

STUDY OF THE EFFECTIVE PARAMETERS ON THE ADSORPTION OF MALONIC ACID FROM AQUEOUS SOLUTIONS BY RICE (*Oryza sativa* L.) BRAN

Vida JODAIAN¹, Narges SAMADANI LANGEROODI², Sepideh MEHRANI³,
Behzad SANI⁴

¹Islamic Azad University, Islamshahr Branch, Department of Chemistry, Tehran, Iran

^{2,3}Golestan University, Science Faculty, Chemistry Department, Gorgan, Iran

⁴Islamic Azad University, Shahr-e-Qods Branch, Department of Agriculture, Tehran, Iran

Corresponding author email: hvidajodaian@yahoo.co.nz

Abstract

*The adsorption of malonic acid on the rice (*Oryza sativa* L.) bran was studied under various conditions such as temperature, contact time, adsorbent dose and concentration of adsorbate. In this case Rice bran is one of the important agricultural wastes which in this study is used from it as adsorbent. The rice bran is a beneficial source of lots of lignin, cellulose and silica with adequate adsorptive capacity that can be uses as a sorbent. In this research Batch adsorption experiments were conducted and the results showed that the adsorption was dependent on all these parameters. 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 mines.*

Keywords: rice bran, adsorption isotherms, malonic acid, various conditions.

INTRODUCTION

Through the physical and chemical processes of sorption, it is possible to remove a significant portion of the total metal concentration, thus lowering the effluent concentration to a level that will be less detrimental to public health and environmental quality (Kumar, 2010). Several workers have reported on the potential use of agricultural by-products as good substrates for the removal of metal ions 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 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 (Dabrowski, 2000; Kocaba, 2007; Al-Anber, 2008; Oei, 2009; Hsieh, 2000; Ho,

2002; Demirba, 2004; Tarley, 2004). Rice bran is one of the important agricultural wastes. In this study is used from it as adsorbent. 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 byproduct 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 (Tarley, 2004). 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°C and density of 1.619 g.cm⁻³. It is used as a chelating agent (Thongtem, 2005) and potential reagent in decontamination processes for Ni-rich alloy surface (Thongtem, 2005). Malonic acid accumulates in the pigments of some flowers (Saito, 2008) and fruits (Muchuweti, 2005) and can be regarded as a reliable indicator of orange fruit senses (Sasson, 1976). 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, adsorbate concentration, contact time and temperature on the adsorption of malonic acid on the rice bran.

MATERIALS AND METHODS

All the chemicals were purchased from Merck. Before the process of adsorption characterization the rice bran must be prepared. Thus, the amounts which are needed were 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, derived in an oven at 50°C for 24 hr and stored in the desiccators. It was further crushed grinded and sieved to average size <0.5 mm in accordance with the American Society for Testing and Materials (ASTM). All experiments were carried out by samples containing 50 cc of different initial concentration (0.01- 0.05 M) of Malonic acid in the range of 28-60°C temperature. Four 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 and 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:

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

where C_0 and C_e (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 (Brown, 2000).

RESULTS AND DISCUSSIONS

The mentioned process was controlled by several operational parameters. In order to

enhance the process performances, the influences of these parameters were studied as follows:

Effect of Adsorbate Concentration

Several stock solutions (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.

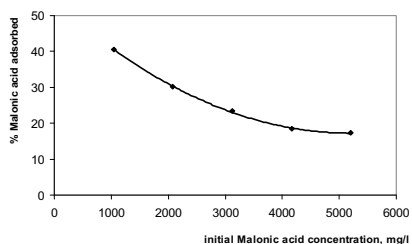


Figure 1. Influence of initial malonic acid concentration on adsorption of malonic acid on rice bran

It was found that the percentage of malonic acid removal decreased with increase in initial malonic acid concentration. This can be explained by the fact that more adsorption sites were being covered as the malonic acid concentration increases. For all these runs, initial malonic acid concentration was fixed as 100 mg/l.

Effect of Adsorbent dose

Fifty 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 an increase in the dosage of adsorbent should yield a corresponding increase in the amount of malonic acid adsorbed on the surface of the adsorbent since there will be more sites for the adsorbate to be adsorbed. Therefore competition for bonding sites between molecules of the adsorbate should decrease with increase in dose of the adsorbent (Wan Ngah, 2008; Bulut and Aydin, 2006). From Figure 2 this trend was

inconsistent and therefore suggests that the use of rice bran as adsorbent partly depend on its dose in aqueous solution. Further increase of adsorbent dose did not cause any significant change because equilibrium was achieved between solution and solid phase.

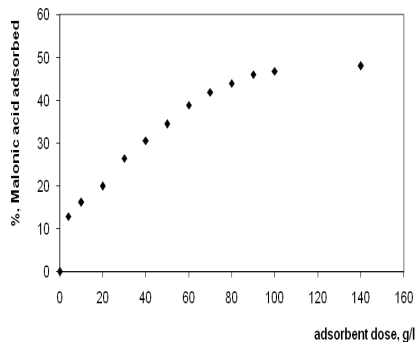


Figure 2. Influence of adsorbent dose on adsorption of malonic acid on rice bran

Effect of Contact Time

Fifty ml each of stock solution of malonic acid was transferred into different 250 cm³ Erlenmeyer flask, corked and labeled. Four 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 metal in each of the filtrate was determined. The results obtained are shown in Figure 3.

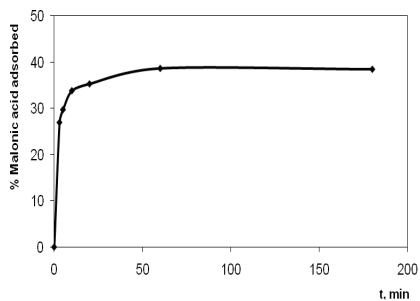


Figure 3. Influence of contact time on adsorption of malonic acid on rice bran

As the contact time was increased, the amount of malonic acid removed also increased. The data showed malonic acid removal from aqueous solution increases initially until equilibrium was attained and then was

constant. In according to Figure 3, the observable time for maximum adsorption is between 50-60 minutes.

Effect of Temperature

Fifty ml each of stock solution was transferred into various 250 cm³ flask containing 4.0g each of the adsorbent, corked and labeled for different temperatures 28, 45, 50, 60°C respectively. The mixture was heated and shaken to the appropriate temperature in a water bath. At the right temperature, the content of the each of the flask was removed, filtered and analyzed. The results obtained are shown in Figure 4.

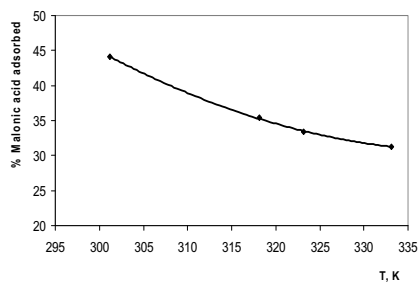


Figure 4. Influence of temperature on adsorption of malonic acid on rice bran

The effect of temperature on the removal of malonic acid from aqueous solution was investigated by varying the temperature of adsorption between 28°C and 60°C (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 hence there is bound to be weak adsorption interactions between the adsorbent and the adsorbate.

CONCLUSIONS

The results showed that the adsorption was dependent on all related parameters. The adsorption capacity was found to be 1.24 mg/g. The sorption of malonic acid on the rice (*Oryza*

sativa L.) bran was rapid during the first 20 minutes and the equilibrium was found to be attained within 50 minutes.

ACKNOWLEDGMENTS

This paper was supported by the Islamshahr Branch, Islamic Azad University (IAU) and Chemistry Department of Golestan University, Gorgan.

REFERENCES

- Al-Anber M., Al-Anber Z.A., 2008. Utilization of natural zeolite as ion-exchange and sorbent material in the removal of iron. *Desalination*, 225 (1-3), p. 70.
- Brown P., Jefcoat I.A., 2000. Evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution. *Advances Environ Res*, 4, p. 19.
- Bulut Y., Aydin H.A., 2006. A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination*, 194 (1-3), p. 259.
- Dabrowski A., 2000. Adsorption - from theory to practice. *Advances in colloid and interface science*. 93, p. 135.
- Demirbas A., 2004. Adsorption of lead and cadmium ions in aqueous solutions onto modified lignin from alkali glycerol delignification. *Hazard J. Mater*, 109, p. 221.
- Garcia D., Bruyere V.I.E., Bordoni Olmedo R.A.M., Morando P.J., 2011. Malonic acid: A potential reagent in decontamination processes for Ni-rich alloy surfaces. *J. Nucl. Mater*, 412 (1), p. 72.
- Ho Y.S., Huang C.T., Huang H.W., 2002. Equilibrium sorption isotherm for metal ions on tree fern. *Proc. Biochem*, 37, p. 1421.
- Hsieh C.T., Teng H., 2000. Influence of mesopore volume and adsorbate size on adsorption capacities of activated carbons in aqueous solutions. *H. Carbon* vol. 38 issue 6 2000, p. 863-869.
- Kocaba S., Orhan Y., Akyuz T., 2007. Kinetics and equilibrium studies of heavy metal ions removal by use of natural zeolite. *Desalination*, 214(1-3), p. 1.
- Kumar S.P., Ramakrishnan K., Gayathri R., 2010. Removal of nickel (II) from aqueous solutions by ceralite IR 120 cationic exchange. *J. Eng. Sci. Technol*, 5, p. 2.
- Muchuweti M., Zenda G., Ndhlala A.R., Kasiyamhuru A., 2005. Sugars, organic acid and phenolic compounds of *Ziziphus mauritiana* fruit. *Eur Food Res Technol*, 221, p. 570.
- Oei B.C., Ibrahim S., Wang S., Ang H.M., 2009. Surfactant modified barley straw for removal of acid and reactive dyes from aqueous solution. *Bioresour. Technol.*, 100 (18), p. 4292.
- Saito N., Tatsuzawa F., 2008. Tetra-acylated cyanidin 3-sophoroside-5-glucosides from the flowers of *Iberis umbellata* L. (Cruciferae). *Phytochemistry*, 69 (18), p. 3139.
- Sasson A., Monselise S.P., 1976. Malonic acid, a proposed indicator of orange fruit senescence. *Experientia*, 32, p. 1116.
- Tarley C.R.T., Arruda M.A.Z., 2004. Biosorption of heavy metals using rice milling byproducts characterisation and application for removal of metals from aqueous effluents. *Chemosphere*, 54, p. 987.
- Thongtem T., Thongtem S., 2005. Synthesis of $\text{Li}_{1-x}\text{Ni}_x\text{O}_2$ using malonic acid as a chelating agent. *Ceram. Int*, 31 (2), p. 241.
- Wan Ngah W.S., 2008. Adsorption of copper on rubber (*Hevea brasiliensis*) leaf powder: Kinetic, equilibrium and thermodynamic studies. *Biochem Eng J*, 39 (2), p. 521.