 1. It was found that the percentage malonic acid removal decreased with increase in initial malonic acid concentration. This can be attributed to the greater number of available sites on the adsorbent for the adsorption of malonic acid with lower concentration.

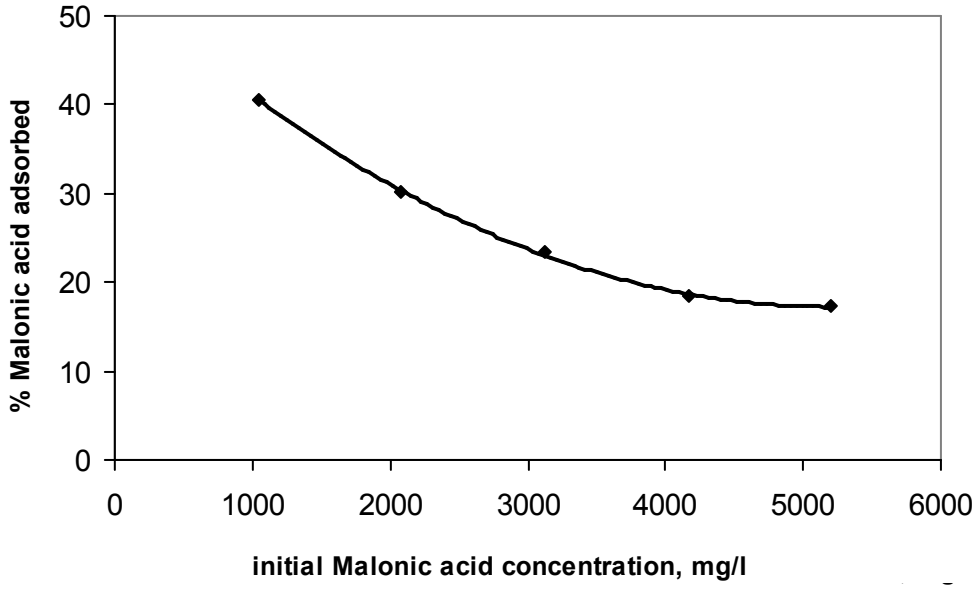

Figure 1. Influence of initial malonic acid concentration on adsorption of malonic acid on rice bran.

Effect of Adsorbent dose

50 ml each of the malonic acid solutions were added to various amount of the adsorbent (0.2-7.0 g) in different 250 ml flasks, flasks were agitated for 1hr on a mechanical stirrer. The content of the flask was filtered and analyzed. The results are presented in figure 2. The maximum removal of malonic acid was obtained in the adsorbent dose of 90 g/l. It is expected that adsorption of malonic acid increases rapidly with increase in the amount of adsorbent due to greater availability of the surface area at higher concentration of the adsorbent. Therefore competition for bonding sites between molecules of the adsorbate should decrease with increase in dose of the adsorbent [20, 21]. Further increase of adsorbent dose did not cause any significant change because equilibrium was achieved between solution and solid phase.

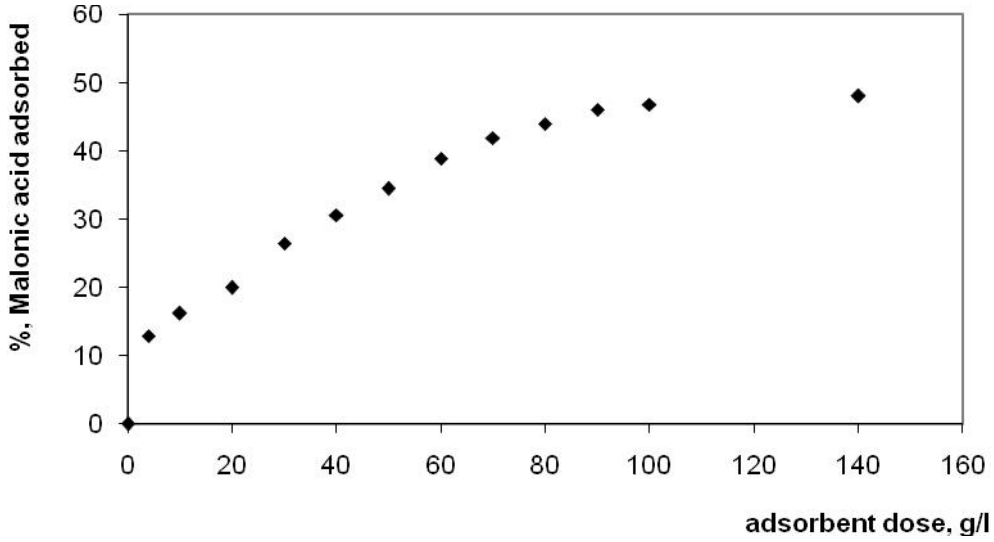

Figure 2. Influence of adsorbent dose on adsorption of malonic acid on rice bran.

Effect of Contact Time

50 ml each of stock solution of malonic acid was transferred into different 250 cm^3 Erlenmeyer flask. 4.0 g each of the adsorbent was weighed into the different labeled flasks and agitated in a shaker for different contact times (3, 5, 10, 20 and 60 minutes). After each agitated time, the content of each flask was filtered. The equilibrium concentration of the malonic acid was determined. The results obtained are shown in Figure 3. As the contact time was increased, the amount of malonic acid removed also increased. From figure 3 the plot reveals that the rate of percent malonic acid removal is higher at the beginning. This is probably due to larger surface area of the adsorbent being available at beginning for the adsorption of malonic acid. In according to figure 3, the observable time for maximum adsorption is between 50-60 minutes.

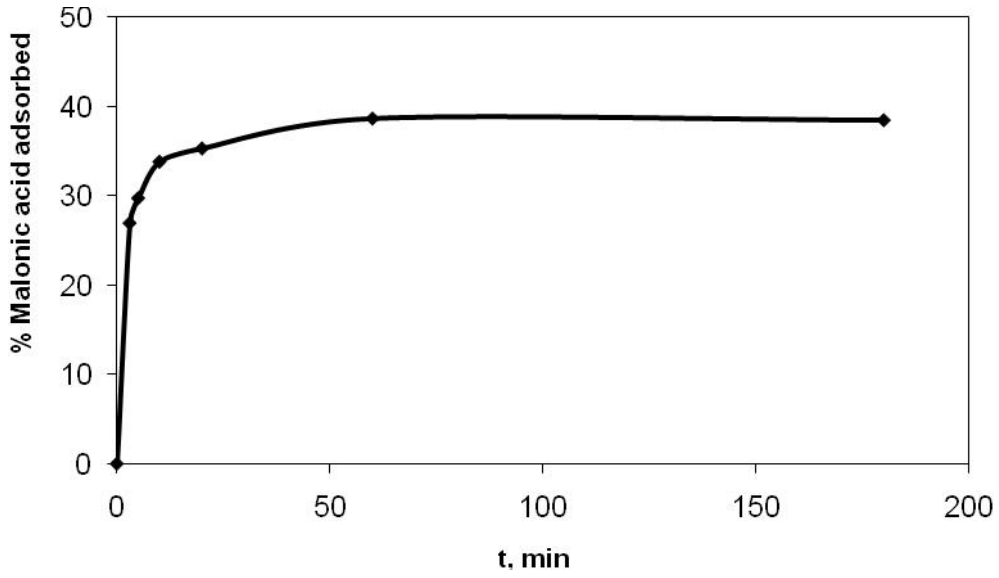

Figure 3. Influence of contact time on adsorption of malonic acid on rice bran.

Effect of Temperature

50 ml each of stock solution was transferred into various 250 cm^3 flask containing 4.0 g of the adsorbent, labeled for different temperatures 28, 45, 50, 60^oC respectively. After the equilibrium time the content of the each of the flask was removed, filtered and analyzed. The results obtained are shown in figure 4. The data showed that with increasing temperature the amount of malonic acid adsorbed on the surface of the adsorbent decreases. The attractive forces between the adsorbent and the adsorbate ion may have been weakened making the adsorption to decrease. At high temperature, the thickness of the boundary layer is expected to decrease due to the increased tendency of the ions to escape from the surface of the adsorbent to the solution phase.

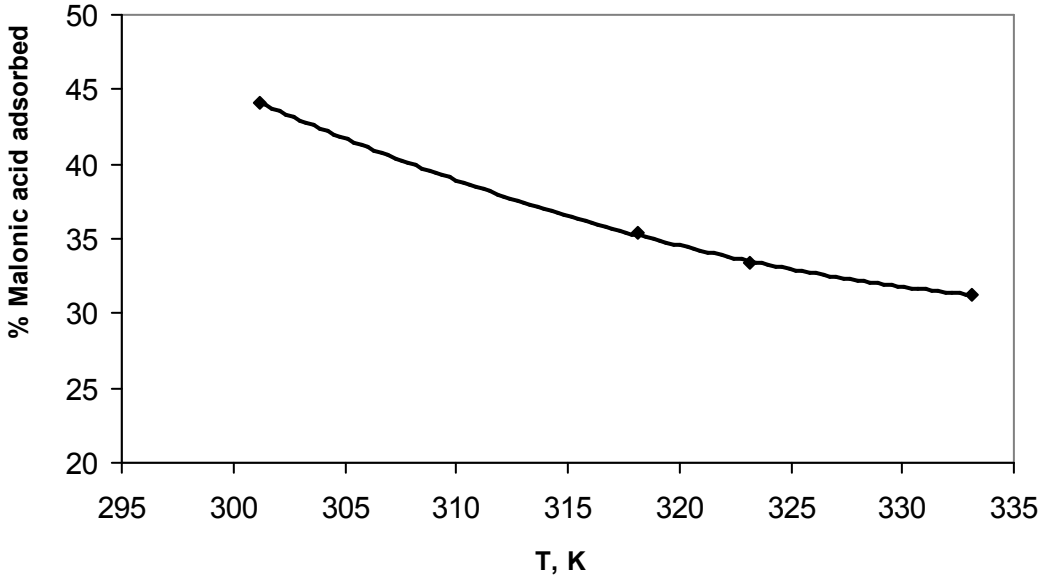

Figure 4. Influence of temperature on adsorption of malonic acid on rice bran.

Adsorption isotherms

The equilibrium adsorption isotherm is one of the most important data to understand the mechanism of the adsorption systems. In this manner, the Langmuir, the Freundlich isotherm equations were used to interpret the experimental data. Langmuir isotherm theory is based on the assumption that adsorption on a homogeneous surface, i.e., the surface consists of identical sites, equally available for adsorption and with equal energies of adsorption and that the adsorbent is saturated after one layer of adsorbate molecules forms onto surface [22]. The linearized form of the Langmuir adsorption isotherm equation is:

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

The Langmuir constants, which are qm and KL values, can be calculated from the plot C_e/q_e versus C_e. The maximum adsorption capacity was determined as 1.24 mg/g at 28°C. Isotherm models constants and correlation coefficients for malonic acid adsorption on rice bran listed in Table 1.

The linearized Freundlich isotherm equation that corresponds to the adsorption on heterogeneous surface is given as:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (3)$$

The Freundlich isotherm constants K_F and 1/n can be calculated from the plot of $\ln q_e$ versus $\ln C_e$. The slope (1/n) measures the surface heterogeneity. Heterogeneity becomes more prevalent as 1/n gets closer to zero. The Langmuir and Freundlich adsorption constants calculated from the corresponding isotherms with the correlation coefficients are presented in Table 1. The correlation coefficient shows that the adsorption process could be described by the both Langmuir and Freundlich model equation.

Table 1. Isotherm Models Constants and Correlation Coefficients for malonic acid adsorption on rice bran.

	Freundlich			Langmuir		
T (K)	K_F, ((mg/g)(l/mg)$^{1/n}$)	n	R^2	K_L (l/mg)	q_m (mg/g)	R^2
301.15	0.177	3.33	0.98	0.0011	2.61	0.98
318.15	0.105	2.96	0.98	0.00085	2.24	0.98
323.15	0.094	2.91	0.98	0.0008	2.12	0.99
333.15	0.082	2.85	0.98	0.00072	2.07	0.98

Thermodynamic studies

Thermodynamic parameters such as change in Gibb s free energy (ΔG°), enthalpy (ΔH°), entropy (ΔS°) were determinated using the following equations [23, 24]:

$$\ln\left(q_e/C_e\right) = \Delta S^\circ/R - \Delta H^\circ/RT \qquad (4)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (5)$$

The values of ΔH° and ΔS° were determined from the slopes $\left(-\Delta H^\circ/R\right)$ and the intercepts

$(\Delta S^{\circ}/R)$ of the plots of $\ln\left(q_e/C_e\right)$ vs. 1/T. The values of thermodynamic parameters are presented in Table 2. The negative values of ΔG° indicate that the adsorption process is feasible and spontaneous in nature. The negative value of ΔH° suggest the exothermic nature and the negative value of ΔS° described the randomness at the adsorbent-solution interface decreased during the adsorption.

Table 2. Thermodynamic parameters for malonic acid adsorption on rice bran.

		ΔG° (kJ/mol)			
ΔS°, (kJ/mol.K^{-1})	ΔH° (kJ/mol)	301.15	318.15	323.15	333.15
-0.022	-11.16	-4.6	-4.2	-4.1	-3.9

Sorption kinetics

Sorption kinetics was studied for adsorption of malonic acid on rice bran of initial concentration 0.01 mol/l. The rate constant of adsorption was determined from the pseudo-second order rate expression [25]:

$$t/q_t = 1/k_2 q_e^{\,2} + t/q_e \quad (6)$$

Where k_2 is the rate constant of adsorption (g/mg/min) and q_t is the amount of malonic acid adsorbed at time t (mg/g) respectively. The values of k_2 and q_e^{cal} were calculated from the intercepts ($1/k_2\ qe^2$) and the slopes ($1/q_e$) of the plots of t/q_e vs. t. respectively, reported in Table. 3. The results show that the values of q_e^{cal} and q_e^{exp} are almost equal and regression correlation coefficient (R^2) is close to unity which confirms that adsorption of malonic acid on rice bran follows pseudo-second order kinetic model.

Table 3. Kinetic parameters for malonic acid adsorption on rice bran.

Pseudo – second order			
q_e^{exp} (mg/g)	q_e^{cal} (mg/g)	k_2 (g/mg.min)	R^2
1.24	1.11	0.5	0.99

FT-IR Experiments

FT-IR spectrum of the reference compounds was obtained by mixing it with KBr powder (5% in weight). The analysis of the rice bran loaded particles by FT-IR (in Figure 5., we showed the case of the malonic acid) shows the appearance of the band at 1650 cm^{-1} clearly associated with the carboxylate bands. Therefore, the results based on infrared spectroscopy suggest the formation of a dicarboxylate film on the rice bran surface. The carboxylate films have a quick kinetic of formation (a few minutes).

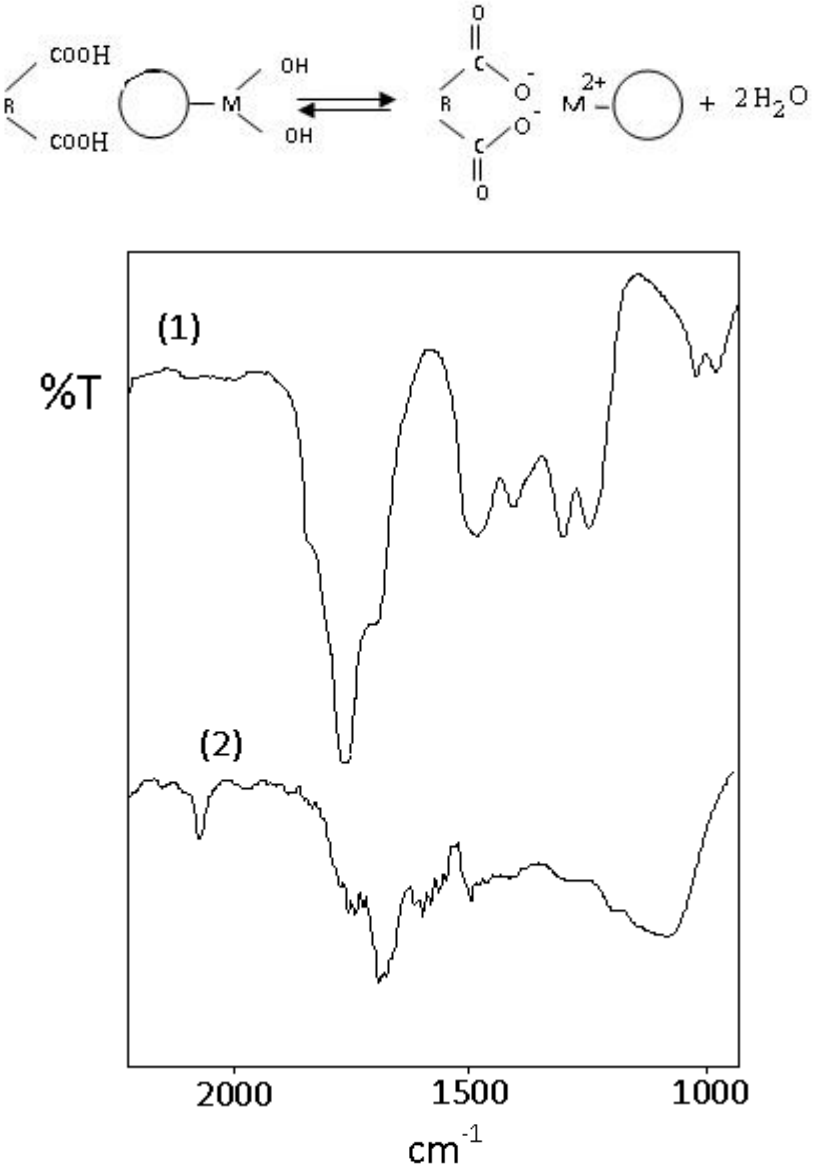

Figure 5. FT-IR spectra of malonic acid in KBr (1) and acid adsorbed on rice bran by direct addition in KBr (2).

Conclusion

Malonic acid is significantly adsorbed on rice bran. The study indicates that removal of malonic acid from aqueous solutions depends on the solution adsorbent dose, contact time and initial malonic acid concentration. The adsorption process obeys both Langmuir and Freundlich adsorption isotherms. The thermodynamic study shows that the adsorption process was exothermic and spontaneous in nature. The adsorption of malonic acid on the rice bran followed reversible second-order rate kinetics. The adsorption is relatively quick and the process is very efficient especially for water containing low concentrations of malonic acid. The results based on Fourier

transform infrared spectroscopy suggest the formation of a dicarboxylate film on the rice bran surface. Dicarboxylate films have a quick kinetic of formation (a few minutes).

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