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Removal of metronidazole from aqueous solution using activated carbon

Habibi Belhassen [1,*], Ibtissem Ghorbel-Abid [1,2] and Lahsini Rim [3]

[1] *Laboratory for Applications of Chemistry to Resources, Natural Substances and Environment, Carthage University, Faculty of Sciences of Bizerte, Zarzouna, Bizerte, 7021, Tunisia*
[2] *Laboratory of Methods and Techniques of Analysis, National Institute of Physico-chemical Analysis, Technological Pole, Sidi Thabet, Ariana, 2020, Tunisia*
[3] *Laboratory of Research and Development, Tunisian Company for Pharmaceutical Industry, Siphat, 2034, Tunisia*

** Corresponding author at: Laboratory for Applications of Chemistry to Resources, Natural Substances and Environment, Carthage University, Faculty of Sciences of Bizerte, Zarzouna, Bizerte, 7021, Tunisia.*
Tel.: +216.20802721. Fax: +216.71382768. E-mail address: habibi_belhassen@yahoo.fr (H. Belhassen).

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ABSTRACT

Metronidazole antibiotic is a medication once discharged into the water after use, can react with living organisms and causing adverse effects to their lives. This kind of contaminant must be removed from wastewater and the technique adopted in this work is the liquid-solid adsorption method. The removal of metronidazole in aqueous solutions is carried out on powdered activated carbon. Different parameters such as solid/liquid ratio, temperature, pH, concentration, and contact time influencing this adsorption are examined. The Langmuir isotherm appears the most satisfactory is best suited for modeling the adsorption of metronidazole. In addition, the pH and the temperature do not seem to have any noticeable effect on the adsorption of metronidazole. The experimental results showed that metronidazole was removed at 64% for concentration of 50 mg/L for contact time of 20 min.

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1. Introduction

Metronidazole is an antibiotic used particularly for anaerobic bacteria and protozoa. It belongs to a class of antibiotics known as nitroimidazoles [1]. It is the commercial name for 2-methyl-5-nitro-imidazole-1-ethanol having molecular formula $C_6H_9O_3N_2$ [2]. The structure of metronidazole is depicted in Figure 1.

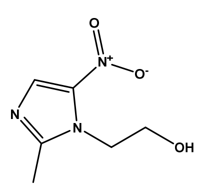

Figure 1. Chemical structure of metronidazole.

Because of its inexpensive and effective, this drug is important and widely used for therapeutic management of several human diseases and husbandry including fish farming particularly for parasitic infections [3]. It has been also reported that metronidazole shows toxic, carcinogenic and mutagenic properties. Due to its environmental side effects, cytotoxicity and genotoxicity European Council Regulation 613/98/EEC announced that any residue detected in food producing animals intended for human consumption in whatever quantity is considered as a violation to European regulation [4]. So, it can appear that no MRL has been set in literature [5]. Investigation of its presence in aquatic and edaphic environment is still very few. Range of sorption values of metronidazole on various soils and sediments (K_d) reported in literature ranged from 0.5 to 0.7 L/Kg [6], whereas, biodegradation is at 5% in 40 days because this lipid soluble antibiotic is not eliminated until it is metabolized to more polar compounds [7].

The aim of this work is to study the capacity of activated carbon in metronidazole adsorption from water especially due to its important specific area (700-1800 m^2/g), its porosity and granulometry (5 to 50 µm), good adsorption ability can be observed. A new HPLC method using UV detection has been also developed.

2. Materials and methods

2.1. Materials and reagents

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Table 1. Suitability parameters for metronidazole.

Retention time (T_R, min)	Number of theoretical plates (N)	Tailing Factor (As)
4.100	8695	0.840

Standards of metronidazole were provided from SIPHAT Tunisia. Acetonitrile were of HPLC-grade. Hydrochloric acid and sodium hydroxide were of analytical grade. HPLC grade water was prepared by purifying demineralized water in Milli-Q filtration system (Millipore, USA).

2.2. HPLC instrumentation and conditions

A rapid and simple new HPLC method was developed and validated for metronidazole determination in water. The HPLC system consists of a PERKIN ELMER instrument equipped with an auto-sampler, quaternary pump and a diode array detector. The analytical column (250 × 4.6 mm i.d.) was made of stainless steel and packed with Inertsil ODS (5 µm particle diameter, Sunfire, waters, USA), the mobile phase was consisting of a mixture of water:methanol (80:20, *v*:*v*). The flow rate was set at 1 mL/min and the injection volume was 20 µL. Best detection with the UV detector was set at 317 nm (Figure 2). All analyses were performed at ambient temperature (25 °C).

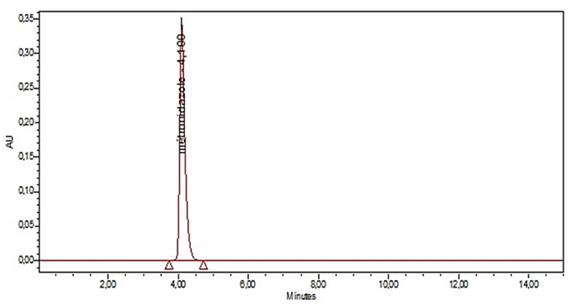

Figure 2. Standard solution of metronidazole chromatogram.

The system suitability parameters for studied compound are reported in Table 1.

The linearity was investigated for solutions containing 10-50 µg/mL of metronidazole. Calibration curves were found to be linear with correlation coefficients of 0.9994 and the variability (RSD) of the slope and intercept were 0.55 and 1.02 %. For the precision intraday RSD values and interday RSD values obtained for retention times and areas were varied from 0.54 and 0.62%. Recoveries ranged between 99.6 and 100.1%; LOD was 0.037 and LOQ was 0.12 µg/mL [8].

2.3. Adsorption isotherms [9]

Retention performance or the adsorbed amount is calculated by the following equations: Q_{ads} (mg/g) is the amount of metronidazole sorbed per gram of sorbent.

$$Q_{ads} = \frac{(C_0 - C_e) \times V}{m} (\frac{mg}{g}) \tag{1}$$

$$\text{Adsorption yield: } R(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \tag{2}$$

with: C_0: Initial concentration (mg/L). C_e: Equilibrium concentration (mg/L). V/m: Report volume of solution/mass of support (L/g).

Different isotherm models are available in the literature. Simple, reliable, and widely used models, such as Langmuir [10] and Freundlich isotherms [11], were used in this present study.

The linear form of Langmuir adsorption isotherm can be expressed as follows:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{3}$$

where, Q_m (mg/g) is the Langmuir constant related to the maximum monolayer adsorption capacity and K_L (L/mg) is the constant related to the free energy or net enthalpy of the adsorption.

The Freundlich model can be applied for multilayer adsorption on a heterogeneous adsorbent surface, with sites that have different energies of adsorption. The Freundlich model is given by the following equation:

$$\text{Ln } Q_e = \text{Ln } K_f + \frac{1}{\text{nf}} \times \ln C_e \tag{4}$$

where K_f (mg/g) and n are Freundlich constants related to adsorption capacity and intensity, respectively.

3. Results and discussion

3.1. Kinetic study and time effect

In order to optimize the contact time and the adsorption kinetic of metronidazole on activated carbon powder, a kinetic study was carried out. 30 mg of sorbent were added to 50 mL of a metronidazole solution (C_0 = 50 mg/L). The measured pH was 6.4. Samples were taken at different times at 25 °C. When increasing contact time, metronidazole removal increased rather rapidly to approach constant value showing attainment of equilibrium.

According to Figure 3, the sorption reaction occurred in two principle phases. In the first step, removal of metronidazole was very rapid, in less than 7 min, which can be explained by the high number of available active sites on the surface of the adsorbent allowing chemical specific interacttions [12]. Then, at 20 min removed rate reached equilibrium because of the non-availability of sorption sites.

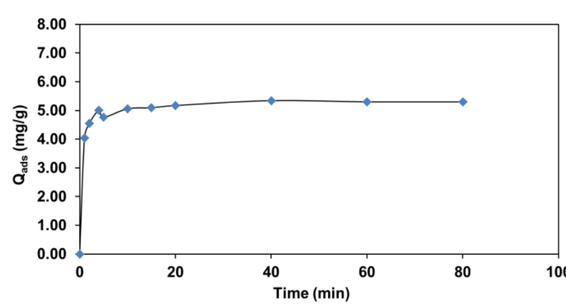

Figure 3. Effect of time on adsorption of metronidazole by activated carbon powder at 25 °C and pH = 6.4.

3.2. pH effect

This parameter is essential in adsorption process because it can affect directly on ionization of adsorbent and adsorbate.

Table 2. Langmuir and Freundlich constants of metronidazole.

Langmuir	
Qm (mg/g)	5.99
K_L	0.095
r^2	0.99
Freundlich	
nf	3.34
r^2	0.964
Kf	1.343

The effect of pH on removal of metronidazole by sorption on activated carbon powder was studied for a pH that ranged from 2 to 12 by adding HCl 0.1 N or NaOH 0.1 N (Figure 4). No significant variation was observed. This, can be explained by the fact that from p*K*a (metronidazole) = 2.6 only one from is present in the solution deprotonated.

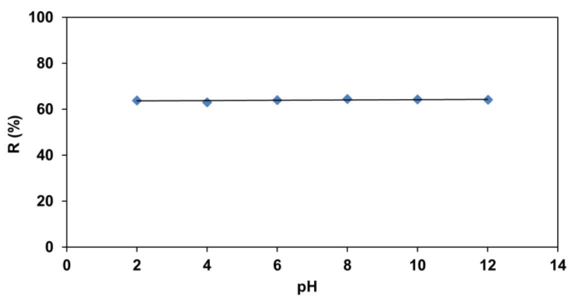

Figure 4. Effect of pH on adsorption of metronidazole by activated carbon powder at 25 °C.

3.3. Temperature effect

In order to obtain optimum temperature for better removal of metronidazole, experiments were carried out at different temperature (25, 30, 35, 40 and 50 °C). Obtained results show temperature doesn't affect adsorption capacity (Figure 5).

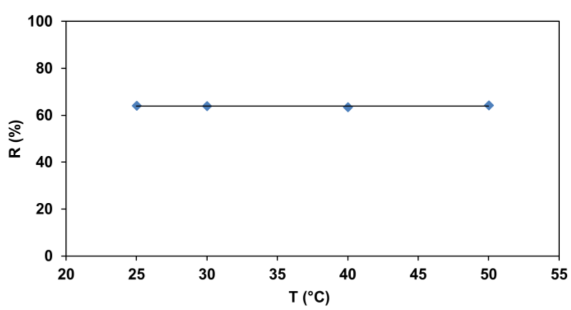

Figure 5. Effect of temperature on the adsorption of metronidazole by activated carbon.

3.4. Effect of ratio adsorbent quantity/Solution volume

The aim of this study is to find the minimum ratio (r) that allow a maximum removal of metronidazole. To the same solution volume (50 mL) different quantities activated carbon powder were added. Contact time was maintained at 30 min and temperature was set at 25 °C. A maximum of removal of 64% was obtained for 0.5 g/L.

3.5. Thermodynamics

Thermodynamic parameters, including changes in the free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) associated with the adsorption process, can be determined by using the following equations [13-18],

$$\Delta G^\circ = -\mathrm{RT}\ \mathrm{Ln}\ K_c \tag{5}$$

$$\Delta G^\circ = \Delta H^\circ - \mathrm{T}\Delta S^\circ \tag{6}$$

$$\mathrm{Ln}\ K_c = \frac{\Delta S^\circ}{\mathrm{R}} - \left(\frac{\Delta H^\circ}{\mathrm{RT}}\right) \tag{7}$$

The heat of adsorption ΔH° and the entropy ΔS° on activated carbon powder was determined graphically by plotting Ln K_c = f(1/T) as shown in the Figure 6.

The positive value of ΔH° (19.6 KJ/mol) confirms that the adsorption of adsorbate on the activated carbon powder is an endothermic process. The negative value (-24.52 J/mol.K) indicates that the entropy of adsorption of adsorbate is accompanied by a disorder of the medium. The adsorption process is thermodynamically possible at room temperature.

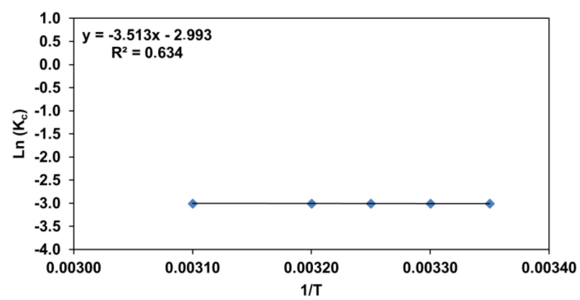

Figure 6. Determination of the enthalpies and entropies of adsorption of metronidazole on activated carbon.

3.6. Adsorption isotherms

We note that the linearization of adsorption isotherms of metronidazole is satisfactory with good coefficients correlation (Figure 7). We can say that the model Langmuir is adequate for a good description of the adsorption isotherm. Constants are depicted in Table 2.

4. Conclusion

A new simple and rapid HPLC method for determination of metronidazole has been validated. The kinetics studies show that pH and temperature parameters have no significant effects on metronidazole adsorption by activated carbon powder. Equilibrium was obtained after 20 min of contact for an adsorption percentage of 64%. The adsorption isotherms of metronidazole are described satisfactorily by the Langmuir model. The positive value of ΔH° confirmed the endothermic nature of adsorption. The negative value indicates that the entropy of the absorption is accompanied by a disorder of the medium. The adsorption process is thermodynamically possible at room temperature. A new support can be used for metronidazole elimination in waste water in pharmaceutical industry.

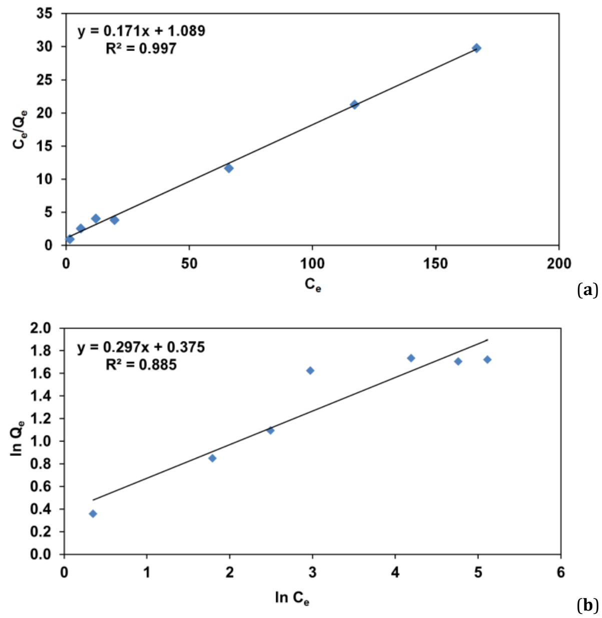

Figure 7. (a) Langmuir isotherm model for the adsorption isotherms of metronidazole on activated carbon powder (T = 25 °C) and (b) Freundlich isotherm model for the adsorption isotherms of metronidazole on on activated carbon powder (T = 25 °C).

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