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Rice husk as a Biosorbent for Antibiotic Metronidazole Removal: Isotherm Studies and Model validation

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Abstract : The present study is on adsorption of Metronidazole (MNZ) by Rice husk. It uses batch adsorption techniques. The influence of contact time, initial concentration, dosage of adsorbent and temperature were investigated. The equilibrium time was found to be 90 minutes at all concentration. The percent removal of the MNZ was increased with increase in temperature and indicated that MNZ adsorption process was endothermic and spontaneous.. Adsorption performance of benign adsorbents was applied to Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm which afford important information on the surface properties of the adsorbent and its affinity for adsorbate. Data correctly fits Langmuir isotherm than Freundlich, Temkin and Dubinin-Radushkevich isotherm proving monolayer and homogenous surface of adsorption with R^2 equal to 0.998. The results indicate that the modified Rice husk is a promising low cost technology adsorbent for the removal of antibiotics.
Keywords: Adsorption, Metronidazole, Isotherm, Rice husk.

Introduction:

The last decades, the presence of emerging contaminants in different types of water appeared as a new environmental threat which needs to be faced by several governments around the word[1-4]. Antibiotics have been at widely used worldwide especially in developing countriesto for treat diseases and to protect the health of humans and animals(5). Antibiotic contamination of water ecological environment has been recognized as one of the common emerging issues worldwide[5,6]. Discharge of the aquatic environment from livestock and pharmaceutical wastewater containing antibiotics exhibits detrimental effects risk to aquatic ecosystem and human[7]. Recently, antibiotics also have been detected in the effluent of sewage treatment plants and the source water of water plant[8].

In recent years, there has been an increasinginterest to the treatment of pollution generated by drug residues, including antibiotics[9,10]. Numerous methods are being used to remove antibiotics: biological treatment, chlorination, advanced oxidation technology, electrochemical treatment, adsorption, the membrane process, and the ultrasonic cavitation effect method[11,12]. However, these treatment processes present a number of drawbacks in terms of low efficiency, usually produce large amounts of sludge and cannot effectively be used to treat a wide[13,14]. Among these methods, the adsorption method has the advantages of easy operation, low cost, high efficiency, and no risk of highly toxic byproducts[15,16].

The activated carbons (ACs) are adsorbents containing high surface area and an appreciable amount of active sites available for adsorption, i.e. which have sufficient affinity to retain certain pollutants[17,18]. Due to these characteristics they are commonly employed in various processes for undesirable chemicals removal[19,20]. However, the removal effectiveness depends on its chemical and physical properties, adsorbate concentration, pH, temperature, and the presence of other species in the solution[21,22]. Although efficient, the wastewater treatment by activated carbons is considered expensive due to its high production costs and restricted application[23,24]. Therefore, many researches have been performed with the aim of obtaining low cost ACs from renewable sources, mainly from agricultural waste[25,26]. Thus, a wide variety of agricultural and industrial waste are frequently used as ACs precursors, such as azolla filiculides, olive husks, buriti shells, lemna minor, plum kernels, fir wood, pistachio nut shells, olive stones, flamboyant pods[27,28]. Agricultural waste Such as Rice husk can prove to be better alternative for sorption process, because it is freely available in countries like Iran (Particularly In the area North Iran) where agriculture is of the major businesses. The aim of the present study was to investigate the MNZ removal from aqueous solution by Rice husk biomass under different experimental conditions in order to optimize the efficiency of the adsorption process. Equilibrium isotherm models were conducted for a better understanding of the adsorption process.

Experimental:

Preparation of Adsorbent

In this study, the Rice husk was used as low cost natural or agricultural wastes for MNZ removal from aqueous solutions. The stalks of Rice husk were collected from research farm of Tabriz agricultural school. The collected Rice husk were washed with de ionised water several times to remove dirt and color. The washing process was continued till the wash water contains no dirt. The biomass were then treated with 0.1M H_2SO_4 for 2 h followed by the washing with distilled water and then was oven dried at 105 °C for 3 h. The washed powders were then completely dried in oven for 3 hr. The dried powders were then ground into small size of powder using blender. In the present study the biomass in the range of 20 mesh particle size were directly used as adsorbent.

MNZ ($C_6H_9N_3O_3$; 99% chemical reagent) was supplied by the Merck Company. Standard MNZ was supplied by the National Institute for the Control of Pharmaceutical and Biological Products and was used for calibration.

Biosorption experiments were performed at room temperature (27±2 °C) in a rotary shaker at 180 rpm using 250 mL Erlenmeyer flasks containing 100 mL of different MNZ concentrations. After 1.5 hr of contact (according to the preliminary sorption dynamics tests), with 0.3 g Rice husk Powder, equilibrium was reached and the reaction mixture was centrifuged for 5 min. The MNZ content in the supernatant was determined using UV Spectrophotometer after filtering the adsorbent with 0.45 µm filter paper. The amount of MNZ adsorbed by Rice husk Powder was calculated from the differences between MNZ quantities added to the adsorbent and MNZ content of the supernatant using the following equation[29,30]:

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

Where q_e is the MNZ uptake (mg/g); C_0 and C_e the initial and final MNZ concentrations in the solution (mg/L), respectively; V the solution volume (mL); M is the mass of adsorbent (g). The pH of the solution was adjusted by using 0.1M HCl and 0.1M NaOH.

Results and Discussions:

Effect of contact time and Initial MNZ concentration

Time course profiles for the adsorption of MNZ from solution are shown in Figure 1. The data obtained from the adsorption of MNZ on the biomass showed that a contact time of 90 min (96.4%, 4.79 mg/g) was required to achieve an optimum adsorption and there was no significant change in concentration of the MNZ with furthur increase in contact time. It is basically due to saturation of the active site which does not allow further adsorption[31,32]. The adsorption rate was found to decrease with increase in time.

Figures 1 and 2 show the effect of MNZ concentration on the adsorption of MNZ by biomass. The data shows that the MNZ uptake increases and the percentage adsorption of MNZ decreases with increase in antibiotic concentration. This increaseis a result of increase in the driving force, i.e. concentration gradient[33-35]. However, the percentage adsorptions of MNZ on biomass were decreased from 96.4 to 76.2%. Though an increase in MNZ uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more MNZ available in the solution[36,37].

Effect of temperature on MNZ adsorption

The effect of temperature on MNZ adsorption onto Rice husk at vary agitation time is shown in Figure 4. As shown in Figure 4, the amount of MNZ removal using Rice husk powdered increases with the increasing of temperature. This arises from the increase in the mobility of MNZ molecule with increasing temperature and more molecules across the external boundary layer and the internal pores of the adsorbent particles. Furthermore, increasing temperature may produce a swelling effect within the internal structure of adsorbent, penetrating the large MNZ molecule further[38,39].

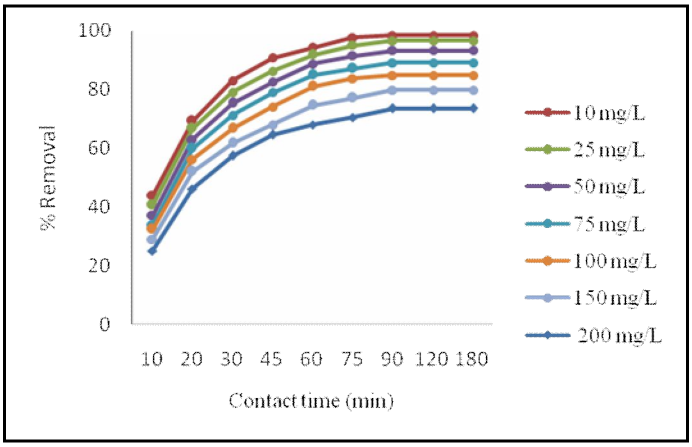

Fig 1. Effect of contact time and concentration on MNZ removal (pH =7, Adsorbent dosage 3 g/L and temperature = 27± 3◦C)

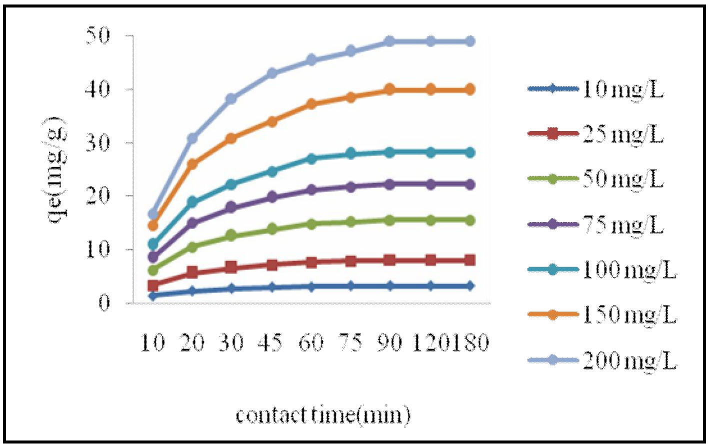

Fig 2. Effect of contact time on adsorption capacity (pH =7, Adsorbent dosage 3 g/L and temperature = 27± 3◦C)

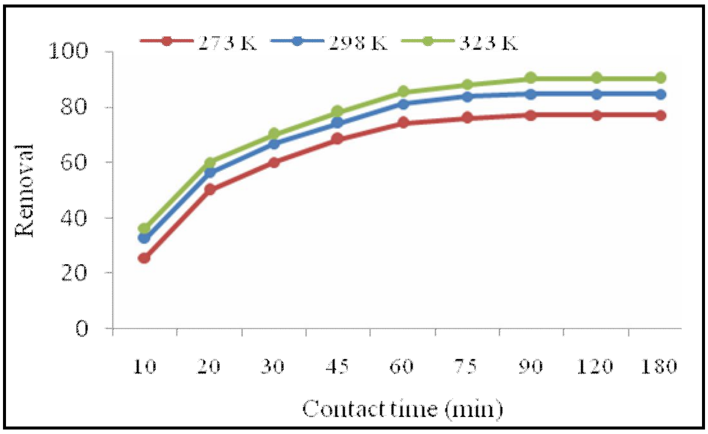

Fig 3. Effect of temperature on MNZ removal (pH =7, Adsorbent dosage 3 g/L, C_0 = 100 mg/L and contact time 90 min)

Isotherm studies

Langmuir, Freundlich, Dubinin-Radushkevich and Temkin adsorption isotherms models were employed to describe the relationship between adsorbate to adsorbent. The Langmuir isotherm model assumes that the adsorption occur at homogeneous sites at adsorbent surface, and saturation happen when the MNZ molecule fill the site where no more adsorption can occur at that site. The Freundlich isotherm is describing the sorption deals with surface heterogeneity. The Temkin isotherm model assumes that the heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage, in adsorbent–adsorbate interactions. Dubinin-Radushkevich (D-R) isotherm model is used to evaluate the sorption free energy and nature of bonding.

The linear form of isotherm models are represented as:

Langmuir isotherm model[40,41]:

$$\frac{Ce}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

Freundlich isotherm model[42,43]:

$$\text{Log } q_e = \frac{1}{n} \log Ce + \log K_F$$

Temkin isotherm model[44-47]:

$$q_e = \frac{RT}{B} \ln A + \frac{RT}{B} \ln C_e$$

Dubinin- Radushkevich isotherm model[48-50]:

$$\text{Ln } q_e = \ln q_m - K\varepsilon^2 \quad \text{and} \quad \varepsilon^2 = RT \ln (1+\frac{1}{C_e})$$

Model validation

In order to evaluate the goodness of the fit of experimental data and the prediction accuracy of the models utilised in the present work, the following statistical indices are employed for the single component system[50-53]:

$$\text{RMSE} = \sqrt{\frac{\sum (q_{e,\exp} - q_{e,\text{cal}})^2}{N}}$$

$$\text{SEP} = \frac{\text{RMSE}}{\sum q_{e,\exp}/N} \times 100$$

$$\text{NSD} = \sqrt{\frac{\sum [(q_{e,\exp} - q_{e,\text{cal}})/q_{e,\exp}]^2}{N}} \times 100$$

$$\text{ND} = \sum \left| \frac{q_{e,\exp} - q_{e,\text{cal}}}{q_{e,\exp}} \right| \times \frac{100}{N}$$

where $q_{e,exp}$ is experimental value of q_e, $q_{e,cal}$ is the predicted value of q_e by models, N indicates the number of data points in the experimental run. To evaluate the goodness of fit of experimental data for the binary system, the statistical indice average relative error (ARE) between the experimental and calculated values is used as given by Eq[54,55]:

$$\text{ARE} = \sqrt{\sum_{i=1}^{N} \left(1 - \frac{q_{e,i,\text{cal}}}{q_{e,i,\exp}}\right)^2} \times \frac{100}{N}$$

Where $q_{e,exp}$ is the equilibrium experimental uptake value of component, $q_{e,cal}$ is the predicted uptake value of component by model, and N indicates the number of experimental data points.

The results of the isotherm constants are displayed in Table 1. The calculated q_e values were in good agreement with experimental q_e values in Langmuir and D-R equation. The R^2 values for Langmuir and D-R equation were comparatively higher than Freundlich and Temkin model. Also the validation values were lower for Langmuir model and low validation values and high coefficient indicates that Langmuir, isotherm equations are much more suitable than the other isotherms in fitting to the data set of MNZ adsorption on Rice husk.

Table 1: Results of isotherm parameters for the adsorption of MNZ onto Rice husk

Langmuir Models		D-R Models		Freundlich Models		Temkin Models	
q_m	25.81	q_m	22.47	K_F	25.28	A	1.194
K_L	0.417	E	0.582	n	2.742	β	56.28
R^2	0.998	R^2	0.979	R^2	0.874	R^2	0.884
ARE	1.44	ARE	9.421	ARE	22.37	ARE	18.45
RMSE	2.734	RMSE	7.235	RMSE	11.95	RMSE	14.66
SEP	4.462	SEP	10.64	SEP	13.44	SEP	11.81
NSD	2.251	NSD	7.825	NSD	21.19	NSD	24.73
ND	3.849	ND	6.466	ND	18.93	ND	15.44

Conclusion:

In the present work, modified Rice husk were applied as adsorbents for the removal of Metronidazole antibiotic from wastewater. The results of this study show that the modified Rice husk is successful in removing the MNZ antibiotic from the aqueous solution. From the batch adsorption studies, the percent removal of MNZ was dependent on contact time, initial MNZ concentration, adsorbent dosage and temperature. Equilibrium data was fitted to the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin adsorption isotherm models and isotherm constants were determined. The equilibrium data were best fitted by the Langmuir isotherm model than other model.

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