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Research article

Removal of norfloxacin in deionized, municipal water and urine using rice (*Oryza sativa*) and coffee (*Coffea arabica*) husk wastes as natural adsorbents

Marcela Paredes-Laverde, Javier Silva-Agredo, Ricardo A. Torres-Palma*

Grupo de Investigación en Remediación Ambiental y Biocatálisis (GIRAB), Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia

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ABSTRACT

The removal of the widely used antibiotic norfloxacin (NOR), the presence of which has been reported in natural water, was evaluated using rice (RH) and coffee (CH) husk wastes as adsorbents. Low particle sizes and natural pH in distilled water favored NOR elimination in both materials. In order to investigate the type of adsorption, the data was adjusted to the Langmuir, Freundlich and Redlich-Peterson isotherms. The best fit for the Langmuir and Redlich-Peterson isotherms suggested a monolayer-type adsorption model. Kinetic models of pseudo first and second order were also evaluated, the latter being the most suitable to represent the NOR adsorption phenomenon. Meanwhile, the intraparticle diffusion model indicated that the adsorption of NOR occurs both at the surface and within the pores of the material. Studies performed on thermodynamic aspects such as activation energy (E_a), enthalpy change (ΔH) and Gibbs free energy change (ΔG) suggest that the physisorption of the pollutant takes place through a spontaneous endothermic process. Additionally, PZC determination, Boehm method, chemical composition, thermodynamic analysis, and FTIR spectra before and after the adsorption of the antibiotic suggest that in CH adsorbents this occurred mainly through electrostatic interactions, while in RH hydrogen bonds also contributed significantly. Finally, the efficiency of natural adsorbents for the removal of NOR was evaluated in synthetic matrices of municipal wastewater and urine, and promising results were obtained despite the complexity of these matrices. The results presented in this work show the potential application of RH and CH residues as a low-cost alternative for the removal of NOR even in complex matrices. However, despite the similarities between the materials, CH waste showed better properties for the removal of the tested NOR due to its higher surface area, lower PZC and higher number of acid groups.

1. Introduction

A wide variety of synthetic and natural compounds, such as antibiotics, are currently used for the treatment of diseases in humans and animals (Ozcan et al., 2016). Norfloxacin (NOR) is an antibiotic of the fluoroquinolone class, which is widely used due to its high antibacterial activity against both Gram-negative and Gram-positive bacteria (Liu et al., 2011). However, it is estimated that about 30–90% of the NOR dose ingested is excreted without modification in urine or feces (Pouretedal and Sadegh, 2014). Due to the inability of conventional water treatment methods to remove this antibiotic, its presence has been detected in both natural and drinking water (Ozcan et al., 2016). In fact, this substance reaches the environment through municipal, hospital and industrial wastewater effluents, as well as through agricultural activities. Consequently, NOR currently represents a serious risk due both to the proliferation of resistant bacteria and to its toxic and acute effects in aquatic species (Darweesh and Ahmed, 2017).

To minimize the pollutant load of this antibiotic, it is necessary to implement treatment systems at source, or as tertiary treatment to complement conventional systems. Some promising alternatives for removal of antibiotics in water are ozone (Alexander et al., 2016), electrochemical oxidation (Jojoa-Sierra et al., 2016; Serna-Galvis et al., 2017), photodegradation (Porras et al., 2016; Rani et al., 2014), membrane separation (Weng et al., 2016a,b), osmosis

* Corresponding author.
E-mail address: ricardo.torres@udea.edu.co (R.A. Torres-Palma).

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Abbreviations

RH	rice husk
CH	coffee husk
NOR	norfloxacin
PZC	point of zero charge
E_a	activation energy
ΔG°	Gibbs free energy
ΔH°	enthalpy
ΔS°	entropy
APE	average percentage errors

(Pan et al., 2015), electrocoagulation (Yoosefian et al., 2017), ion exchange processes (Wang et al., 2016a,b) and adsorption (Li et al., 2017). The last of these is one of the most attractive options, due to its easy operation, efficiency and relatively low cost in the removal of even trace levels of antibiotics (Li et al., 2017). Consequently, many adsorption materials have been tested. Activated carbon is the adsorbent currently preferred for removing antibiotics from water (Xie et al., 2011). However, the use of activated carbon is not always convenient due to its relatively high production costs (Pavan et al., 2014). Therefore, further research is necessary to identify efficient and easily accessible low-cost materials for this purpose.

The manufacture and transformation of agroindustrial products results in large amounts of solid organic waste, with the consequent cost of collection, treatment and disposal of this (Panesar et al., 2015). Moreover, harmful toxic gases are usually generated during the elimination of these residues (Ponnusami et al., 2008). Therefore, it is necessary to seek alternative options for the use of such waste in order to reduce its negative impact on the environment. Therefore, in the last decade the scientific community has investigated the replacement of activated carbon with materials obtained from biomass as an interesting alternative option for water treatment. Indeed, the efficiency of biomass in the adsorption of pollutants has been demonstrated. This efficiency results from the presence of several polar functional groups (e.g. alcohols, aldehydes, ketones, carboxylic acids, phenols and ether groups) on the surface of biomass (Jia et al., 2017). The most promising vegetable waste products used as natural adsorbents for the treatment of contaminants include grapefruit peel (Zou et al., 2012), papaya seeds (Pavan et al., 2014), watermelon peel (Hameed, 2009), peanut shells (Ali et al., 2016), lentil and wheat husks (Aydın et al., 2008), mango and banana peels (Bhatnagar et al., 2015), and guava (Ponnusami et al., 2008).

The use of rice husk (RH) and coffee husk (CH) are of special interest because they are considered a serious environmental problem in many developing countries. In Colombia, around 400,000 tons of RH (Piñeros-Castro et al., 2011) and 2,000,000 tons of CH (Rodriguez Valencia, 2013) are generated per year. Both RH and CH have been used in the removal from water of dyes such as congo red (Han et al., 2008), fast green (Ahalya et al., 2014), and methylene blue (L. S. Oliveira et al., 2008a,b; Sharma et al., 2010); as well as heavy metals such as Pb^{2+} and Zn^{2+} (Ahmaruzzaman and Gupta, 2011; Berhe et al., 2015; Chuah et al., 2005; Oliveira et al., 2008a,b). Therefore, the use of RH and CH as adsorbents could address two serious environmental problems: the disposal of RH and CH waste and the removal of antibiotics from water.

In spite of the fact that RH and CH have significant potential in the removal of antibiotics such as fluoroquinolones, no works on the elimination of this kind of pollutant using these materials have been reported. As such, the objective of this work is to investigate for the first time the potential of RH and CH in the removal of NOR from water. In this sense, in the next section, the materials and methods used to evaluate and understand the NOR elimination using RH and CH are detailed. Then, in the results and discussion section, initially physicochemical characterization of RH and CH was presented and discussed taking into account the specific surface area, chemical composition, acid and basic groups according to the Boehm method, the point of zero charge (PZC) and surface morphologies. Next, experimental conditions such as the effect of pH and particle size were evaluated. Additionally, to better understand the results, the experimental data was adjusted to Langmuir, Freundlich and Redlich-Peterson adsorption isotherms; and kinetics models of pseudo first order, pseudo second order and intraparticle diffusion were tested. Additionally, the thermodynamic parameters activation energy (E_a), Gibbs free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) were calculated, and a mechanism for NOR adsorption on RH and CH was proposed. In order to evaluate the effects of matrices, NOR adsorption in municipal waters and urine was also investigated. Finally, the most important findings were presented in the conclusions section.

2. Material and methods

2.1. Reagents

Source of reagents and chemicals are provided in the Supplementary Material (SM) Text SM 1. All solutions were prepared with distilled water, except for those used for chromatographic analysis, which were prepared with purified water from a Millipore Milli-Q® system.

2.2. Natural adsorbents preparation

RH and CH were collected from agroindustrial waste from the Huila department in Colombia. The materials were washed repeatedly with distilled water to remove dust and soluble impurities, and then dried in an oven at 60 °C for 48 h. The RH and CH were then ground to powder and sieved to obtain different particle sizes (<75, 75–300, 300–500 and > 500 μm). The materials were then stored in plastic bottles before use.

2.3. Characterization of natural adsorbents

The specific surface area of the adsorbents was determined by nitrogen adsorption at 77 K using an ASAP 2020 Micrometrics instrument according to the Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938). Surface functional groups were investigated with Fourier transformed infrared spectroscopy (FTIR) on a Bruker Tensor 27 spectrometer with a MCT (Mercury-Cadmium-Tellurid) detector, using the diamond lens attenuated total reflectance (ATR) accessory. PZC was obtained by the solid addition method (Guechi and Hamdaoui, 2015a). Surface morphologies of RH and CH were examined by scanning electron microscopy (SEM), using a JEOL JSM-6490LV model. Additionally, an energy dispersive spectrometer (EDS) was coupled to the SEM to identify the relative content of elements.

The lignin content was measured according to the D1106-96 method (ASTM, 2013a). Holocellulose (cellulose + hemicellulose) and cellulose were determined by the TAPPI T19m-54 method (Oliveira et al., 2017). Extractable materials content was quantified according to the D1107-96 and D1110-84 methods (ASTM, 2013b)-(ASTM, 2007). The ash concentration was determined by the D1102-84 method (ASTM, 2013c). Finally, the acidic and basic groups of samples were calculated using the Boehm titration method (Al-khaldi et al., 2015).