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Eficiência do Biochar de Borra de Café na Adsorção de Diclofenaco

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R E S U M O

A crescente presença de compostos farmacêuticos em ambientes aquáticos gera desafios ambientais significativos. Os sistemas tradicionais de tratamento de água têm dificuldade em remover completamente esses poluentes, resultando em sua liberação no ambiente com impactos de longo prazo nos ecossistemas aquáticos e na saúde pública. Este estudo investiga a eficácia do biochar derivado de borra de café (CGB) na remoção de diclofenaco de soluções aquosas, utilizando uma abordagem dinâmica via simulação de barreiras 2D em colunas multicamadas sob condições controladas. As propriedades hidrodinâmicas das colunas foram caracterizadas usando Br^- como traçador. A retenção de diclofenaco foi então analisada, juntamente com sua mobilidade em um fluxo de água realista. Os resultados mostraram boa reprodutibilidade dos experimentos e uma retenção moderada de diclofenaco pelo CGB testado, com coeficientes de distribuição variando entre 8,30 e 12,97 $cm^3\ g^{-1}$. Sem otimização do processo, a eficiência de remoção foi calculada em 40% (± 14%) para um tempo de contato de apenas 7 horas. As curvas de ruptura do traçador e do diclofenaco foram ajustadas à equação de convecção-dispersão (modelo CDE) e suas versões CDE-2SS e CDE-MIM. Os resultados foram bem representados pela abordagem CDE, fornecendo parâmetros consistentes para transporte reativo e adsorção efetiva de diclofenaco no CGB, com fatores de retardo oito vezes maiores do que para o KBr. Em conjunto, nossos resultados sugerem que, embora não otimizado, o CGB oferece uma abordagem promissora para a remoção de fármacos como o diclofenaco da água. Investigações adicionais são necessárias para melhorar tanto a reatividade do biochar quanto as condições de transferência em colunas.

Palavras-chave: biochar de borra de café, modelo de convecção-dispersão, adsorção de diclofenaco, remediação ambiental.

Efficiency of Coffee Ground Biochar in the Adsorption of Diclofenac

A B S T R A C T

The increasing presence of pharmaceutical compounds in aquatic environments triggers significant environmental challenges. Traditional water treatment systems struggle in fully removing such pollutants, leading to their environmental release and long-term impacts on aquatic ecosystems and public health. This study investigates the effectiveness of biochar derived from coffee grounds (CGB) to remove diclofenac from aqueous solutions. The capacity of diclofenac retention of this biochar was evaluated using a dynamic approach, simulating a 2-D barrier with three-layer columns under controlled conditions. The hydrodynamic properties of these biochar columns were characterized using Br^- as a non-reactive tracer. The retention of diclofenac was then characterized along with its mobility at a realistic water flow. The results showed a good reproducibility of the experiments and a low to moderate retention of diclofenac by the tested CGB, with distribution coefficients ranging between 8.30 and 12.97 $cm^3\ g^{-1}$. Without process optimization, removal efficiency was calculated to be 40% (± 14%), with a short contact time of around 7h. The breakthrough curves of both the tracer and diclofenac were fitted with the convection-dispersion equation (CDE model) and with its CDE-2SS and CDE-MIM versions. Results were well represented with the convection dispersion approach, giving consistent reactive transport parameters, suggesting that CGB effectively adsorbed diclofenac, with retardation factors eight times larger than on KBr. Altogether, our results suggest that, although not optimized, CGB offers a promising approach for removing pharmaceuticals such as diclofenac from water. Further investigations are needed to improve both biochar reactivity and transfer conditions in columns.

Keywords: coffee grounds biochar, conversion-dispersion model, diclofenac adsorption, environmental remediation.

Introduction

The contamination of surface water and groundwater by pharmaceutical compounds has become an increasingly important environmental concern in recent decades (Chapman, 2006; Archundia et al. 2018; Noronha et al., 2021; da Silva et al., 2023; Sanusi et al., 2023). The presence of these pharmaceuticals and drugs in water bodies is a challenge for conventional water treatment systems, such as Waste-water Treatment Plants (WWTP), which are unable to completely remove this family of contaminants (Ghiselli, 2006; Aguiar and Machado, 2022). This situation is particularly worrying because of the potential toxic effects on aquatic fauna, as well as the growing antimicrobial resistance associated with prolonged exposure to pharmaceutical products (Noronha et al., 2021).

Diclofenac (DCF), widely used in human and veterinary treatments, is a drug with a high environmental impact, released into the environment mainly through excretion and inappropriate disposal of medicines (da Silva et al., 2023). DCF is a widely prescribed non-steroidal anti-inflammatory drug. It is characterized by its high toxicity and low biodegradability. It is frequently detected in wastewater and water bodies throughout the world (Sundararaman et al., 2022). In addition, DCF contamination of water, generally produces adverse effects ranging from hormonal changes in aquatic organisms to the mortality of sensitive species such as fish and birds (Chapman, 2006; da Silva et al., 2023). Some authors have demonstrated cytological effects in the liver, kidneys, gills, and intestines of rainbow trout exposed to the drug (Schwaiger et al., 2004; Triebskorn et al., 2004). Adverse effects of DCF on brown mussels have also been reported (Fontes et al., 2018), highlighting bioaccumulation and tissue damage at low environmental concentrations (Lonappan et al., 2016), as well as inhibition of immune responses in freshwater fish exposed to DCF (Ribas, Zampronio and de Assis, 2016). Therefore, the effective removal of this drug from wastewater could be considered an environmental priority, mainly because traditional water treatment techniques, such as filtration and biological processes, have proven insufficient for the complete removal of DCF and many other emerging compounds (Gamarra Jr. et al., 2015; Noronha et al., 2021). In this context, the use of alternative adsorbents to collect or filter contaminants appears to be a promising solution (Carvalho et al., 2021).

Biochar is one of such solutions, which has proved to reduce organic residues and removal of toxic compounds from the environment (Hoslett et al., 2021), mitigate the pollution regarding unsecured waste disposal and green remediation (Al Masud et al., 2023), improve soil quality and fertility (Sisay et al., 2023), and as complementary treatment of contaminated water (Carvalho et al., 2021; Présiga-López, Rubio-Clemente and Pérez, 2021). Biochar is a carbon-rich material produced through the pyrolysis of biomass at high temperatures under oxygen-limited conditions. Most pyrolytic biochars exhibit high specific surface areas, ranging from 50 to 500 $m^2\ g^{-1}$ depending on the feedstock and pyrolysis

conditions; moderate porosity with a predominance of micropores; permeability; and abundant functional groups (mainly at the micro surface level), such as carboxyl, hydroxyl, and phenolic groups, which enhance their adsorption capacity by promoting interactions with contaminants, especially negatively charged ones (Wang and Wang, 2019; Liu et al., 2022; Wood et al., 2023). These characteristics make biochars ideal adsorbents for mitigating surface waters and groundwater contamination, mainly from organic and pharmaceutical pollutants (Carvalho et al., 2021).

Biochar prepared from pyrolysis of various agro-wastes, including coconut, rice straw and husks, coffee grounds, bamboo, cassava, sawdust, Prosopis juliflora, has been successfully applied for removing antibiotics such as ibuprofen, tetracycline, sulfamethoxazole, norfloxacin, trichloroethylene, carbamazepine, diclofenac, acetaminophen, and ofloxacin (W. Wang et al., 2022; Ashebir et al., 2024). Biochar from organic feedstock of homes, businesses and agricultural waste was able to reduce the presence of antibiotics in the environment (Hoslett et al., 2021). Acetone washing biochar and nitric-acid washing biochar derived from bagasse showed promising potential for antibiotic contaminants removal from water under multi-interference conditions (W. Wang et al., 2022). Out of the liquid phase, biochars have been an efficient and low-cost application for removing the gaseous pollutants in combustion flue gas, including SO_2, NO_X, Hg, CO_2 and VOC (Wen et al., 2023), and on catalytic applications, for tuning gasification process during sustainable approaches for hydrogen production (Bartoli, Giorcelli and Tagliaferro, 2023).

Among these agro-wastes, coffee grounds is a relatively inexpensive and easily available row material (Maged et al., 2021; Nunes et al., 2023). Indeed, coffee is one of the most widely consumed products globally, which generates large volumes of waste, making it a promising source for the production of biochars with environmental applications (Zungu et al., 2022; Khan et al., 2023). It is also important to highlight that the production of biochar from coffee grounds aligns with the principles of the circular economy, maximizing the use of organic waste and reducing the environmental impacts associated with improper disposal (Skorupa, Worwąg and Kowalczyk, 2023). This contributes not only to the management of agricultural residues but also to the development of more sustainable technologies.

Coffee grounds biochar (CGB) has been considered as absorbent material in numerous environmental applications, such as soil improvement and remediation, mainly for fertility, carbon sequestration, and wastewater treatment (Sohi, 2012; Wang and Wang, 2019; Présiga-López, Rubio-Clemente and Pérez, 2021; Al Masud et al., 2023). It has been effective for a tetracycline derivative antibiotic removal by adsorption and catalytic degradation (Y. Wang et al., 2022); was considered a good adsorbent for the emerging pollutant Norfloxacin, removing 99.85% from a 24.69 $mg\,L^{-1}$ contaminated wastewater (Nguyen et al., 2022); was recently highlighted as an efficient adsorbent for removing textile dyes from effluents (Nascimento et al., 2024), and for recovery phosphate from wastewater, in that case, by using a Mg/Zr modified nanobiochar (Sisay et al., 2023). Similarly, CGB obtained by carbonization at 500 ºC and then functionalized with hydrogen peroxide was reported as efficient for fluoride (F^-) removal from aqueous solutions (dos Santos et al., 2024).

Nevertheless, concluding remarks about the effectiveness of CGB in the removal of pharmaceuticals and reliable sorption rates are still limited, mainly because major part of these studies is supported by batch mode experiments at chemical equilibrium. Maged et al. (2021) indicate that the porous structure of biochar can promote contaminant adsorption in batch conditions; and sorption rates are largely overestimated for longer contact times with the biochar (Qiu et al., 2022). Besides, batch sorption experiments do not account for frequent kinetic effects linked to the co-existence of micro- and macro-porosity fractions present in most biochar materials. Thus, further research is needed to better understand and describe sorption process in CGB, in more realistic conditions. Authors defend the hypothesis that using column experiments conducted under saturated conditions on multi-material layers, mimicking common on-site treatment set-ups, will provide more reliable experimental data about the capacity of CGB to remove DCF from aqueous solutions, as well as hydrodispersive parameters for simulations, evaluating its effectiveness as an adsorbent material.

This study evaluates the DCF retention capacity by CGB, using saturated sand/biochar columns under very simple controlled laboratory conditions. Columns consist of a layer of finely ground CGB placed between two layers of inert sand, which stabilize the biochar, avoid clogging of

the column membranes and limit biochar leaching out of the columns. The parameters quantifying the reactive transfer of DCF in columns were obtained by fitting the data with 3 CDE models such as the dispersion coefficient and the retardation factor, both essential for understanding the reactive transfer of DCF through the biochar columns. The authors wish to contribute to the development of an accessible and sustainable technology for the removal of pharmaceuticals from effluents, in order to promote the protection of water resources and environmental health in areas lacking efficient pharmaceutical treatment plants.

Material and Methods

Coffee ground biochar

The biochar was produced from coffee grounds, a low-cost waste product collected in cafés of the city of Garanhuns, in the Brazilian state of Pernambuco. The pyrolysis process was carried out at 530 °C in a low-oxygen environment for 10 to 12 hours, in order to maximize the formation of fixed carbon and reduce unwanted volatile compounds (Lima et al., 2018). After production, the biochar was washed with distilled water (DW) to remove impurities and residual volatile compounds that could interfere with adsorption.

The point of zero charge (PZC) of the biochar produced was estimated by measuring the initial pH (pH_0) and the final pH (pH_f) of several biochar suspensions, adjusting pH_0 from 1.0 to 11.0 at room temperature (26 °C ± 2 °C), and reading pH_f after stirring for 24 hours (Rufasto and Huamani, 2023). The PZC was obtained by plotting the $pH_f - pH_o$ differences vs. pH_0 and taking the pH value where the difference is zero.

Sand

The quartz sand was first washed and sifted with an average diameter of 0.5 mm. This sand was used as support material, forming the upper and lower layers to fix the biochar to the center of the infiltration columns and to ensure uniform flow and stability during the experiments.

Column setup

Three Cytiva XK26 glass column setup, all conforming to three layers with a total height of 5 cm each: 1 cm of the sieved quartz sand at the bottom, followed by 3 cm of biochar, and a further 1 cm of the same quartz sand at the top. The pressure applied at the top to set up the columns was carefully controlled to avoid the formation of voids that could affect the tracing results, and sorption and transport assays.

Calcium chloride

A solution of 5.5 g L^{-1} $CaCl_2$ in DW was used to saturate the adsorption columns from bottom to top. Saturation is necessary to stabilize the adsorbent materials prior to the contaminant injections, thus preventing variations in sorption capacity. This is the common practice in solute transport studies (Scheytt, Mersmann and Heberer, 2006; Mastrocicco et al., 2011; Archundia et al. 2019) and aims to reproduce real environmental conditions where dissolved salts are often present, with the interest of stabilizing soil colloidal phases, thus limiting column clogging.

Potassium bromide

KBr is a conservative compound with that exhibits almost no interactions with pyrolytic porous media (Mastrocicco et al., 2011). The bromide ion (Br^-) is frequently used as a tracer to assess the hydrodynamic characteristics (advection and dispersion) of porous media usd for displacement experiments. Tracing experiments permit to obtain accurate estimates of the hydrodispersive parameters (Martins and Mermoud, 1998; Mastrocicco et al., 2011; Labrecque and Blanford, 2021). A solution of KBr at 3.57 g L^{-1} in DW was used as a non-reactive water tracer (bromide ion, Br^-).

Diclofenac

Diclofenac (2 - [2 - (2,6 dichlorophenyl) amino] phenylacetic acid) is a model contaminant (DCF), widely used as an anti-inflammatory in human medicine, with notable persistence in aquatic environments (Lonappan et al., 2016; Sundararaman et al., 2022; Sanusi et al., 2023). It is a weak organic acid with a pKa of 4.15, indicating that anionic DCF species dominate in solution above pH 4.15. DCF used in all experiments (CAS 15307-79-6 and EC 239-346-4) was purchased from Sigma-Aldrich® (São Paulo, Brasil).

A DCF stock solution was prepared by dissolving the appropriate quantity in DW with 1% CH_3OH to obtain a stock solution of around 1.0 g L^{-1}. The solution was stored at 4°C in obscurity to ensure stability throughout the study.

Column saturation procedure with $CaCl_2$

All experimental columns were initially weighed after careful introduction of dry sand and

biochar, as described by Martins and Mermoud (1999), and then saturated with a 0.05 mol L^{-1} $CaCl_2$ solution as described above, by upward injection into the columns (bottom to top), at a flow rate of 0.18 mL min^{-1}, using a 4-channel Ismatec Reglo ICC peristaltic pump. The saturation process was maintained for 24h, ensuring complete stabilization of the adsorbent material (Scheytt et al., 2006; Mastrocicco et al., 2011). Pore volume of each column was estimated by mass difference before and after saturation and also controlled before and after each breakthrough experiment.

Transport assays with KBr and diclofenac

These are the central experiments in this study. Sorption and transport test were carried out first with the Br^- tracer in aqueous solution, and then with the DCF solution in the three columns, under identical set-up conditions. KBr was injected into the columns at flow rates ranging between 10.12 to 13.47 mL h^{-1}, corresponding Darcy flux between 1.89 and 2.51 cm h^{-1}, and effluent samples were collected during 8 min. using a Spectrum CF-2 Fraction Collector for further analysis.

Bromide and DCF analysis

All samples collected during the tracer tests were analyzed for Br^- concentration using a Thermo Scientific Orion Star A214 Ionometer, after electrode calibration against a series of Br- standard solutions of increasing concentration. DCF concentrations were determined by High-Performance Liquid Chromatography (HPLC): Waters ArcHPLC equipped with an XSelect C18 column and a diode array detector (PDA DAD), with chromatographic conditions including a mobile phase composed of methanol (35%) and ultrapure water (65%), a flow rate of 1 mL min^{-1}, and DCF detection at 204 nm.

Convection-Dispersion Equation (CDE) models
CDE model

The CDE is one of the fundamental equations for describing solute transport in porous media (Scheytt et al., 2006). It considers transport by convection, which is the advective movement of solutes driven by the flow of water, and dispersion, the spreading of the solute due to molecular diffusion and variations in the flow velocity and characteristics of the porous medium. This formalism can be written as follows:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} \quad (1)$$

where R is the retardation factor, useful to quantify the interactions between DCF and biochar; C is the DCF normalized concentration (C/C_0) in the fluid phase; D is the hydrodynamic dispersion coefficient, which combines the effects of molecular diffusion and mechanical dispersion; z is the vertical normalized height in the column; v is the average advective pore velocity; and t is time.

This model was used to describe the global transport of the bromide tracer and DCF in saturated columns. To evaluate the potential existence of complex DCF interactions with Biochar, involving at least two different retention sites (strong and weak sorption), we also fitted the data with the CDE-2SS model. Similarly, to evaluate the effect of the potential water fractionation into mobile and immobile phases on the two solutes transport inside the columns, we also fitted the data with the CDE-MIM model.

CDE-2SS model

The CDE model with two sorption sites (CDE-2SS) considers that the solute can interact with two different sites of biochar varying in affinity and with instantaneous and kinetic sorption. If such types of retention sites are present in biochar, DCF breakthrough curves should present asymmetrical shape and the CDE-2SS model will correctly fit the data. Such variable adsorptive affinities of adsorbent surface areas have already been described for biochar (e.g. Labrecque and Blanford, 2021). The CDE-2SS model is described with the following equations:

$$\beta R\frac{\partial c_1}{\partial T} + \omega\,(c_1 - c_2) = x - \mu c_1 \quad (2)$$

$$\omega\,(c_1 - c_2) = (1-\beta)R\frac{\partial c_2}{\partial T} \quad (3)$$

$$x = \frac{1}{P_e}\frac{\partial^2 c_1}{\partial z^2} - \frac{\partial c_1}{\partial z} \quad (4)$$

where β is the partition coefficient between the two sites; c_1 and c_2 are the solute concentrations at sites with (1) and without (2) equilibrium, respectively, or the equivalent faster and slower sorption sites; T is time on a dimensionless scale; μ is a solute degradation constant; P_e is the Péclet number; and ω is the Damköhler number. The remaining

parameters are the same as for the CDE general equation.

CDE-MIM model

The CDE model with two regions (mobile and immobile, CDE-MIM), considers that solute flow does not occur homogeneously throughout the porous medium (Gaudet et al., 1977; Van Genuchten and Wagenet, 1989). In some regions of the porous medium, the solute may diffuse to immobile water regions and remain "immobilized" for some time, while in others, the solute flows freely in mobile water regions (Martins and Mermoud, 1999; Mastrocicco et al., 2011; Larin and Polunina, 2023). This heterogeneity can affect solute transport since part of the solute may be retained in immobile water zones, resulting in additional retardation with usually a progressive elution of the solute as a curve tailing (Larin and Polunina, 2023). The CDE-MIM model is described as follows:

$$\frac{\partial \theta_m \cdot C_m}{\partial t} + \frac{\partial \theta_{im} \cdot C_{im}}{\partial t} = \frac{\partial K_m}{\partial z} - v_m \frac{\partial \theta_m \cdot C_m}{\partial z} \quad (5)$$

$$K_m = \theta_m D_m \frac{\partial C_m}{\partial z} \quad (6)$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \quad (7)$$

where C_m and C_{im} are the solute concentrations in the mobile and immobile regions, respectively; θ_m and θ_{im} are the volumetric water contents of the mobile and immobile fractions, respectively; v_m is the average water velocity in the mobile region, t is time; z is the vertical position along the column; D_m is the hydrodynamic dispersion coefficient in the mobile water region; and α is the exchange coefficient between the two water fractions. This model is especially relevant to fit asymmetrical breakthrough curves by efficiently reproducing curve tailing induced by the progressive restitution of solute trapped in immobile water regions.

Software

The STANMOD software is widely used for evaluating solute transport in porous media using analytical solutions of the Equations 1 to 7 (Van Genuchten, 1980; Van Genuchten et al., 2012). STANMOD 2.08 was used in this study for fitting experimental data with the three models in the CXTFIT 2.0 package. It was used to identify independently the hydrodynamic parameters (P_e, ω and β) by fitting the observed tracer breakthrough curves (BTCs) (Martins and Mermoud, 1999). Assuming that hydrodynamic parameters remain constant in the columns, the other DCF transport parameters (R, D, f) were determined by fitting DCF BTCs, in a dimensionless form expressed by the following relations:

$$P_e = \frac{V_m L}{D} \quad T_0 = \frac{V t_p}{L} \quad R = 1 + \frac{\rho_d K}{\theta} \quad (8)$$

$$\beta = \frac{\theta_m + f \rho_d K}{\theta + \rho_d K} \quad \omega = \frac{\alpha L}{q} \quad \psi = \frac{\mu L}{V} \quad (9)$$

where P_e is the Péclet number; T_0 is the dimensionless pulse duration, V is the pore water velocity, R is the retardation factor; β is the mobile water zone for the tracer; ω is the solute dimensionless transfer coefficient between the mobile and immobile water zones; and L is the total column length (Martins and Mermoud, 1999).

Results and Discussion

As a result of simultaneous and numerous sorption mechanisms, the sorption capacity and sorption distribution coefficient of biochars are largely dependent on pH (Peiris et al., 2017; Sharma et al., 2022). The pH of the produced CGB was measured as 9.65, higher than the pH of the coffee grounds (in natura), which was 5.25. This pH increase agrees with previous observations related to similar biomass, and it is assumed to be due to alkaline groups generated in biochar during pyrolysis (Yuan et al., 2011; Kim et al., 2014).

The results of the measurement of the Point of Zero Charge (PZC) of biochar are presented in Figure 1. The crossing point in Figure 1 indicates that the PZC of the CGB is around 8.29, which means that the biochar's surface charge is positive below this pH value, neutral in solutions or surrounding medium conditions with pH ≈ 8.29 (Wang and Wang, 2019), and negative above this value. The PZC in this study was found to be almost 2.5 units higher than the reported value for similar biochar preparation (Zungu et al., 2022), suggesting that the obtained biochar surface needs more basic solutions to be negatively charged. In the Sand-Biochar columns used in this study, solution pH was measured around 6.8 ± 0.2, confirming that the biochar surface should exhibit a net positive charge at this pH (because it is lower than the PZC value).

The pH of the column effluents was around 7.34. Since the pKa of DCF is 4.24, it appears that anionic DCF species dominate above the pKa, and

especially at the pH of the column effluent above, at which the biochar is positively charged, thus favoring interactions with DCF and enhancing the adsorption capacity of the used CGB.

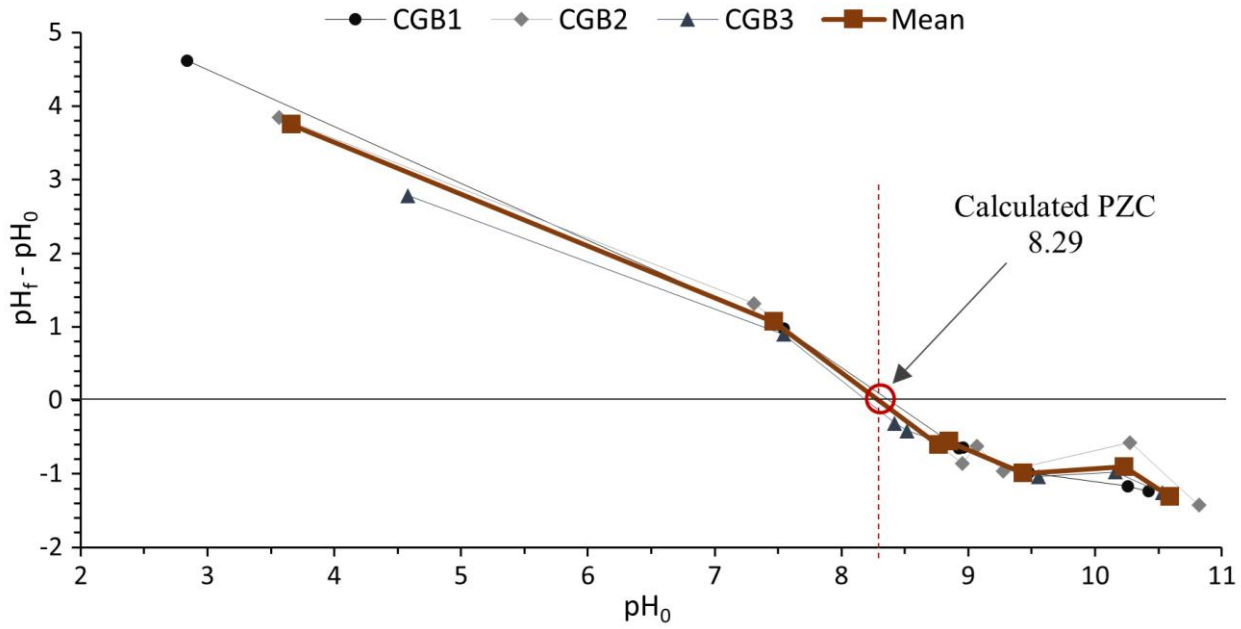

Figure 1. Point of zero charge (PZC) of coffee grounds biochar (CGB). Three replicates were considered (CGB1, CGB2, and CGB3), and the PZC value was obtained from where $pH_f - pH_0 = 0$ in the curve of the mean differences.

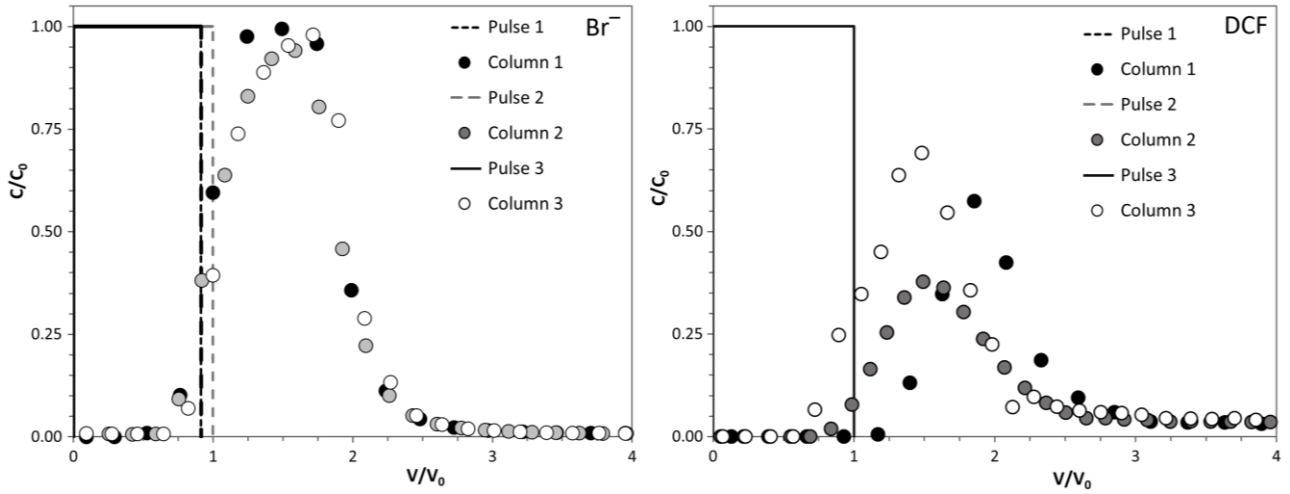

Figure 2. Breakthrough curves of Bromide tracer (left) and Diclofenac (right) measured in three water-saturated Sand-Biochar columns. C/C_0 is the ratio of the effluent to influent concentrations, V/V_0 is the eluted pore water velocity q from 1.89 to 2.51 cm h^{-1}, $[KBr]_o$ = 3.45 g L^{-1}, pH = 7.3 ± 0.2.

Table 1. Experimental parameters used in the miscible displacement assays with Br^- in sand-biochar columns.

Column	n	ρ_d (g cm^{-3})	V_p (cm^3)	θ_s	q (cm h^{-1})	v (cm h^{-1})	T_{pulse} (h)
1	0.61	0.937	8.88	0.363	2.49	6.86	0.564
2	0.61	0.937	9.96	0.372	2.51	6.74	0.742
3	0.61	0.937	8.71	0.326	1.89	5.81	0.861

n – average porosity; ρ_d – sand-biochar apparent density; V_p – pore volume; θ_s – saturated volumetric moisture; q – Darcy flux; v – average pore water velocity; T_{pulse} – pulse duration.

Br^- tracer experiments in Sand-Biochar columns

Table 1 reports the pre-set parameters and experimental conditions applied in the miscible displacement assays for the Br^- tracer. These parameters characterize the experimental assembly of the columns and are fundamental for understanding the results of this research. The bromide breakthrough curves (BTC) obtained in the three Sand-Biochar columns are presented in Figure 2 (left). The three BTCs appear symmetrical and with similar shapes in the three columns, indicating a good experimental reproducibility, despite the difficulty of finely reproducing introduction of CGB into columns. The residence times of Br^- tracer were 45, 46 and 52 minutes in columns 1, 2, and 3, respectively.

Characterization of hydrodynamic parameters

To characterize the hydrodynamic properties of the Sand-Biochar columns, bromide BTCs were fitted the CDE, CDE-MIM and CDE-2SS models. Figure 3 presents these fittings in the three Sand-Biochar columns obtained with the CXTFIT 2.0 module in STANMOD software; and Table 2 shows the values of the hydrodynamic parameters optimized by fitting the bromide tracer BTCs in the STANMOD software (Van Genuchten et al., 2012). It can be observed that the three models give very similar fittings for the three curves (Figure 3), along with similar parameter values (Table 2). This shows that the simplest CDE model can be used to correctly model water movement in the three independant Sand-Biochar columns. Neither of the 2-regions or 2-sites models improve significanltly Br^- BTCs fittings. This suggests that the whole water inside the column is mobile and contributes to water flow. The 2-sites model is also useless as the tracer is conservative and presents not interaction with biochar and consequently no retardation.

Bromide has been widely used as a water tracer in many reactive transport studies in porous media, due to its non-reactive properties (Martins et al., 1999; Mastrocicco et al., 2011; Labrecque and Blanford, 2021). As a conservative non-reactive tracer, Br^- retardation factor (R) was set to 1 and, depending on the model used, the v, D, f, and ω parameters were adjusted. The conservative property of Br^- was confirmed as the recovery rates were 100%, 94.08%, and 98.57% for columns 1, 2 and 3, respectively.

Analysis of the coefficients of determination (r^2 in Table 2) shows that the CDE model fits the Br^- experimental BTCs very well, with values greater than 0.99 for the three columns.

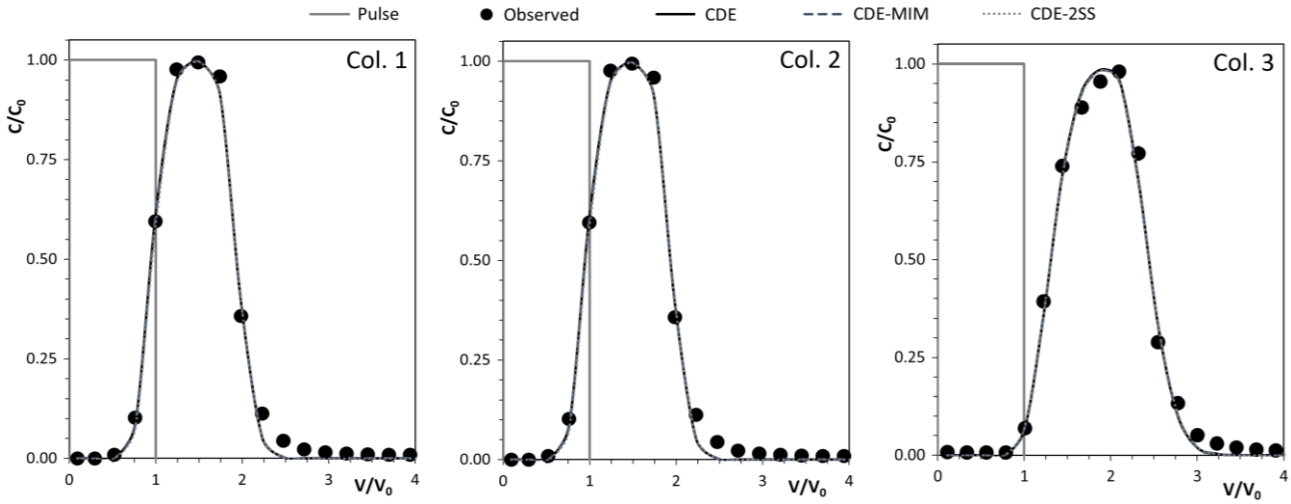

Figure 3. Fitting of bromide breakthrough curves with the CDE, CDE-MIM and CDE-SS models. The corresponding parameters are presented in Table 2.

Table 2. Hydrodispersive parameters obtained by fitting the miscible displacement assays of the KBr tracer via the three models (CDE, CDE-MIM and CDE 2SS). Font: Vasconcelos et al. (2024).

Column	Model	$D\ (\mathrm{cm^2\ h^{-1}})$	R	β	r^2	P_e
1	CDE	0.311 ± 0.031	1.04		0.996	
	CDE-MIM	0.316 ± 0.033	1.02	0.975 ± 0.096	0.996	110.65
	CDE-2SS	0.346 ± 0.076	1.05	0.985 ± 0.201	0.980	
2	CDE	1.111 ± 0.057	1.00		0.997	34.67

	CDE-MIM	0.863 ± 0.041	1.08	0.913± 0.016	0.999	
	CDE-2SS	0.944 ± 0.071	1.05	0.952 ± 0.022	0.999	
3	CDE	0.371 ± 0.035	1.00		0.995	
	CDE-MIM	0.384 ± 0.044	1.00	0.999 ± 0.126	0.995	76.45
	CDE-2SS	0.387 ± 0.001	1.00	0.999 ± 0.126	0.995	

D – hydrodynamic dispersion coefficient; R – retardation factor; β – partition coefficient between mobile and immobile water fractions; r^2 – coefficient of determination, P_e – Peclet number. The D and β values are reported as the mean ± standard error interval.

With regard to the Peclet number (P_e) values, it is possible to verify that Br^- transport is predominantly convective, showing $P_e > 10$ at the tested pore water velocity (around 6.5 cm h^{-1}) in the three columns (around 110.65 in column 1).

Reactive transport tests with DCF

The elution curves depict the ratio of the effluent DCF concentration (C) to the initial DFC concentration (C_0) as a function of the pore-volume fraction (V/V_0). They provide valuable insights into the hydrodynamic and adsorption profile of diclofenac in the sand-biochar columns. The pre-set parameters and experimental conditions applied in the miscible displacement assays for DCF were the same as for Br^- tracer (Table 2), except for the DCF pulse duration, which were 34, 52 and 51 minutes, for columns 1, 2, and 3, respectively.

Diclofenac breakthrough curves are presented in Figure 2 (right). Different from Br^-, these BTCs present much lower dimensionless concentrations, suggesting the existence of complex irreversible interactions with column material, and are also significantly asymmetrical and retarded (R > 1), indicating the existence of reversible interactions with CGB, with further slow restitution of the pharmaceutical in the effluent. This is confirmed by low recovery rates calculated for the three BTCs (see below).

Assuming that hydrodynamics remain constant in the columns for Br^- tracer and DCF displacement assays, it is useless to use the CDE-MIM model for fitting the DCF curves (no mobile water). In the other hand, the CDE-2SS model can be further applied to DCF experimental results in order to evaluate the presence of several retentions sites at biochar surface. Therefore, the three DCF BTCs were fitted with the CDE and CDE-2SS models. The corresponding curves and parameters are presented in Figure 4 and Table 3.

The results show that the two models correctly fit the three DCF BTCs (Figure 4). However, the CDE model can clearly not fit the tailing observed in each of the three curves that is characteristic of a process of slow restitution of solutes retained on kinetic sorption sites of biochar.

On the contrary, the CDE-2SS model fits very well the whole curve, including the tailing. This was expected with this model that accounts for two retention sites of variable affinity and strength. Table 3 shows that the three BTCs present significant retardation factors (R), ranging between 2.47 and 6.77, with an average value of 4.04, in agreement with previous studies, which obtained similar diclofenac retardation factors, *e.g.*, 4.80 (Scheytt et al., 2006).

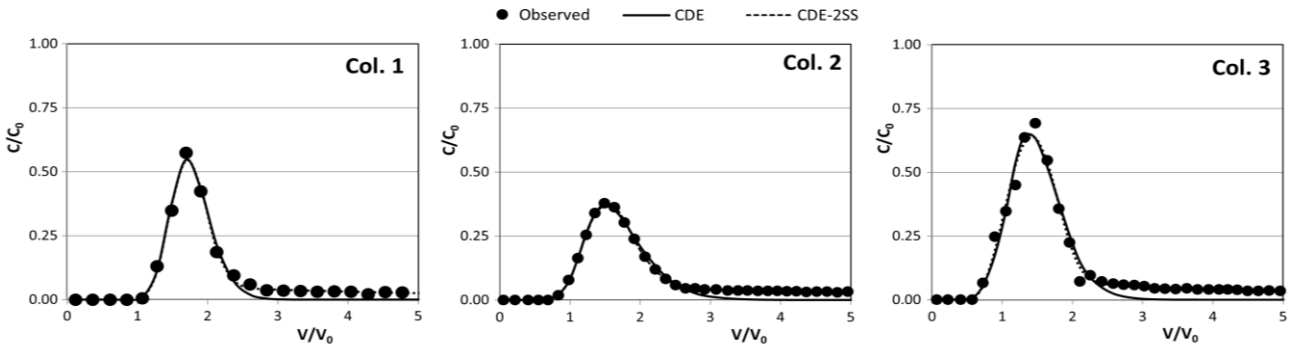

Figure 4. Fitting of Diclofenac breakthrough curves with the CDE and CDE-2SS models. The corresponding parameters are presented in Table 3.

Table 3. Hydro-dispersive parameters obtained by fitting the CDE-2SS model to the miscible displacement data of DCF in the three adsorptive columns. Font: Vasconcelos et al. (2024).

Column	r (%)	$D\ (\mathrm{cm^2\ h^{-1}})$	R	β	ω	P_e	$K_d\ (\mathrm{cm^3\ g^{-1}})$	r^2	τ (h)
1	60.80	0.30 ± 0.02	2.90 ± 0.3	0.48 ± 0.05	0.49 ± 0.04	112.7	4.17	0.994	1.113
2	46.40	1.01 ± 0.02	6.77 ± 0.34	0.25 ± 0.01	0.75 ± 0.02	33.40	6.61	0.999	1.450
3	72.51	0.67 ± 0.11	2.47 ± 0.40	0.44 ± 0.07	0.44 ± 0.05	43.29	2.80	0.985	1.074
Average	59.90	0.66	4.04	0.39	0.56		4.53		1.212

r – Recovery; D – hydrodynamic dispersion coefficient; R – retardation factor; β – partition coefficient; ω - Damköhler number; P_e – Peclet number; K_d – distribution coefficient; r^2 – coefficient of determination; τ – residence time, calculated as $\tau = L/vR$. The D, R, β and ω values are reported as the mean ± standard error interval.

The use of the CDE-2SS model allowed clearly for a more accurate assessment of the transport and retention processes of DCF in the Sand-Biochar columns tested. For this model, β represents the partition coefficient of DCF between the sorption sites. The β values range from 0.25 ± 0.01 to 0.48 ± 0.05, which indicates a moderate and consistent fraction of DCF in the fast-sorbing sites within the CGB. On the other hand, the Damköhler numbers (ω in Table 3) provide important insights into the relationship between the kinetics of sorption and the transport processes in the columns. Very small values (< 1) suggest that transport is faster than sorption; values around the unit (≈ 1) indicate that both sorption kinetics and transport processes are significant and co-dominate the overall rate of sorption; and finally, greater values (> 1) indicate that sorption is faster and controls the overall process (Scheytt et al., 2006). The ω values for this study were around 0.56 (Table 3), which suggest conditions where both transport and reaction kinetics play a significant role.

Both parameters (β and ω) are consistent over all CGB columns in the CDE-2SS model, indicating that it well captures the transport behavior of DCF in the columns; and P_e numbers for both models (CDE-2SS and CDE-MIM) denote predominantly convective transport in all columns.

The significant interactions of DCF with CGB is confirmed by low mass balances calculated for the three curves, permitting to calculate recovery rates of 60.80%, 46.40%, and 72.51% for columns 1, 2, and 3, respectively, with an average recovery of 59.9% (± 13.8%). These results indicate that even without any optimization of the CGB (*i.e.*, production, activation, drying), and with quite low residence times ($\tau \approx 1.212$ h, Table 3) in the columns, the CGB has the capacity to retain around 40% of the injected DCF. This corresponds to approximately 71 $\mathrm{mg\ g^{-1}}$ in the used set-up column experiments, which agrees with the range reported as appropriate in order to use biochars for the removal of contaminants from water environments (9–309 $\mathrm{mg\ g^{-1}}$), as for instance, ibuprofen (Zhan, Ye and Hou, 2023).

Favre et al. (2022) observed similar values with activated biochar (45% retention), while non-activated biochar presented lower retention, 19%. However, other studies using activated biochars obtained higher retention efficiencies (Jung et al., 2015; Czech et al., 2021). Other works based on molecular modeling offer interesting perspectives with the use of specifically activated biochars (Mrozik et al., 2021; Sochacki et al., 2024).

Noteworthy that the retention capacity obtained in this study (40% ≈ 71 $\mathrm{mg\ g^{-1}}$) is higher than the 38.52 $\mathrm{mg\ g^{-1}}$ observed when using CGB with a 232 $\mathrm{m^2\ g^{-1}}$ surface area (Zungu et al., 2022); and very close to the removal capacity of *Prosopis juliflora* biochar for sulfametoxazol in real wastewater treatment, 76.7% (Ashebir et al., 2024); However, it is very small related to the adsorption capacity of biochar from sunflower seed to DCF, 692 $\mathrm{mg\ g^{-1}}$, estimated under activated conditions by fitting the Langmuir isotherm to batch-experiment data (Alvear-Daza et al., 2023). This is the main difference between batch and column modes. The batch sorption experiments enforce biochar to be in contact with the contaminated solution for a long time until equilibrium (more than 500 minutes in the referred works), with possibly higher adsorption rates and no hydrodispersive considerations. In the present study, the total residence time in the column was only 73 minutes, thus considering rates by unit time, retention in this work is better described.

Using the equation of the R factor (Equation 8), we calculated theoretical solid/water distribution coefficients (K_d) for DCF in the three columns, which ranged between 2.80 to 6.61

$cm^3\ g^{-1}$, with an average value of 4.53 (Table 3). According to Labrecque and Blanford (2021), these K_d values are moderate (in the range of 5-50 $cm^3\ g^{-1}$), and this indicates a moderate DCF sorption capacity of the CGB. These values agree with other works on DCF retention by biochar such as Lima-Schillo et al. (2021) and suggest that after adapted activation (to be further studied), coffee-grounds biochar (produced from a massive urban waste) could be a sustainable and effective alternative for diclofenac removal from polluted aquatic systems.

All these results show that CGB is capable of significantly retaining DCF, mainly through physical adsorption via non-bonded long-range interactions like van der Waals forces, with more limited chemical interactions. This was formerly suggested when using non-activated biochars to retain organic compounds (Wang and Wang, 2019). Furthermore, the process is likely to occur predominantly on the surface due to large available surface areas, around 3.36 $m^2\ g^{-1}$ in coffee grounds biochars (Changotra et al., 2023), but as high as 40 $m^2\ g^{-1}$ when obtained at 500 °C or high increasing temperature rates (Islam et al., 2022), or low porosity ($2.32 \cdot 10^{-3}\ cm^3\ g^{-1}$), and small pores ranging from 8.88 nm to 9.44 nm (Changotra et al., 2023).

Finally, the first dissociation constant (pKa) of DCF is 4.16, which is below the pH of the used biochar columns (9.6) and also below the PZC (8.29) and the column effluent (6.8). These features also reinforce the DCF sorption capacity of the CGB, because the medium conditions exhibit twice the basicity of diclofenac, supporting stronger Lewis acid base interactions between the contaminant and the aromatic carboxyl and hydroxyl groups of the carbonaceous surface.

Conclusions

This study highlights the potential of coffee grounds biochar (CGB) as an effective adsorbent for removing diclofenac from aqueous solutions, particularly in sand-biochar column systems, which was evaluated through a series of column transport experiments. The use of biochar derived from coffee grounds could represent a sustainable and low-cost option for environmental remediation, offering an alternative to more expensive and less accessible adsorbents.

The use of bromide ion as a non-reactive tracer helped to characterize the hydrodynamics of the 3-layer porous medium, showing no interaction with the biochar, and verifying that convective transport dominated the systems, ensuring effective solute movement through the columns. On the other hand, the experimental results revealed that the CGB exhibited significant adsorption capacity for diclofenac, predominantly due to its surface properties and favorable pH environment. The pH increase from the initial coffee grounds (in natura) to the biochar, along with its PZC at 8.29, suggests that CGB surfaces are positively charged under saturated conditions (pH ≈ 6.8 – 7.34), thus enhancing interaction with the anionic species of DCF at the column effluent's pH, which exceeds the pKa of DCF (4.24). This pH and surface charge environment create optimal conditions for electrostatic attraction, which enhances CGB's adsorption efficiency.

When modeling DCF transport, the CDE-2SS model emerged as the most accurate, capturing the adsorption tailing effects that simpler models could not. The observed asymmetry and retardation factor of DCF breakthrough curves, with an average value of 4.04, further underscore CGB's ability to retain DCF in its structure, reflecting the complex, partially reversible interactions occurring on the biochar's surface.

Additionally, the partition coefficient calculated in this study aligns with previous studies on biochar-DCF interactions and reveals that sorption kinetics play a significant role in DCF transport, with both convective transport and chemical interactions, likely driven by physical adsorption mechanisms, such as van der Waals forces. The estimated recovery rate of 60% for DCF in CGB columns further indicate substantial removal of this contaminant, even without extensive biochar optimization.

Future work should explore both the CGB activation possibilities and its regeneration capacity for upscaling its application in larger-scale treatment systems. Examining the biochar's stability under varied environmental conditions and its capacity to absorb other organic contaminants would further elucidate its practical applications in real-world scenarios. This study thereby lays a foundation for advancing biochar-based solutions in water treatment and environmental management, especially in addressing pharmaceutical pollution in water systems.

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