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Nitroimidazoles adsorption on activated carbon cloth from aqueous solution

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ABSTRACT

The objective of this study was to analyze the equilibrium and adsorption kinetics of nitroimidazoles on activated carbon cloth (ACC), determining the main interactions responsible for the adsorption process and the diffusion mechanism of these compounds on this material. The influence of the different operational variables, such as ionic strength, pH, temperature, and type of water (ultrapure, surface, and waste), was also studied. The results obtained show that the ACC has a high capacity to adsorb nitroimidazoles in aqueous solution. Electrostatic interactions play an important role at pH < 3, which favors the repulsive forces between dimetridazole or metronidazole and the ACC surface. The formation of hydrogen bonds and dispersive interactions play the predominant role at higher pH values. Modifications of the ACC with NH_3, $K_2S_2O_8$, and O_3 demonstrated that its surface chemistry plays a predominant role in nitroimidazole adsorption on this material. The adsorption capacity of ACC is considerably high in surface waters and reduced in urban wastewater, due to the levels of alkalinity and dissolved organic matter present in the different types of water. Finally, the results of applying kinetic models revealed that the global adsorption rate of dimetridazole and metronidazole is controlled by intraparticle diffusion.

1. Introduction

Nitroimidazoles are the most widely used pharmaceuticals to treat infections in humans and animals caused by anaerobic and protozoan bacteria, such as *Trichomonas vaginalis* and *Giardia lamblia* [1]. Among nitroimidazoles, only five are useful as antibacterial and antiparasitic drugs [2,3]. Metronidazole (MNZ) is used in human, and dimetridazole (DMZ) is applies to animals. Metronidazole is the most widely used nitroimidazole. It is one of the 100 most commonly prescribed drugs in the USA [4] and one of the 10 most frequently administered drugs during pregnancy [5]. Moreover, MNZ is the only nitroimidazole included in the WHO list of essential drugs. This has produced an accumulation of these drugs in the animal organism, in fish-farm waters, and especially in the effluents from meat industries [6–8].

Nitroimidazoles have high water solubility, low biodegradability [9], and high toxicity [10,11] and show mutagenic and carcinogenic characteristics [2]. These characteristics make nitroimidazoles potentially dangerous compounds because of their persistence in water, which favors their bioaccumulation. According to the International Agency for Research on Cancer, there is sufficient evidence to consider MNZ as a potentially carcinogenic substance [12]. For all these reasons, nitroimidazoles are considered emerging water micropollutants.

Adsorption on carbon materials, one of the oldest water treatment technologies has been recognized by the U.S. Environmental Protection Agency as one of the best methods available to remove organic and inorganic compounds from water intended for human consumption [13–22]. The value of activated carbons in this field resides in the chemical and textural properties of their surfaces. However, this technology is not very widely used to treat wastewater and industrial effluents, mainly because of their high organic matter content. Importantly, some experimental parameters of activated carbon adsorption remain unknown, and the mechanisms involved in each system have yet to be elucidated. This knowledge is essential for optimizing the use of activated carbon in water treatments.

Nitroimidazole adsorption on granular activated carbon (GAC) has not been extensively studied in the literature. In previous works, Méndez-Díaz et al. [23] investigated the adsorption kinetics of four nitroimidazoles (DMZ, MNZ, ronidazole, and tinidazole) on three activated carbons (C, S, and M) and reported that the time to reach equilibrium was 60 h. The nitroimidazole adsorption rate increased in the order C < S < M, which was attributed to the hydrophobicity values of these activated carbons. Rivera-Utrilla et al. [24,25] studied the behavior of activated carbons with different chemical and textural characteristics in nitroimidazole adsorption in static and dynamic regime in ultrapure, surface, ground, and

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Nomenclature

a	Prausnitz–Radke isotherm constant, L g^{-1}
b	Prausnitz–Radke isotherm constant, $L^{1-\beta}$ $mmol^{\beta}$ g^{-1}
C_1	concentration in equilibrium at q = constant and $T = T_1$, mg L^{-1}
C_2	concentration in equilibrium at q = constant and $T = T_2$, mg L^{-1}
C_A	concentration of solute, mg L^{-1}
C_{A0}	initial concentration of solute in aqueous solution, mg L^{-1}
C_{Ar}	concentration of solute within the particle at distance r, mg L^{-1}
$C_{Ar\|r=R}$	concentration of solute at the external surface of the ACC at $r = R$, mg L^{-1}
C_{Ae}	concentration of solute at equilibrium, mg L^{-1}
D_{AB}	molecular diffusion coefficient at infinite dilution, cm^2 s^{-1}
D_{ep}	effective pore volume diffusion coefficient, cm^2 s^{-1}
d_f	average diameter of the fibrils of ACC, μm
k	equilibrium constant of Freundlich isotherm, $mg^{1-1/n}$ $L^{1/n}$ g^{-1}
k_L	external mass transfer coefficient in liquid phase, cm s^{-1}
K	Langmuir constant related to the adsorption heat, L mg^{-1}
m	mass of ACC, g
n	Freundlich isotherm constant related to the adsorbent–adsorbate affinity
N	number of experimental data
q	mass of solute adsorbed, mg g^{-1}
q_e	mass of solute adsorbed at equilibrium, mg g^{-1}
q_m	maximum solute mass adsorbed on the adsorbent, mg g^{-1}
r	distance in radial direction of ACC, cm
R	universal gas constant, 8.314 J mol^{-1} K^{-1}
S	external surface of the fibrils of ACC per unit mass of ACC, cm^2 g^{-1}
T	temperature, K
V	volume of the solution, L
V_a	molar volume of solute at its boiling temperature, cm^3 mol^{-1}

Greek letters

β	Prausnitz–Radke isotherm constant
ε_p	void fraction of ACC
ϕ_A	dimension less concentration of solute in solution
ϕ_{exp}	experimental dimension less concentration of solute in solution
ϕ_{pred}	dimensionless concentration of solute in solution predicted with diffusional model
λ	ratio of the solute molecular diameter to the pore diameter
ρ_p	apparent density of ACC, g cm^{-3}
τ	tortuosity factor
ΔH_{ads}	isosteric heat of adsorption, J mol^{-1}

wastewaters. They also assessed the influence of the chemical nature of the solution (pH and ionic strength) on the adsorption of these compounds. They found that the activated carbons had a high capacity to adsorb nitroimidazoles, which was directly related to the electron density of the nitroimidazole aromatic ring. The authors concluded that the interactions governing the adsorption process were dispersive between the electrons of the graphene planes of the carbon and the aromatic rings of the nitroimidazoles.

Recently, a new form of activated carbon has recently been developed based on the carbonization and activation of cloths from different polymeric materials, including nylon, rayon, cellulose, phenolic resins, polyacrylonitrile, and pitch. This novel material is known as activated carbon fiber (ACF), which is manufactured in the form of cloth or felt. The properties of ACF depend on the precursor, preparation method, and activation process [26].

In contrast to GAC, which possess a complex pore structure formed by macropores (pore diameter > 50 nm), mesopores (2 ⩾ pore diameter ⩾ 50), and micropores (pore diameter < 2 nm), ACF has a completely microporous structure. Moreover, most ACF shave larger specific areas in comparison with GAC and PAC and therefore show higher adsorption capacities in some cases. A further advantage of ACF is that the diameter of its fibers is 0.006–0.017 mm, which is on average 100-fold smaller than the diameter of GAC particles (1–3 mm), yielding much faster global adsorption rates because the intraparticle diffusion distance is markedly reduced. For these reasons, ACF has been increasingly employed for the removal of organic pollutants in aqueous phase over the past few years [27]; however, the behavior of this type of adsorbents in the nitroimidazoles removal has not been analyzed yet.

With this background, the objective of this study was to investigate the equilibrium and adsorption kinetics of nitroimidazoles on activated carbon cloth (ACC), determining the main interactions responsible for the adsorption process and the diffusion mechanism of these compounds on ACC. A further objective was to study the influence on this process of different operational variables, i.e., ionic strength, pH, temperature, and type of water (ultrapure, surface, and wastewater).

2. Experimental

2.1. Nitroimidazoles

The two antibiotics used in this study were metronidazole (MNZ), as representative of the group of nitroimidazoles prescribed to humans, and dimetridazole (DMZ), as representative of the nitroimidazoles used in animals; both were supplied by Sigma–Aldrich. The two antibiotics have a similar chemical structure, i.e., they have a five-membered aromatic heterocycle with a nitrite-group located in position five of the ring. Fig. B1 depicts the chemical formula and Table 1 shows the main physicochemical properties of the nitroimidazoles.

The species distribution diagrams for these compounds were obtained from the pK_a values of the nitroimidazole molecules (Fig. 1).

2.2. Activated carbon cloth

The activated carbon cloth (ACC) used in this study was supplied by Kynol Europe. It has a fiber diameter of 9 μm, and its chemical and textural properties were reported by López-Ramón et al. [28] (see Table 2).

2.3. Modification of the activated carbon cloth

ACC was modified with NH_3 and $K_2S_2O_8$ by placing 1 g of the material in contact with 100 mL of 5 M solutions of NH_3 and $K_2S_2O_8$ for 24 h. Then, the ACC was separated from solutions, filtered, and washed several times with ultrapure water until the