Scientific Paper

Evaluation of a pilot system for removal of the herbicide 2,4-dichlorophenoxyacetic acid and absorbance determination after clarification and adsorption on granular activated carbon

Avaliação de uma instalação piloto na remoção do herbicida 2,4-diclorofenoxiacético e absorvância por clarificação e adsorção em carvão ativado granular

Edumar Ramos Cabral Coelho[1]* ⓘ, **Renata Santos Brega[1]** ⓘ

ABSTRACT

The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) has been detected in water bodies worldwide, precluding their use for water supply. Despite this, scientific studies assessing the behavior of herbicides in water treatment systems are scarce, which motivated this study on 2,4-D removal. 2,4-D removal and its relationship with absorbance were investigated using a pilot system comprising coagulation, sedimentation, filtration, granular activated carbon (GAC) adsorption, and chlorinated disinfection. 2,4-D removal ranged from 15 to 64% after sedimentation, from negative values to 19% after filtration, and from 5 to 16% after chlorination, with total removal rates of 19 to 70%. Breakthrough curves showed an adsorption capacity of 0.70 mg g^{-1} GAC for a C/C_0 ratio of 0.50 and a V_{TW}/V_{GAC} ratio of 3.598 for a breakthrough concentration of 30 ± 3 μg L^{-1}. The positive correlation between absorbance and 2,4-D ($R^2 = 0.78$) in the GAC column effluent indicated that absorbance can be used for early prediction of 2,4-D breakthrough. GAC column adsorption associated with coagulation produced treated water in accordance with the criteria for turbidity, apparent color, and 2,4-D concentration established by the Minister's Office/Ministry of Health — GM/MS Ordinance No. 888/2021, representing a promising technological alternative for 2,4-D removal from water treatment systems.

Keywords: adsorption; activated carbon; 2,4-dichlorophenoxyacetic acid; pilot plant; water treatment.

RESUMO

O herbicida 2,4-diclorofenoxiacético (2,4-D) tem sido encontrado em mananciais de todo o mundo comprometendo o uso para o abastecimento público. Apesar disso, as publicações científicas que avaliam o comportamento de herbicidas em sistemas de tratamento de água são escassas e justificam o estudo para avaliar a remoção do herbicida 2,4-D com o objetivo de gerar informações para a aplicação em sistemas de tratamento de água. Foram investigadas a remoção do 2,4-D e a sua relação com absorvância em uma instalação piloto constituída de coagulação, decantação, filtração e adsorção em carvão ativado granular (GAC) seguida de desinfecção com cloro. A remoção do 2,4-D variou de 15 a 64% na decantação, de negativa a 19% na filtração e na cloração de 5 a 16% com remoção total entre 19 e 70%. Nos ensaios de adsorção, foi determinada a capacidade de adsorção de 0,70 mg de 2,4-D/g GAC para a relação C/C_0 igual a 0,50 e V_A/V_{GAC} igual a 3.598, para condição de ruptura de 30 ± 3 μg L^{1}. A correlação positiva entre a absorvância e o 2,4-D ($R^2 = 0,78$) no efluente da coluna de GAC indicou que a absorvância pode ser utilizada como parâmetro para previsão antecipada de ruptura do 2,4-D. A adsorção em coluna de GAC associada à coagulação produziu água tratada que atendeu aos limites estabelecidos na Portaria GM/MS nº 888/2021 para turbidez, cor aparente e 2,4-D, apresentando-se como opção tecnológica para remoção de 2,4-D em sistemas de tratamento de água.

Palavras-chave: adsorção; carvão ativado granular; 2,4-diclorofenoxiacético; instalação piloto; tratamento de água.

INTRODUCTION

The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) was the first organic herbicide synthesized by the chemical industry. It began to be used around the time of World War II and continues to be an important chemical agent in agriculture to the present day. In fact, 2,4-D is the second most widely used active ingredient in soybean, corn, sugarcane, coffee, wheat, oat, rye, rice, and pasture

production worldwide. The herbicide has been detected in water springs and water supply systems in Brazil and in other countries at very high concentrations. For instance, the 2,4-D concentration detected in the Karun River, Iran, was 121 µg L^{-1} (NAM et al., 2014; MOJIRI et al., 2020). In Brazil, 2,4-D concentrations can reach 220 µg L^{-1}, greatly exceeding regulatory limits for class 2 (4 µg L^{-1}) and class 3 (30 µg L^{-1}) springs (BROVINI et al., 2021; GALVAN et al., 2020).

Pesticides have deleterious effects on human health, disrupting the endocrine system and increasing the risk of cancer, which justifies their monitoring and control in water supply systems for human consumption (ISLAM et al., 2018). The most restrictive legislation is that of the European Commission: it states that the maximum permissible concentration of total pesticides in treated water is 0.5 µg L^{-1} and sets the maximum limit for any single pesticide at 0.1 µg L^{-1} (EUROPEAN UNION, 1998). In Brazil, the Minister's Office/Ministry of Health — GM/MS Ordinance No. 888/2021 states that the maximum permissible concentration of 2,4-D is 30 µg L^{-1}.

Coagulation treatments have limited capacity to remove microcontaminants, necessitating the combined use of other technologies, such as advanced processes, to produce drinking water in accordance with regulatory standards, consequently reducing health risks. Activated carbon adsorption is one such technology that can be associated with conventional water treatment processes (MOJIRI et al., 2020).

Adsorption is influenced by chemical characteristics of the adsorbent and adsorbate, temperature, water physicochemical properties, and operating conditions of water treatment systems (CORWIN; SUMMERS, 2012). As for the adsorbate, the main characteristics that influence adsorption are molecular size, solubility, pK_a, and substituent groups on aromatic rings. 2,4-D is a polar molecule with a molecular weight of 221.04 g mol^{-1}, pK_a of 2.73 at 20–25°C, log K_{ow} of 2.81 (moderate hydrophobicity), water solubility of 600 mg L^{-1} at 25 °C, and molecular diameter of 2.074 Å (MOJIRI et al., 2020). The first intermediate of 2,4-D degradation is 2,4-dichlorophenol (2,4-DCP), as depicted in Figure 1.

Pilot tests performed on a granular activated carbon (GAC) column can be used to obtain breakthrough curves and thus gain insight into interactions between the adsorbent surface and water contaminants under industrial-scale conditions (CORWIN; SUMMERS, 2012; KENNEDY et al., 2015). The presence of natural organic matter (NOM) has an important impact on adsorption efficiency (JARVIE et al., 2005; HUMBERT et al., 2008; ERSAN et al., 2016). Because of the complexity of identifying and quantifying NOM, researchers have suggested evaluating the presence of NOM by indirect parameters, such as ultraviolet (UV) absorbance at 254 nm, total organic carbon content, dissolved carbon content, and fluorescence (BENSTOEM et al., 2017). Microcontaminants are also difficult to quantify, and studies have sought strategies to reduce the analytical complexity of quantification methods, focusing on molecules that
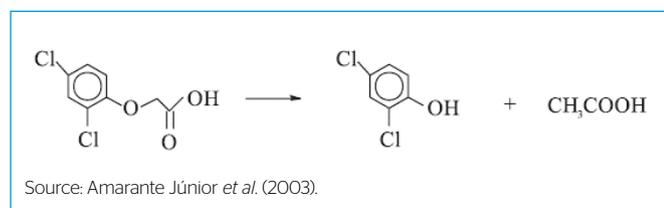
could serve as indicators of the presence and removal of microcontaminants. Anumol et al. (2015) used GAC microcolumns to study the removal of microcontaminants, such as personal hygiene products and pharmaceuticals, in secondary wastewater from domestic sewers. The authors observed a positive linear relationship between microcontaminant concentration and absorbance and recommended the use of this parameter to predict the breakthrough point of activated carbon columns.

In this study, we investigated the ability of a pilot system comprising coagulation, flocculation, sedimentation, filtration, GAC adsorption, and chlorination in removing 2,4-D and determined the adsorption capacity of the column. The feasibility of using absorbance as an indirect parameter for prediction of the breakthrough point of 2,4-D on the GAC column was also assessed. Given that studies of 2,4-D removal by adsorption on a pilot scale are scarce, the results of this research may contribute to the identification of parameters that represent adsorption capacity, facilitating the monitoring of 2,4-D adsorption on GAC columns.

METHODS

Pilot system

The pilot system comprised a rapid mixing unit, a V-notch weir, a three-chamber mechanized flocculation unit, a high flow rate decanter, a downward rapid filtration unit with anthracite/sand double layer, a GAC column, and a disinfection tank.

2,4-D removal was evaluated over four treatment cycles. Runs 1 (R1) and 2 (R2) consisted of the conventional steps used for water treatment, as follows: coagulation, flocculation, decantation, filtration, and chlorinated disinfection. Runs 3 (R3) and 4 (R4) included an advanced treatment process, that is, a GAC column connected to the system after the rapid filtration unit. The pilot installation is shown in Figure 2.

The pilot system was fed with untreated surface spring water containing 2,4-D. The herbicide was added by a dosing pump installed upstream of the rapid mixing unit, before the point of coagulant addition (Figure 2). 2,4-D solutions were prepared by diluting the commercial product DMA 806 BR-DOW, whose active ingredient is 2,4-D, with distilled water. After preparation, which was carried out at the beginning of each test, solutions were stored in opaque plastic bottles and kept away from light under constant stirring by air injection. The initial concentration should be in the range of twice the concentration permitted by GM/MS Ordinance No. 888/2021 (30 µg L^{-1}) and the highest concentration reported in the literature (220 µg L^{-1}). 2,4-DCP, the major degradation product of 2,4-D, was monitored in effluents collected after decantation, filtration, GAC adsorption, and chlorination. This procedure was used to assess the possibility of 2,4-D removal by processes unrelated to adsorption.

The operating conditions for coagulant dosage were defined using preliminary jar tests. The coagulant was 0.5% liquid aluminum sulfate, and the dose was set at 5–10 mg L^{-1}. Water disinfection was performed using a commercial product based on sodium dichloroisocyanurate dihydrate (25% available chlorine) at a dose ranging from 1.50 to 2.25 mg L^{-1}. At the end of each run, rapid filters were washed until the turbidity of wash water decreased to less than 0.5 turbidity units (TU). Table 1 summarizes the operational parameters of the pilot system.

Source: Amarante Júnior et al. (2003).

Figure 1 – Structural formula of 2,4-dichlorophenoxyacetic acid and its main degradation product, 2,4-dichlorophenol.
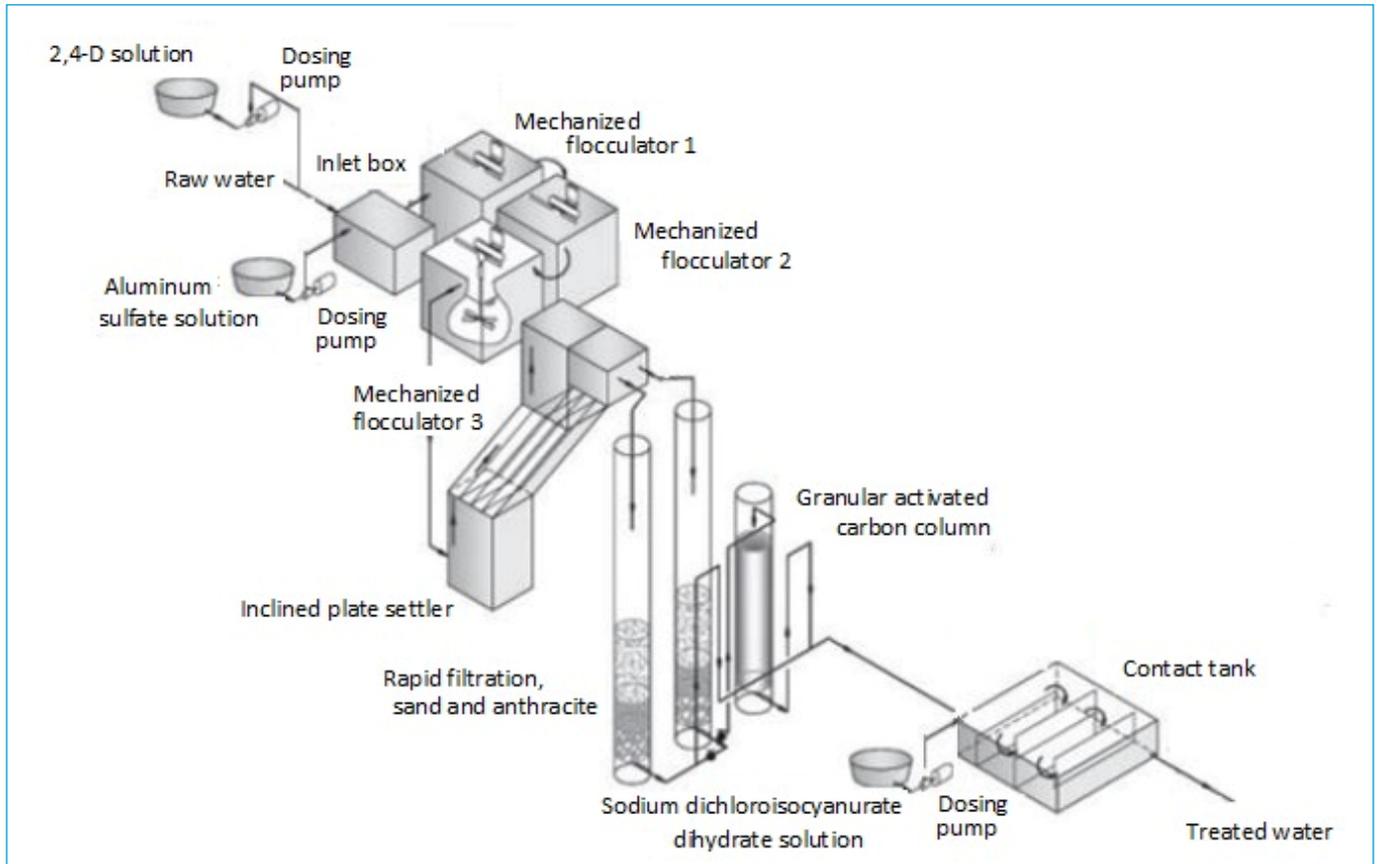
Figure 2 – Schematic of the pilot plant. 2,4-D, 2,4-dichlorophenoxyacetic acid.

The GAC column was operated with downward flow. Water samples were collected from three points, hereafter referred to as GAC_5, GAC_{15}, and GAC_{95}, located 5, 15, and 95 cm from the top of the column and corresponding to contact times of 0.4, 1.1, and 7 min, respectively. The operating conditions of the GAC column are described in Table 2.

Column adsorption capacity (q_b) was calculated according to Equation 1,

$$q_b = \frac{V}{w} (C_0 - C_b) \tag{1}$$

Where:

q_b: the adsorption capacity at breakthrough (mg adsorbate g^{-1} adsorbent);

V: the solution volume (L);

w: the weight of adsorbent (g);

C_0: the initial concentration of adsorbate in aqueous phase (μg L^{-1});

C_b: the concentration of adsorbate in aqueous phase at breakthrough (μg L^{-1}).

Analytical procedures

For physicochemical characterization, influents and effluents were analyzed for pH, turbidity, apparent and true color, absorbance at 254 nm, and total organic carbon according to the *Standard Methods for the Examination of Water and Wastewater* (APHA; AWWA; WEF, 2000). Turbidity was determined on a HACH 2100P turbidimeter. Color was measured using a UV-Vis Spectro 580UVP-Marte spectrophotometer. The pH was measured using a Denver UB-10 benchtop digital pH meter. Absorbance measurements were taken at 254 nm using a UV-Vis Spectro 580UVP-Marte spectrophotometer. Total organic carbon was

Table 1 – Operational properties of the pilot system.

Property	Value
Nominal flow rate (m³ h⁻¹)	1
Velocity gradient during rapid mixing (s⁻¹)	500
Velocity gradient during flocculation (s⁻¹)	70, 30, 10
Application rate during decanting (m³ m⁻² d⁻¹)	30
Application rate during filtration (m³ m⁻² d⁻¹)	120
Sand/anthracite bed height (cm)	25/55
Sand/anthracite particle size (mm)	0.4-1.3/0.71-2
Contact time in chlorination tank (min)	30

Table 2 – Operational properties of the granular activated carbon column.

Property	Value
Column diameter (cm)	25
Nominal flow rate (m³ h⁻¹)	0.4
Superficial flow rate (mL min⁻¹)	6.67
Maximum bed height (cm)	95
Particle size (mesh)	8 × 30 (0.59 × 2.38 mm)

quantified using a Shimadzu TOC-L analyzer. Chlorine was measured using a portable digital colorimeter (Policontrol AquaColor-Cloro).

Detection and quantification of 2,4-D and 2,4-DCP were performed using a Shimadzu CBM-20A liquid chromatography system equipped with a solvent degasser (DGU-20AS), a quaternary gradient pump (LC-20AT),

an automatic sample injector (SIL-20AHT), a diode array detector (SPD-M20A), and a column oven (CTO-M20A). The chromatographic column was XTerra MS C18 (150 × 4.6 mm, 3.5 μm). The mobile phase consisted of acetonitrile (ACN) and 10 mM ammonium formate acidified with 0.10% phosphoric acid (47:53 v/v ACN/NH$_4$COOH). Elution was performed in isocratic mode at a flow rate of 1.2 mL min^{-1}. The sample injection volume was 50 μL. The column temperature was set at 30°C. Identification and quantification of analytes were performed at 200 and 206 nm. The maximum absorption wavelength was found to be 200 nm for both 2,4-D and 2-4-DCP. Solid phase extraction was achieved using a 500 mg/6 mL Agilent C18 cartridge. All solutions used to prepare the mobile phase were previously filtered through a 0.45 μm polytetrafluoroethylene membrane (Millipore) and degassed in an ultrasound bath (Limpsonic) for 15 min under vacuum.

Coconut shell activated carbon, produced by physical activation, was provided by Bahiacarbon Agroindustrial Ltda. The material was characterized for iodine number (ABNT, 1991), Brunauer-Emmett-Teller (BET) specific surface area and pore distribution (N$_2$ adsorption isotherms determined at 77 K using a Quantachrome Autosorb-1 instrument), and pH (ASTM, 1999).

The parameters evaluated for validation of solid phase extraction by high-performance liquid chromatography with diode array detection (SPE-HPLC-DAD) were linearity, limit of detection, and limit of quantification. Recovery and precision were determined in accordance with Resolution No. 899/2003 of the Brazilian Health Regulatory Agency (BRASIL, 2003).

RESULTS AND DISCUSSION

Adsorbent characterization
GAC was classified as predominantly microporous (< 20 Å) (Table 3), according to the International Union of Pure and Applied Chemistry. Given that 2,4-D has a molecular width of 2.074 Å, the herbicide can be adsorbed onto the micropores of GAC. GAC properties were compared with values recommended by the American Water Works Association (AWWA, 2005) for GAC adsorption treatment in water supply systems. Iodine content was within the recommended range, between 600 and 1,050 mg g^{-1}. The specific surface area (561 m^2 g^{-1}) was lower than the recommended (650–1,000 m^2 g^{-1}). The pH of GAC was 9.24, demonstrating the presence of basic surface groups.

Table 3 – Properties of granular activated carbon.

Parameter	Value
Iodine number (mg g^{-1})	824
pH	9.24
BET surface area (m^2 g^{-1})	561
Total pore volume (cm^3 g^{-1})	0.3355
Primary micropore volume (d < 8 Å) (cm^3 g^{-1})	0.1936
Secondary micropore volume (8 < d < 20 Å) (cm^3 g^{-1})	0.0915
Mesopore volume (20 < d < 500Å) (cm^3 g^{-1})	0.0503

BET: Brunauer-Emmett-Teller.

Removal of 2,4-dichlorophenoxyacetic acid by coagulation-flocculation-decantation and chlorination
The 2,4-D quantification method had detection limits of 3.63 μg L^{-1} for 2,4-D and 3.60 μg L^{-1} for 2,4-DCP. The quantification limit was 20 μg L^{-1} for both compounds, below the value determined by GM/MS Ordinance No. 888/2021. Two runs were conducted for evaluation of 2,4-D removal by coagulation (R1 and R2). R1 lasted 10 hours, with three collections every 2 hours, and R2 lasted 30 hours, with four collections (2 hours between the first three collections and 22 hours between the third and last collection). The time elapsed between the beginning of each test and the first collection was defined according to hydraulic stabilization of the pilot plant. As access to the pilot facility was not allowed at night, collections were restricted to daytime, limiting the interval between collections. Tests were terminated when the turbidity of the filter effluent reached 0.5 TU.

The variation in 2,4-D concentration in raw water was attributed to the low solubility of the commercial product in water and the limitation of the type of agitation applied. Values remained within the limits reported in the literature. On the other hand, this condition allowed assessing the variation in the presence of herbicide in raw water, which is common under real conditions. The results of the characterization of raw water and effluents from coagulation-flocculation-decantation are described in Table 4.

Decantation played an important role in the removal of true color (> 81%), absorbance (46–63%), and 2,4-D (30–52%). During filtration, particle removal ranged from 91 to 95%, as assessed by turbidity, with nominal values lower than 0.5 TU. Apparent color removal was greater than 86%, and organic carbon removal ranged from 10 to 35%. After chlorination, water quality met the requirements of GM/MS Ordinance No. 888/2021, except for 2,4-D concentration. During filtration, 2,4-D removal ranged from negative values to 19%. Negative values were interpreted as 2,4-D desorption. The total 2,4-D removal ranged from 35 to 59% after chlorination, with nominal values of 54 to 68 μg L^{-1}.

Nam *et al.* (2014) achieved 2,4-D removal efficiencies of 51% with decantation, 50% with filtration, and 0% with chlorination, from influent containing 33.6 ng L^{-1} 2,4-D at a water treatment plant in Seoul, South Korea. Differences in the results of the current and cited study can be explained by differences in water properties, operating conditions, and initial 2,4-D concentrations. Such a finding reinforces the need for pilot plant tests, as the variation in water physicochemical properties influences treatment efficiency.

Removal of microcontaminants by coagulation may occur through adsorption on organic or inorganic particles, electrostatic interactions between contaminants and hydrolyzed species of the coagulant, and photodegradation (STACKELBERG *et al.*, 2007; JIN; PELDSZUZ, 2012). 2,4-D has a pK_a of 2.87, suggesting the occurrence of electrostatic interactions associated with coagulant hydrolysis products (NAM *et al.*, 2014). Although high 2,4-D removal was achieved after chlorination, the nominal value was still greater than the threshold defined by GM/MS Ordinance No. 888/2021, i.e., 30 μg L^{-1}. Therefore, we assessed the feasibility of 2,4-D adsorption on a GAC column as a complementary treatment.

Adsorption of 2,4-dichlorophenoxyacetic acid on a granular activated carbon column
For this experiment, we performed two runs of filtration, followed by GAC column adsorption and chlorination (R3 and R4). Samples were collected at

the beginning (GAC_5), middle (GAC_{15}), and end (GAC_{95}) of the GAC column. The contact time was equal to 0.4, 1.1, and 7 minutes for GAC_5, GAC_{15}, and GAC_{95}, respectively.

R3 lasted 48 hours, with five collections (2 hours between the first three collections, 22 hours between the third and fourth collections, and 18 hours between the fourth and fifth collections). The mean 2,4-D removal was 20% at GAC_5 ($68 \pm 5\,\mu g\,L^{-1}$) and 99% at GAC_{95} ($< 3.6\,\mu g\,L^{-1}$, detection limit). Two runs lasting 24 hours were conducted between R3 and R4. Samples were collected at the end of each run at GAC_5 and GAC_{95}, totaling 96 hours of operation. 2,4-D concentration at GAC_5 was greater than $30\,\mu g\,L^{-1}$; thus, collections were also made at 15 cm from the top of the column (GAC_{15}) in R4.

R4 lasted 6 hours, with three collections every 2 hours. The run was stopped because of a sudden increase in turbidity in raw water, compromising the quality of treated water. At GAC_{15}, the 2,4-D concentration was 50%, with an influent concentration of $60 \pm 9\,\mu g\,L^{-1}$ and effluent concentration of $30 \pm 3\,\mu g\,L^{-1}$ after 102 hours of operation. These findings are promising for the design of GAC columns in water treatment plants. At GAC_{95}, 2,4-D removal was 97%, with an effluent concentration of 2–$4\,\mu g\,L^{-1}$. The presence of 2,4-DCP was not observed in any stage of treatment, suggesting that biodegradation or photodegradation did not contribute to 2,4-D removal during coagulation or adsorption.

There are gaps in the understanding of adsorption processes involving GAC with regard to adsorbent surface characteristics, chemical characteristics of the contaminant, pH, and interactions between organic matter and other compounds. The pH of GAC used in this study was higher than the pK_a of 2,4-D, suggesting that 2,4-D removal involved phenomena other than electrostatic interactions. Barbosa *et al.* (2014) studied the adsorption of phenols onto activated carbon and concluded that phenol adsorption in basic medium is very complex and that there is great difficulty in elucidating adsorption phenomena. The results of 2,4-D removal from raw water in R3 and R4 are depicted in Figure 3.

A breakthrough curve was constructed for 2,4-D and normalized concentrations to estimate parameters and investigate the possible relationship between absorbance and 2,4-D concentration. The curve is defined as the relationship between 2,4-D concentration in the influent (C_0) and effluent (C) as a function of time (Figure 4). The breakthrough point was defined for an effluent concentration of $30\,\mu g\,L^{-1}$, the maximum value allowed by Brazilian regulation for drinking water. This concentration corresponds to C/C_0 values of 0.41–0.68, achieved at GAC_{15} after 96 hours of operation.

The amount of 2,4-D adsorbed at GAC_5 was $0.20\,mg\,g^{-1}$ GAC, with a C/C_0 of 0.9 and a volume of treated water per GAC bed volume (V_{TW}/V_{GAC}) of 15,673 after 96 hours of operation. At GAC_{15}, the amount of adsorbed 2,4-D was 0.70

Table 4 – Minimum and maximum values of physicochemical parameters of raw spring water after decantation, rapid filtration, and chlorination (runs 1 and 2).

Parameter	Unit	Raw water (min-max)	Decantation (min-max)	Filtration (min-max)	Chlorination (min-max)
pH	dimensionless	6.8-6.9	-	6.5-6.8	6.6-6.8
Turbidity	TU	7-11	3.8-5.2	0.1-0.5	0.2-0.4
Apparent color	HU	51-69	26-41	nd-12	nd-5
True color	HU	5-8	nd-5	nd-1	nd-5
Absorbance at 254 nm	cm⁻¹	0.046-0.056	0.017-0.024	0.018-0.022	0.016-0.022
Total organic carbon	mg L⁻¹	1.454-8.024	1.677-1.887	1.068-1.506	1.567-4.295
2,4-D*	µg L⁻¹	79-186	60-89	72-75	54-68
2,4-DCP	µg L⁻¹	BDL	BDL	BDL	BDL

2,4-D: 2,4-dichlorophenoxyacetic acid; 2,4-DCP: 2,4-dichlorophenol; TU: turbidity units; HU: Hazen units; nd: not detected; BDL: below detection limit (3.63 HU for 2,4-D and 3.60 HU for 2,4-DCP); *added to raw water.
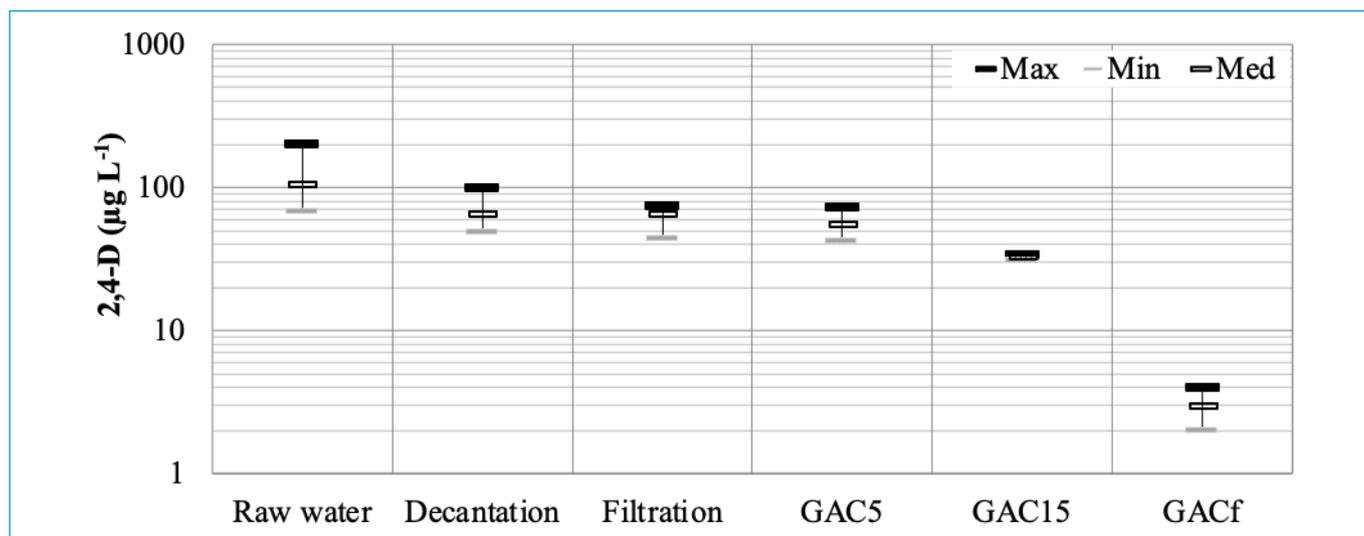
Figure 3 – 2,4-Dichlorophenoxyacetic acid concentration in raw water after treatment steps in runs 3 and 4 ($n = 13$). GAC, granular activated carbon; GAC_5, GAC_{15}, and GAC_{95}, collection points at 5, 15, and 95 cm from the top of the column, respectively.

mg g^{-1} GAC, with a C/C_0 of 0.5 and V_{TW}/V_{GAC} of 5551 after 102 hours of operation. As a result, treated water had a 2,4-D concentration of 30 ± 3 µg L^{-1}. These treatment conditions may serve as a reference for GAC column design for the treatment of waters with similar characteristics to the one used in the current study. After 102 hours of operation, at GAC$_{95}$, the effluent exhibited final 2,4-D concentrations of 2–4 µg L^{-1}, with a C/C_0 of 0.05, indicating that the column could have been used for a longer time, taking advantage of its entire length (95 cm). The amount of 2,4-D adsorbed was 0.96 mg g^{-1} GAC, with a C/C_0 of 0.05 and V_{TW}/V_{GAC} of 876.

As shown in Figure 4, over time, there was an approximation between absorbance and 2,4-D curves, demonstrating that organic compounds and 2,4-D molecules compete for different active sites. Organic matter desorption was not observed, and there was a balance between adsorbate and adsorbent. The occurrence of organic compound adsorption on GAC, assessed here as absorbance, was prior to that of 2,4-D adsorption.

After 10 hours of operation, the saturation of absorbance was reached but that of 2,4-D removal was not, with a C/C_0 equal to 0.77, i.e., there were still active sites available for 2,4-D adsorption. The same behavior was observed until the end of the experiment at GAC$_5$ and GAC$_{95}$, demonstrating the possibility of using absorbance as a measure to predict the occurrence of 2,4-D breakthrough. 2,4-D breakthrough occurred at a C/C_0 of 0.41–0.68 at GAC$_{15}$, whereas the C/C_0 value for absorbance was equal to 0.9 after 98 hours of operation.

Similar results were reported by Altmann *et al.* (2016) in secondary sewage effluent treated with powdered activated carbon and by Anumol *et al.* (2015) in effluents treated with GAC under laboratory conditions, with the aim of producing reuse water. Therefore, in the current study, we sought to find correlations between 2,4-D concentration and absorbance. In decantation, the stage with the greatest 2,4-D removal by conventional treatment, the linear correlation between 2,4-D concentration and absorbance was 0.73 for all assays ($n = 12$). In Figure 5, the positive linear correlation between absorbance and 2,4-D

concentration in the GAC column effluent ($R^2 = 0.78$) can be observed, further corroborating the feasibility of monitoring absorbance to predict 2,4-D breakthrough. We underscore the gap in the understanding of microcontaminant removal from water treatment systems and reinforce the need for studies investigating the influence of water properties on removal and the possibility of using certain parameters for predicting GAC column breakthrough. GAC column adsorption showed promise as an alternative for 2,4-D removal to obtain treated water within the limits defined by GM/MS Ordinance No. 888/2021. It is suggested that absorbance may serve as an indirect parameter to predict 2,4-D breakthrough.

CONCLUSIONS

This pilot study showed the limitation of coagulation-sedimentation-filtration-chlorination treatment for 2,4-D removal and the notable efficiency of GAC column adsorption for 2,4-D removal. Under the conditions of this study, it was possible to conclude the following:
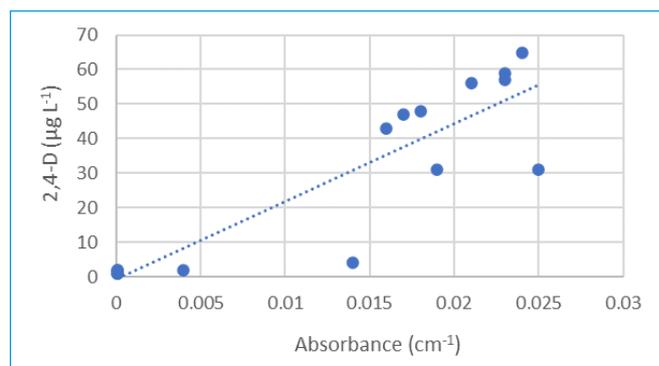
Figure 5 – Correlation between absorbance and 2,4-dichlorophenoxyacetic acid (2,4-D) concentration in the effluent collected at 5 ($n = 4$), 15 ($n = 3$), and 95 cm ($n = 7$) from the top of a granular activated carbon (GAC) column.
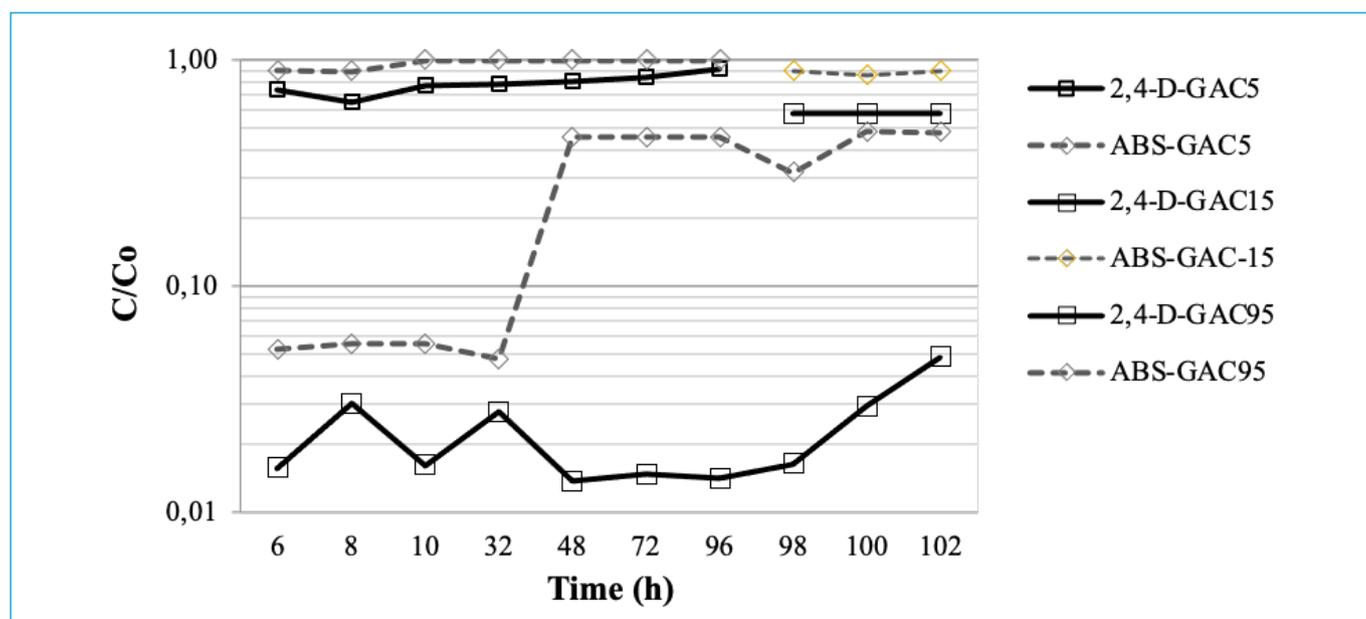
Figure 4 – Breakthrough curve for 2,4-dichlorophenoxyacetic acid (C_0 = 44–74 µg L^{-1}) and absorbance (C_0 = 0.019–0.023 cm^{-1}) at GAC$_5$, GAC$_{15}$, and GAC$_{95}$ as a function of time. Lines were added to help visualize trends. GAC, granular activated carbon; GAC$_5$, GAC$_{15}$, and GAC$_{95}$, collection points at 5, 15, and 95 cm from the top of the column, respectively.

- Conventional treatment achieved 2,4-D removal rates of 35 to 59%, depending on influent concentration;
- 2,4-D removal was attributed to adsorption, given that 2,4-DCP, a degradation product of 2,4-D, was not detected in any treatment stage;
- GAC produced from coconut shell was characterized as predominantly microporous with alkaline characteristics; the material was able to produce effluent that met the criteria of GM/MS Ordinance No. 888/2021 for 2,4-D ($< 30\,\mu g\,L^{-1}$);
- The adsorption capacity of 2,4-D in natural water was 0.70 mg g^{-1} GAC, with a C/C_0 of 0.50 and V_{TW}/V_{GAC} of 5555; these data can be used as a reference for the design of GAC columns in water treatment systems;

- The saturation of GAC for organic compounds, evaluated here as absorbance, occurred earlier ($C/C_0 = 0.9$) than 2,4-D breakthrough ($C/C_0 = 0.5$), and a positive relationship was observed between absorbance and 2,4-D concentration ($R^2 = 0.78$), indicating that absorbance can be used as an indirect measure for early prediction of 2,4-D breakthrough.

AUTHORS' CONTRIBUTIONS

Coelho, E.R.C.: Supervision, Validation, Funding Acquisition, Writing—Review and Editing. Brega, S.B.: Investigation, Methodology.

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