Original Article

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Removal of Metronidazole Antibiotic from Hospital Wastewater by Biosorbent Prepared from Plantain Wood

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ABSTRACT

BACKGROUND AND OBJECTIVE: The overuse of antibiotics in hospitals and the entry of these pollutants into water resources is one of the major challenges to the health of the community and the environment. Removal of antibiotics from hospital wastewater and other aquatic environments is possible through the adsorption process. This study was performed to evaluate antibiotic removal using plantain wood due to being cheapn and natural.

METHODS: In this in vitro study, the effect of pH (2, 4, 6, 8, 10 and 12), contact time (5, 10, 20, 40, 60, 80, 100 and 120 minutes), initial metronidazole concentration (10, 50 and 100 mg/L) and biosorbent dose (0.2, 0.4, 0.6, 0.8, 1, 1.2 and 1.4 g) on metronidazole removal rate in synthetic solution were evaluated, and the isothermal kinetic and thermodynamic results of the adsorption process were investigated in this study. Concentration of metronidazole in aqueous solution was measured by Hach DR 5000 UV-Vis Laboratory Spectrophotometer.

FINDINGS: Maximum removal of metronidazole (91%) was obtained at pH=6.5, 60 min, initial concentration of 50 mg/l, adsorbent dose of 0.8 g and 25 °C and maximum adsorption capacity (11.38 mg/g) was obtained at a dosage of 0.1 g. In this study, the reaction rate followed the pseudo-second order and adsorption isotherm followed Langmuir equation. The adsorption thermodynamic results showed that the adsorption process is physical in nature and is a spontaneous endothermic reaction.

CONCLUSION: The results of the study showed that biosorbent prepared from plantain wood is a natural material and has the ability to remove metronidazole antibiotics from hospital wastewater and other aquatic environments.

KEY WORDS: *Adsorption, Biosorbent, Metronidazole, Hospital wastewater, Kinetics, Isotherms.*

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Introduction

During the last decade, a large number of scientists have investigated the presence of drugs in the environment and their adverse effects on living things (1–3). The most important reason for evaluating and monitoring of environmental contaminants is the entry of these pollutants into the food cycle and their detrimental effects on human health (4,5). Today, more than 80 types of environmentally active pharmaceuticals, in microgram concentrations, have been detected from the effluents of wastewater treatment plants, surface water, groundwater and drinking water (6,7). The metronidazole antibiotic is used to treat infectious diseases caused by anaerobic bacteria and a variety of protozoa in humans (8). Removal of this compound from aqueous solutions and hospital wastewater as a highly used antibiotic, due to its non-biodegradability and high carcinogenicity, has always been of interest to environmental researchers (9). The adsorption process is an efficient and economical method of separating and removing organic and inorganic pollutants from water sources (10,11). In order to remove organic matter in water and wastewater, various adsorbents such as activated carbon, sorbents produced from natural and agricultural wastes and mineral wastes have been used (12–16). In the study of Zazouli et al., eucalyptus bark was used as biosorbent to remove methylene blue pollution from aqueous solutions. In this study, the adsorption equilibrium time for different concentrations of this compound was 60 min (17). In the study of Belhassen et al., the removal of metronidazole antibiotic from aqueous solutions using powdered activated carbon, the effect of pH, temperature, initial solution concentration and contact time were evaluated (18). In the study of Fang et al., the efficiency of metronidazole removal from aqueous media by iron nanoparticles was investigated. In this study, complete removal of this antibiotic from aqueous solution was obtained at a concentration of 80 mg/l for 5 min, pH= 5.6 and adsorbent dose of 0.1 g/l iron nanoparticles (19). In the study of Flores-Cano et al., the adsorption of metronidazole and dimetridazole antibiotics by biosorbents produced from coffee and almond shell was investigated (20). In the study of Ding et al., adsorption of metronidazole antibiotic from aqueous solutions was evaluated using a type of iron-modified sepiolite mineral (21). Plantain is one of the trees found in most parts of the world and in different climates. In Iran, this tree is planted in different cities. Therefore, in this study, plantain was used as biosorbent in the removal of metronidazole antibiotic from hospital wastewater due to being cheap and accessible. The aim of this study was to evaluate the effect of pH, contact time, biosorbent dose, initial metronidazole concentration and temperature on removal of metronidazole from aqueous media and to investigate the kinetics, isotherms and thermodynamics of adsorption process in the produced biosorbent.

Methods

This in vitro study was conducted following the approval of the Ethics Committee of Guilan University of Medical Sciences under the code of ethics IR.GUMS.Rec.1397.309. The samples were first prepared, grinded and washed several times with distilled water. The product was carbonized at 400 °C for 2 hours and then activated at 800 °C for 2 hours under carbon dioxide (22). Metronidazole has a molecular weight of 171.15 g/mol, solubility in water of 7.02 g/l, octanol/water partition coefficient (pK_{ow}) of 0.02 and its ionization state is (pKa1= 2.85 and pKa2= 14.44, respectively) (8,23). The molecular structure of the metronidazole is shown below (Figure 1).

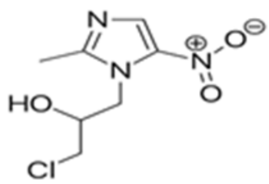

Figure 1. Molecular structure of the metronidazole antibiotic

In vitro metronidazole powder (98% purity) with the formula "$C_6H_9N_3O_3$" was prepared and used with molecular weight of 171.15 g/mol produced by Sigma and prepared from Behvarzan Co. Metronidazole at 1 g/l (1000 mg/l) in distilled water was prepared with ethanol as a stock solution and then, standard solutions were prepared at the desired concentrations in 50 ml Erlenmeyer flask using deionized distilled water. Determination of the adsorbent pH_{pzc} was done by direct pH method; 50 ml of 0.1 M sodium chloride solution was poured into 150 ml Erlenmeyer flasks and pH of the samples was adjusted by sodium hydroxide and hydrochloric acid solutions in the range of 2 to 12. Then, 0.04 g of adsorbent was added to the solutions and the containers were closed and stirred for 48 hours with an electric stirrer and the final pH was measured and its curve was plotted against initial pH. A point in the curve that cut the bisector was designated as PH_{pzc} of activated carbon (21,22). In each experiment, 50 ml of metronidazole solution of varying concentrations were poured separately into the Erlenmeyer flasks. The pH of the solution was also adjusted to the desired level with sodium hydroxide or 0.1 N Hydrochloric Acid. Predetermined concentrations of metronidazole were added to aqueous and biosorbent solution and mixed at 150 rpm. After complete mixing, the samples were smoothed by centrifugation at 5000 rpm and residual metronidazole concentration was measured by Hach DR 5000 UV-Vis Laboratory Spectrophotometer at 320 nm using a standard curve. Calculation of the level of metronidazole adsorption on the produced biosorbent was calculated based on the removal percentage and adsorption capacity (24). Curves and shapes were also drawn by Excel software 2019.

Equation 1:

$$\text{Metronidazole removal percentage} = \frac{C_0 - C_t}{C_0} \times 100$$

C_0= initial antibiotic concentration, Ct= antibiotic concentration after contact time

Equation 2:

$$\text{Metronidazole adsorption capacity (mg/g)} = \frac{V(C_0 - C_t)}{M}$$

V= volume of antibiotic solution in reactor, M= mass of carbon poured into reactor

Results

Evaluation of the effect of pH of solution on the efficacy of metronidazole adsorption by produced biosorbent: In this study, the PH_{pzc} of produced biosorbent was 7.5 (Figure 2). Optimal efficacy of metronidazole adsorption (91%) was obtained by biosorbent at initial concentration of 50 mg/l metronidazole, 60 minutes, adsorbent dose of 0.8 g/l and pH of 6.5. The percentage of metronidazole removal increased in the pH range of 2 to 6.5 and then decreased as the pH increased above 6.5 (Figure 3).

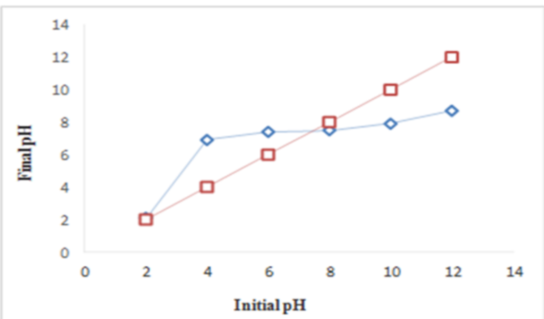

Figure 2. Representation of the PH_{pzc} of biosorbent produced from plantain

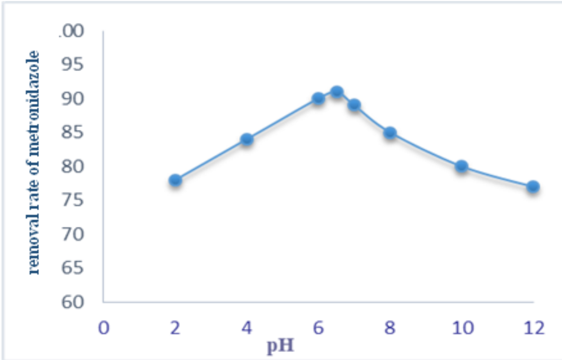

Figure 3. Effect of soluble pH on removal rate of metronidazole by produced biosorbent (Concentration of 50 mg/l, contact time of 60 min, adsorbent dosage of 0.8 g/l and temperature of 25°C)

The effect of the dosage of biosorbent produced on efficiency of metronidazole adsorption: In this study, the effect of biosorbent dosage on metronidazole removal rate and biosorbent adsorption capacity were investigated in the range of 0.2 to 1.4 g/l. As the adsorbent dosage increased, metronidazole removal percentage increased (Fig. 4a) and biosorbent adsorption capacity decreased (Fig. 4b).

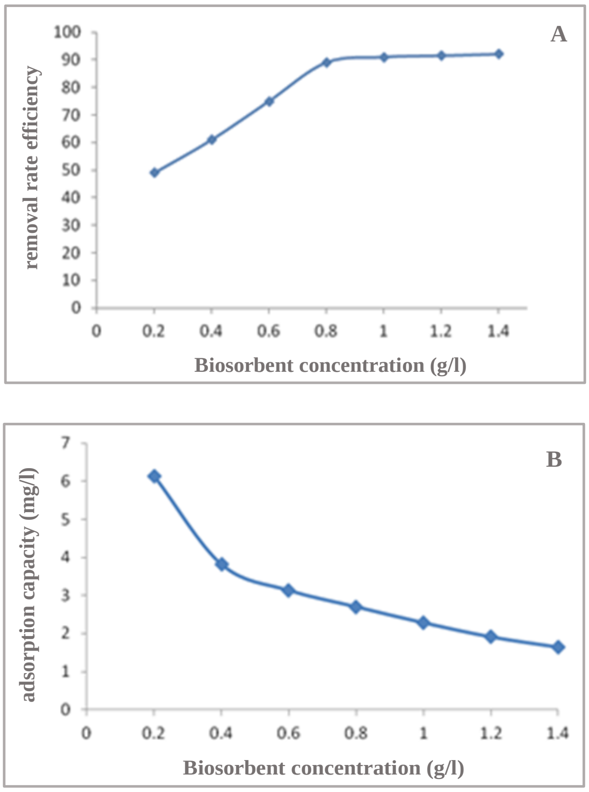

Figure 4. Effect of adsorbent concentration on metronidazole removal rate (Fig. A) and adsorption capacity (Fig. B) by produced biosorbent (pH= 6.5, 60 min contact time, initial concentration of 50 mg/l, temperature of 25 °C).

Evaluation of the effect of concentration and contact time on the efficiency of metronidazole adsorption by produced biosorbent: In this study, the effect of different concentrations of metronidazole (10, 50 and 100 mg/l) on efficiency of produced biosorbent was investigated under certain conditions. The efficacy of metronidazole removal by biosorbent at initial concentrations of 50 and 100 mg/l for 60 minutes and 0.8 g dose were 91% and 73%, respectively. However, at the same conditions and at 10 mg/l concentration of metronidazole, 99% metronidazole removal occurred within 20 minutes (Fig. 5).

Investigation of kinetic model of adsorption of metronidazole by produced biosorbent: In this study, kinetic parameters of metronidazole adsorption on biosorbent surface at concentrations of 50 and 100 mg/l metronidazole are presented (Table 1). According to the correlation coefficient (R2), the reaction rate of metronidazole adsorption at different concentrations follows the pseudo-quadratic kinetic model.

Investigation of isotherm of metronidazole adsorption by produced biosorbent: In this study, the efficiency of metronidazole adsorption based on Langmuir and Freundlich isotherms has been investigated (25). Due to the higher amount of adsorption correlation coefficient in the Langmuir isotherm (R2 = 0.992) (Fig. 6) than the Freundlich isotherm (R2 = 0.939) (Fig. 7), the adsorption process of metronidazole by biosorbent is more in line with the Langmuir isotherm.

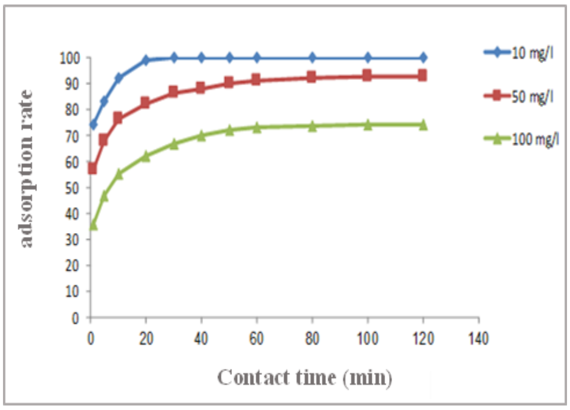

Figure 5. Effect of initial solution concentration on the adsorption rate of metronidazole by the produced biosorbent (pH= 6.5, adsorbent dose of 0.8 g/l, temperature of 25 °C).

Table 1. Kinetic data of metronidazole adsorption by the produced biosorbent

Concentration level	Pseudo– first– order kinetic model			Pseudo– second– order kinetic model		
--------	$K_1(min^{-1})$	q_e (mg/g)	R^2	K_2(g/mg.min)	q_e (mg/g)	R^2
50 (mg/l)	0.043	21.66	0.971	0.005	62.11	0.998
100 (mg/l)	0.029	54.78	0.937	0.002	97.09	0.991

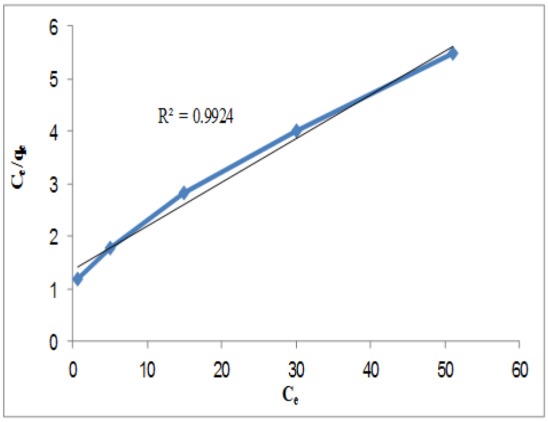

Figure 6. Langmuir isotherm curve in the adsorption process of metronidazole by biosorbent

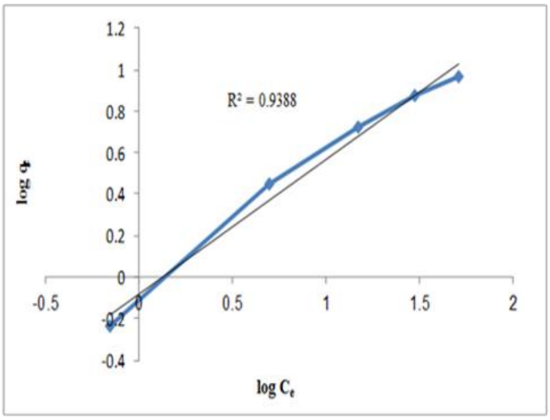

Figure 7. Freundlich isotherm curve in the adsorption process of metronidazole by the produced biosorbent

Discussion

In this study, the maximum removal rate of metronidazole by the produced biosorbent at pH= 6.5 was 91%. Considering the levels of biosorbent PH_{pzc} (PH_{pzc}= 7.5), it is found that at pH= 7.5, the biosorbent is electrically neutral. However, at pH below 7.5 (pH= 6.5), the positive charges on the biosorbent surface increased and in this case, due to the pKa_1 of metronidazole solution (e.g., pKa_1< 7), the negatively charged functional groups dominated in the solution. In this case, the removal efficiency in the adsorption process increased due to the van der Waals force between the positively charged groups present in the adsorbent surface and the negatively charged groups in the contaminant solution. The results of other studies in this area are in line with the findings of this study (26,27). At pH above 7.5, the biosorbent provides its positive charge (H^+) and the adsorbent surface has a negative charge. In this case, if the pKa_2 of solution is in alkaline pH (pH > 7.5) and the negative functional groups predominate in the solution, then the electrostatic repulsion between the negative charges on the biosorbent surface and the negative functional groups in the solution decreases the adsorption process efficiency (18).

A study by Çalışkan et al. on the adsorption of metronidazole and methoxazole antibiotics by activated carbon showed that changes in solution pH did not affect the increase in metronidazole removal rate (9). The reason for the differences between these two studies may be due to the difference in the type and properties of the biosorbent used, especially the difference in the pH of the two biosorbents. The concentration or dose of the biosorbent is also an influencing factor on the adsorption rate of the biosorbent (28,29).

Increasing the biosorbent dose increased the efficiency of metronidazole removal and decreased the adsorption capacity of this contaminant. To justify this phenomenon, it can be said that with increase in biosorbent content, the level of active surfaces and the number of exchange sites for the adsorption of pollutants increases. This leads to increased efficiency in metronidazole separation and adsorption. However, due to the adsorption capacity relationship, increasing the amount of biosorbent increases the denominator of this equation and decreases the adsorption capacity (27,28).

In this study, although the maximum removal rate of metronidazole based on the biosorbent dose was 1.4 g, the optimum and economical biosorbent dose produced was 0.8 g with respect to its appropriate removal efficiency (91%). According to the results of this study, the maximum removal efficiency (99%) of metronidazole was obtained at 20 mg/l metronidazole solution for 20 minutes. The high specific surface area and the presence of empty spaces in the structure of the produced biosorbent and the low concentration of metronidazole are the main reasons for complete absorption of this antibiotic by the desired biosorbent (29,30). At a concentration of 50 mg/l metronidazole, a longer removal time was required to achieve a higher removal efficiency, as the concentration of the solution increased and the level of biosorbent dose was constant. Although, over time, the percentage of metronidazole removal increased, but the rate of changes in metronidazole removal decreased at a concentration of 50 mg/l. This is also due to the high concentration of contaminants and the occupation of empty spaces and micropores of biosorbent by molecules of metronidazole (31,32).

Adsorption kinetics equations are used to investigate the mechanisms controlling the adsorption process such as diffusion, surface adsorption, intramolecular diffusion, and chemical adsorption (33). If the adsorption – controlling factor is infiltration at the boundary layer, the adsorption kinetics follows a pseudo– first– order model, where changes in the rate of absorption over time are proportional to the number of sites not occupied at the adsorbent surface (19). In the pseudo – second – order kinetic model, it is assumed that the chemical adsorption reaction controls the adsorption process and the rate of occupation of the adsorption sites is proportional to the square of the number of unoccupied sites (34).

According to the correlation coefficients of the pseudo– first and pseudo– second– order kinetic models at concentrations of 50 and 100 mg/l, and given the higher coefficient of correlation for the pseudo – second – order kinetic model (0.998, 0.991), it can be concluded that the adsorption mechanism follows a pseudo – second – order kinetic model. In the study of Çalışkan et al. using activated carbon, the adsorption kinetics of metronidazole and sulfamethoxazole at two concentrations of 20 and 34 mg/l followed the pseudo– second– order equation with correlation coefficient (R> 0.995) (9).

Due to the higher value of adsorption correlation coefficient in Langmuir isotherm (R^2= 0.992) compared to Freundlich isotherm (R^2= 0.939), the adsorption process of metronidazole by the biosorbent is more consistent with the Langmuir isotherm. This means that the adsorption of metronidazole molecules onto the biosorbent particles is better described by the Langmuir isotherm and the metronidazole molecules have uniform distribution in the adsorption sites (19,20). In this study, the HΔ value was 11.69 kJ/mol, and the fact that this value is positive indicates the endothermic and physical reaction. The change in entropy, or SΔ, is another thermodynamic variable. SΔ in this study was 5.56 and its positive value indicates the orderly and optimal state of adsorption process in the solid – liquid phase at the biosorbent surface. According to the results of this study, biosorbent prepared from plantain is an efficient and inexpensive adsorbent and has the potential to remove metronidazole from hospital wastewater. This adsorbent, at a dose of 0.2 g, has a maximum adsorption capacity (11.38 mg/g) under certain conditions. The highest removal efficiency of metronidazole (91%) was obtained at 50 mg/l metronidazole concentration, 60 min, 25 °C, 0.8 g biosorbent dosage and pH = 6.5. With increasing adsorbent dose, the efficiency of metronidazole removal increased and its adsorption capacity decreased. In this research, the pseudo– second– order kinetic equation and Langmuir isotherm model were in good agreement with the experimental data, with correlation coefficients of 0.998 and 0.992, respectively. The results obtained from the thermodynamic parameters GΔ, HΔ and SΔ confirm the physical and spontaneous nature of the reaction as well as desirable adsorption of the target biosorbent.

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