REVISTA CONTRIBUCIONES A LAS CIENCIAS SOCIALES

Removal of ibuprofen in aqueous medium by adsorption in biochar produced from coffee grounds and activated with hydrogen peroxide

Remoção de ibuprofeno em meio aquoso por adsorção em biocarvão produzido de borra de café e ativado com peróxido de hidrogênio

Remoción de ibuprofeno en medio acuoso por adsorção en biocarvón produzido de borra de café e ativado com peróxido de hidrógeno

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ABSTRACT
The presence of drug compounds in the environment, especially in water, is harmful to humans and to the balance of the ecosystem. The entry of drug residues into the environment can occur by the release of treated or raw domestic sewage in water bodies, since most sewage treatment

plants are not efficient in the removal of these compounds. Therefore, research on methods of drug and other contaminants removal is extremely important. Considering that ibuprofen is one of the most consumed drugs in the world, the aim of this study is to verify the removal of ibuprofen from aqueous medium using adsorption in H2O2-activated biochar (ABC) produced from coffee grounds. For the characterization of the biochar produced, zero charge point determination and identification and quantification of functional surface groups were performed. The adsorption process was evaluated by pH influence tests, influence of ABC mass and adsorption kinetics. The efficiency of biochar produced was 70.2% (qe = 46.57 mg/g) for an initial concentration of 120 mg/L and for a contact time of 2 h. Thus, it can be concluded that the biochar produced presented satisfactory results, contributing to the removal of ibuprofen in aqueous medium

Keywords: adsorption, activated biochar, ibuprofen, coffe grounds.

RESUMO

A presença de compostos farmacêuticos no ambiente, especialmente na água, é prejudicial aos seres humanos e ao equilíbrio do ecossistema. A entrada de resíduos de fármacos no ambiente pode ocorrer por meio do lançamento de esgoto doméstico tratado ou bruto em corpos hídricos, uma vez que a maioria das estações de tratamento de esgoto não é eficiente na remoção desses compostos. Portanto, pesquisas sobre métodos de remoção de fármacos e outros contaminantes são extremamente importantes. Considerando que o ibuprofeno é um dos medicamentos mais consumidos no mundo, o objetivo deste estudo é verificar a remoção de ibuprofeno de meio aquoso por meio de adsorção em biocarvão ativado com H2O2 (ABC) produzido a partir de borra de café. Para a caracterização do biocarvão produzido, foram realizadas a determinação do ponto de carga zero e a identificação e quantificação dos grupos funcionais na superfície. O processo de adsorção foi avaliado por meio de testes de influência do pH, influência da massa de ABC e cinética de adsorção. A eficiência do biocarvão produzido foi de 70,2% (qe = 46,57 mg/g) para uma concentração inicial de 120 mg/L e tempo de contato de 2 h. Assim, pode-se concluir que o biocarvão produzido apresentou resultados satisfatórios, contribuindo para a remoção de ibuprofeno em meio aquoso.

Palavras-chave: adsorção, biocarvão ativado, ibuprofeno, borra de café.

RESUMEN

La presencia de compuestos farmacéuticos en el ambiente, especialmente en el agua, es perjudicial para los seres humanos y para el equilibrio del ecosistema. La entrada de residuos de fármacos al ambiente puede ocurrir mediante el vertido de aguas residuales domésticas, tratadas o sin tratar, en cuerpos de agua, dado que la mayoría de las plantas de tratamiento de aguas residuales no son eficientes en la eliminación de estos compuestos. Por lo tanto, la investigación sobre métodos de eliminación de fármacos y otros contaminantes es de suma importancia. Considerando que el ibuprofeno es uno de los medicamentos más consumidos en el mundo, el objetivo de este estudio es verificar la eliminación de ibuprofeno de un medio acuoso mediante adsorción en biocarbón activado con H2O2 (ABC) producido a partir de residuos de café. Para la caracterización del biocarbón producido, se realizaron la determinación del punto de carga cero y la identificación y cuantificación de los grupos funcionales superficiales. El proceso de adsorción se evaluó mediante pruebas de influencia del pH, influencia de la masa de ABC y cinética de adsorción. La eficiencia del biocarbón producido fue del 70,2 % (qe = 46,57 mg/g)

para una concentración inicial de 120 mg/L y un tiempo de contacto de 2 h. Así, se puede concluir que el biocarbón producido presentó resultados satisfactorios, contribuyendo a la eliminación de ibuprofeno en medio acuoso.

Palabras clave: adsorción, biocarbon activado, ibuprofeno, borra de café.

1 INTRODUCTION

Population growth combined with increased life expectancy, especially in large urban centers, is currently one of the main factors associated with increased drug consumption, and this, in turn, has attracted the attention of researchers in the area of environmental sanitation in view of the possibility of these compounds being introduced into different environmental compartments by different routes.

The drug compounds that have been detected belong to a class of products called emerging pollutants, in which endocrine disruptors and nonsteroidal anti-inflammatory drugs (NSAIDs) are specified. The presence of these substances in water is harmful to human and ecosystem balance in general due to toxicity, genotoxicity, endocrine disturbance and the development of resistant pathogenic bacteria (Tambosi *et al.* 2010).

Among NSAIDs is ibuprofen, which is one of the most consumed drugs in the world. This compound, even at low concentrations, on the order of μg/L or ng/L, is harmful to the environment (Farias *et al*. 2019).

For NSAIDs, conventional sewage treatment is not fully efficient, which is why they are often found in water bodies (Santos 2016).

Among the treatment techniques usually adopted for the removal of these microcontaminants is adsorption, which in addition to demonstrating good efficiency for this purpose (Maia 2017), presents the possibility of having adsorbent material to be produced from lignocellulosic residues that give to the technology an economically viable and environmentally responsible character (Anas *et al*. 2020)

Therefore, the purpose of this work is to verify whether biochar produced from a lignocellulosic residue and activated with hydrogen peroxide is able to satisfactorily remove the ibuprofen present in aqueous medium.

2 MATERIALS AND METHODS

2.1 PREPARATION AND ACTIVATION OF BIOCHAR

Biochar was prepared from coffee grounds previously washed with distilled water to remove impurities or soluble substances. Then, the material was dried in an oven at a temperature of 105 °C for a period of 24 h until residual moisture was removed. Pyrolysis was performed at 450 °C for a period of 1.5 h in a muffle oven with an oxygen- poor atmosphere. The activation of the biochar obtained was performed according to the method proposed by Huff and Lee (2015). Thus, 100 g of biochar was kept under agitation with 500 mL of hydrogen peroxide at room temperature for a period of 2 h. After this period, the biochar was washed with distilled water at a temperature between 50 and 60 °C, filtered and dried in an oven at 105 °C for 24 hours. The material obtained was stored in polyethylene bottles at room temperature. The concentration of hydrogen peroxide was 40%.

2.2 CHARACTERIZATION OF ACTIVATED BIOCHAR (ABC) AND THE ADSORPTION PROCESS

The tests were carried out in batch reactors under constant agitation of 120 rpm in an orbital agitator shaker (Solab 180/A) at room temperature. For the characterization of ABC, the following assays were performed: i) determination of the zero charge point, assay of 11 points and ii) identification and quantification of functional surface groups, Boehm titration analyses and FTIR. The adsorption process was evaluated by means of the following tests: i) influence of pH on adsorption; ii) influence of ABC mass on adsorption; iii) adsorption capability with the analysis of data adjusted to Langmuir and Freundlich models; and iv) adsorption kinetics with the adjustment of the data to the pseudofirst and pseudosecond-order models.

2.3 ADSORPTION AND EQUILIBRIUM KINETICS TESTS

For this test, 0.1 g of ABC was kept in contact under constant agitation with 50 mL of ibuprofen solution that had initial concentrations of 50 mg/L and 75 mg/L under pH 2 conditions. The readings of ibuprofen concentrations in solution were performed at predetermined time intervals (1, 2.5, 5, 10, 15, 30, 60, 90 and 120 min) until equilibrium was reached, which was verified by means of a constant concentration of ibuprofen. To obtain the kinetic parameters, the ibuprofen adsorption data as a function of time were fitted to pseudofirst- and pseudosecond-order models, and the R^2 coefficient was used as a parameter to evaluate the adequacy of the fits.

2.4 PHYSICOCHEMICAL ANALYSES

Ibuprofen determination was performed according to the method proposed and validated by Roveri *et al*. (2012), which consists of the spectrophotometric analysis of ibuprofen in the UV region (264 nm) in alkaline medium. A spectrophotometer (Hach DR5000) was used. pH analyses were performed by the potentiometric method. The calibration curve was constructed from a solution prepared with 99% ibuprofen and distilled water. For this, concentrations were in the range between 10 mg/L and 200 mg/L ($R^2 = 0.9986$).

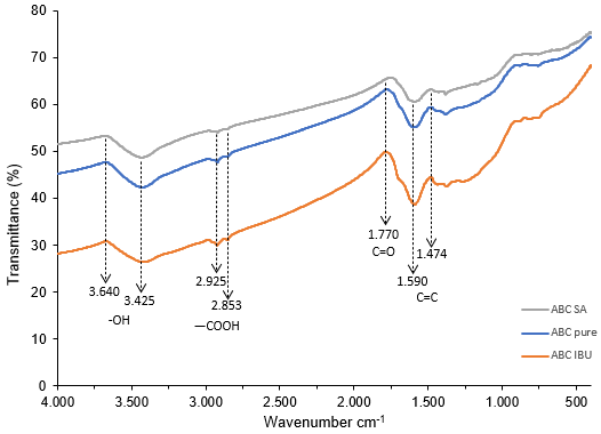
3 RESULTS AND DISCUSSION

The carbonization of coffee grounds presented a yield of approximately 33% of mass. The pH measured after washing the biochar varied between 9 and 10. After activation with hydrogen peroxide, however, there was a decrease in pH, which was approximately 7. The zero charge point (ZCP) test result showed that pH 5 corresponds to the range in which the constructed graph presented a constant behavior of the final pH regardless of the initial pH value. Thus, in the cationic region (pH values below the ZCP), the surface of the ABC is positively charged, while in the anionic region (pH values above the ZCP), it is negatively charged.

Regarding the identification and quantification of functional surface groups, the results of Boehm titration showed that biochar activated with hydrogen peroxide presented on its surface hydroxyls (OH-) corresponding to phenolic functional groups (84.52%), carboxylic acids

(6.65%) and lactone (2.17%). For the infrared assay, three different samples were analyzed: i) biochar without activation (ABCSA); ii) biocarbon activated with hydrogen peroxide (ABCpure) and biochar after adsorption of ibuprofen (ABCIBU) (Figure 1).

Figure 1. Infrared spectrum for ABC samples i) without activation, ii) activated with hydrogen peroxide and iii) after adsorption of ibuprofen.



Source: the authors

Since the region between 3700 cm-1 and 3400 cm-1 suggests the presence of OH- normally associated with hydrogen (Silverstein *et al*. 2005), it is believed, depending on the infrared result, that the hydroxyl group of ibuprofen is binding to hydroxyl groups of biochar by means of hydrogen bonds. As 84.52% of the surface of ABCpure corresponds to the phenolic functional group, hydrogen bonds may occur predominantly between the hydroxyl of the ibuprofen molecule and the hydroxyl of the phenolic functional group. In turn, in the range between 3300 cm-1 and 2500 cm-1, pronounced peaks correspond to axial deformations of OH- bonds of carboxylic acid groups. In this case, activation with hydrogen peroxide may have inserted carboxylic acids, since peaks in wavelengths 2925 cm-1 and 2853 cm-1 are more significant in ABCpure than in ABCSA.

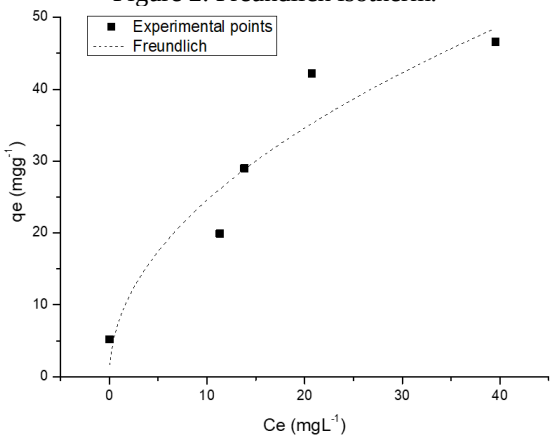
On the other hand, the pH determination assay showed that using pH 2, a more favorable ibuprofen adsorption was obtained with a removal of 71.2% (7.84 mg/g). As the ibuprofen molecule has a pka value of approximately 4.91, it is expected that at pH 2, the carboxylic acid group of the ibuprofen molecule is in its undissociated form, which would facilitate intermolecular interactions, such as hydrogen bonds between the adsorbent and adsorbate.

Regarding the mass assay, the value at which the highest adsorption capacity was obtained, i.e., the highest amount of ibuprofen adsorbed by ABC mass, was 0.1 g ABC (qe =

40.6 mg/g). For this qe value, the removal obtained was 75%. Thus, for the capacity and kinetic tests of adsorption, the mass of ABC was 0.1 g.

Regarding the adsorption capacity assay, there is no standardization regarding the number of points that an isotherm should have. Isotherms with 3, 4 or 5 points are found in scientific works. Thus, the adsorption capacity assay is presented in Figure 2, and the results were adjusted to the Freundlich model ($R^2 = 0.879$).

Figure 2. Freundlich isotherm.



Source: the authors

The Freundlich model describes the occurrence of adsorption on a heterogeneous and amorphoussurface that presents different adsorption energies and is not restricted to monolayer coverage.

The experimental results obtained for the adsorption of ibuprofen by the produced ABC indicate that the maximum value experimentally achieved for adsorption was 46.57 mg/g. Figueiredo (Figueiredo 2012), using activated carbon, also produced from coffee grounds and chemically activated with K2CO3 at 700 °C, obtained a maximum adsorption capacity of ibuprofen at 30

°C, equal to 149.5 mg/g, while using commercial activated carbon the adsorption capacity was 143.8 mg/g.

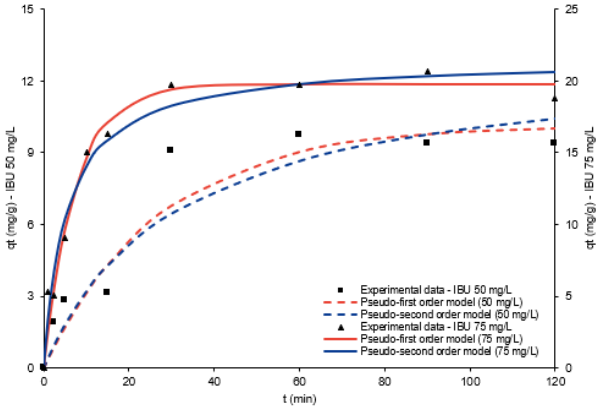
A satisfactory fit was not obtained for the Langmuir model, so it was removed from the results.

For the evaluation of the experimental data of ibuprofen adsorption kinetics in activated biocarbon, the experimental results obtained were adjusted using pseudofirst-order and pseudosecond-order kinetic equations. Thus, two different initial concentrations of ibuprofen

solution (50 and 75 mg/L) were established, and the results are presented in Figure 3.

From the analysis of the graphs, it is observed that the adsorption of ibuprofen occurred relatively quickly. In the first 15 min, a greater variation in the removal rate was noticed; however, equilibrium was established approximately 120 min from the beginning of the assay.

Figure 3. Adjustments for pseudofirst-order and pseudosecond-order models for IBU 50 mg/L and 75 mg/L solutions.



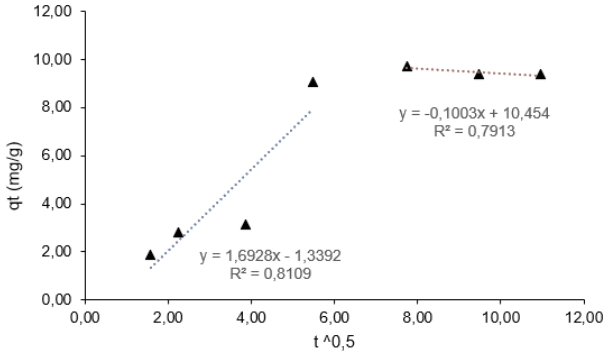
Source: the authors

Regarding the influence of the initial concentration of ibuprofen solution on the kinetics of the reaction, it can be observed that for the highest concentration (75 mg/L), an ibuprofen removal of 47.9% was obtained in the first 15 min, while for the concentration of 50 mg/L, the removal obtained in the same time interval was 14.6%.

In addition, the model for which the best fit was obtained was the pseudofirst-order with R^2 values of 0.9272 and 0.9798. Thus, the removal of ibuprofen achieved in equilibrium for IBU 50 mg/L solution was 9.407 mg/g and for IBU 75 mg/L solution was 18.815 mg/g. Therefore, as the pseudofirst-order kinetic model is characterized by not sharing or exchanging electrons between the adsorbent and the adsorbent, the adsorption rate is proportional to the number of free sites, describing a physisorption process.

For the IBU 50 mg/L solution, the kinetic model of intraparticle diffusion proposed by Weber and Morris was also applied (Dos Santos 2019). The results presented in the graph in Figure 4 demonstrate multilinearity, indicating that the adsorption process involves more than one mass transfer mechanism.

Figure 4. Adjustment of the kinetic assay for the intraparticle diffusion model for IBU 50 mg/L solution.



Source: the authors

4 CONCLUSSIONS

From the tests performed in the laboratory, the results indicated that for the ABC produced, the ZCP corresponds to pH 5.

The results of Boehm titration showed that ABC presented phenolic functional groups, carboxylic acids, and lactone on its surface. The infrared assay, in turn, indicated that the possible interaction between the ibuprofen molecule and the functional groups of activated biochar occurred through hydrogen bonds, mainly between the hydroxyl of the ibuprofen molecule and the hydroxyl of the phenolic functional group.

It was also verified that the best ibuprofen removal rates occurred at pH 2 and using an ABC mass of 0.1 g.

The model that obtained the best fit was the Freundlich model ($R^2 = 0.942$). The removal efficiency for an initial ibuprofen concentration of 120 mg/L was 70.2%.

In the study of adsorption kinetics, for the pseudofirst-order model, a removal of 9.407 mg/g was obtained for ibuprofen solution at 50 mg/L, and a removal of 18.815 mg/g was obtained for ibuprofen solution at 75 mg/L.

In the kinetic model of intraparticle diffusion proposed by Weber and Morris, it was possible to verify that the adsorption process under study involved more than one mechanism of mass transfer, that is, there was external diffusion and intraparticle diffusion.

After the tests and data analysis, it can be said that biochar produced from coffee grounds and activated with hydrogen peroxide presented satisfactory results, contributing to the removal of ibuprofen in aqueous medium.

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