



A green strategy for desorption of trihalomethanes adsorbed by humin and reuse of the fixed bed column

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ABSTRACT

The objective of the present work was to develop a thermal desorption method for the removal of trihalomethanes (THM) adsorbed by humin, followed by multiple recycling of the fixed bed column in order to avoid excessive consumption of materials and reduce operating costs. The results obtained for adsorption on a fixed bed column confirmed the effectiveness of humin as an adsorbent, extracting between 45.9% and 90.1% of the total THM (TTHM). In none of the tests was the column fully saturated after 10 h. Experiments involving thermal desorption were used to evaluate the potential of the technique for column regeneration. The adsorptive capacity of the humin bed increased significantly ($p < 0.05$) between the first and fifth desorption cycle, by 18.9%, 18.1%, 24.2%, 20.2% and 24.2% for CHBr_3 , CHBr_2Cl , CHBrCl_2 , CHCl_3 and TTHM, respectively.

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1. Introduction

The twentieth century was characterized by the rapid development of human civilization, although huge economic growth and improvements in the standards of living in both industrialized and developing countries has resulted in negative impacts on the environment [1]. Problems with water quality caused by poor conditions of water sources and contamination by sewage are of particular concern, and necessitate the use of various chemical substances (such as chlorine) in water treatment stations (WTS).

Chlorination is a widely adopted and proven method for microorganism deactivation, especially in water treatment. It is the most important method of drinking water disinfection, and is used worldwide because of its efficacy and low cost [2]. The chlorination of water has been the focus of many studies, including those that have investigated the formation and sources of trihalomethanes (THM) and related halogenated compounds. In natural waters, the formation of THM is mainly a result of the reaction of chlorine with organic matter.

The THM formed as disinfection by-products (DBP) include chloroform (CHCl_3), dichlorobromomethane (CHCl_2Br), dibromochloromethane (CHClBr_2) and bromoform (CHBr_3) [3]. Due to their toxicity, THM must be measured at very low levels in environmental and biological samples, as well as in food products. In

Brazil, the concentration limit for total THM (TTHM) in drinking water is $100 \mu\text{g L}^{-1}$ [4]. The United States Environmental Protection Agency (US EPA) has established a maximum contamination level for THM of $80 \mu\text{g L}^{-1}$ [1].

Activated charcoal is the material that is most widely used for THM removal in water treatment stations, following its recommendation by the US EPA [5,6]. However, its efficiency is dependent on the need for large dosages in short time periods, which increases the waste generated, and its use is also limited by the associated cost.

There is a growing demand for the development of new methodologies that are perceived to be more environmentally friendly, and that are able to reduce or eliminate reagent use, minimize the amount of the waste generated and enable the reuse of materials [7–9]. These concerns have motivated the design and use of chemicals that are more environmentally benign [1,10,11].

Various synthetic and natural materials have been studied for wastewater remediation. One of the adsorbents that have been investigated is peat, an organic soil formed continuously by a complex process of decomposition and humification of plant residues by microbiological oxidation in flooded environments [12–14]. Humin is the soil organic matter that remains after removal of humic and fulvic acids. It is also defined as the fraction that is insoluble in aqueous solution at any pH, and possesses higher molecular weight and carbon content compared with other peat humic fractions. Previous studies have demonstrated that humin is a promising and efficient adsorbent for several micropollutants, including polycyclic aromatic hydrocarbons [15], chlorophenols

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[16] and THM [6]. The use of humin can result in inexpensive systems [13].

Although notions of green chemistry are growing in all areas of chemistry, such techniques still need to be better incorporated into the procedures used for environmental remediation. Selection of a suitable bioadsorbent should include consideration of its potential for multiple reuses, as well as the ability to desorb compounds without any need for solvents.

In the laboratory, solvent-free techniques using thermal desorption can be effective for the extraction of volatile and semi-volatile organic compounds present in aqueous samples [1].

The objective of the present work was to develop a thermal desorption method for the removal of THM adsorbed in humin, with multiple reuse and recycling of the fixed bed column. Implementation of the technique (for example, in WTS) would reduce both usage of materials and operating costs, and contribute to the goal of environmental sustainability with implementation of green chemistry practices that help reduce or eliminate the generation of hazardous waste products. Furthermore, thermal desorption would allow the desorbed THM to be used in other chemical manufacturing processes.

2. Materials and methods

2.1. Reagents

Chloroform, dichlorobromomethane, dibromochloromethane, bromoform, and an internal standard (*p*-fluorobromobenzene) recommended by the American Public Health Association [17] were high purity (99%) analytical standards produced by AccuStandard. The stock solutions were prepared in methanol (99%, J.T. Baker, USA).

2.2. Sample collection and preparation

A tropical peat sample was collected from a peatland in the vicinity of Santo Amaro das Brotas, Sergipe State, Brazil. The sample was air-dried, ground using a pestle and mortar, and sieved first through a 9 mesh grid to remove roots and twigs, and then through a 48 mesh grid to obtain a uniform particle size. *In natura* peat was not used as adsorbent because of the dissolution of humic and fulvic acids at water pH values in the range 6.5–9.0. Hence humin was used, corresponding to the insoluble fraction present throughout the pH range. The International Humic Substances Society (IHSS) recommends an alkaline extraction procedure, using 0.1 mol L⁻¹ NaOH under a nitrogen atmosphere, to extract the humic and fulvic acids, with humin being the insoluble material remaining after this process.

2.3. Preparation of immobilized humin

Humin immobilized on sodium silicate was used in the present work, since it was impossible to use *in natura* humin in the fixed bed column experiments due to problems of bed blockage. The procedure used for the immobilization of the humin on the sodium silicate was similar to that described by de la Rosa et al. [18]. 20.0 g of humin was first passed through a 100 mesh sieve, and then washed twice with 0.01 mol L⁻¹ HCl and once with deionized water. The supernatant was evaporated, and the solid was weighed in order to measure any loss of biomass. 300 mL of 5% H₂SO₄ was added to a 2.0 L beaker containing the dry humin, followed by addition of 6% sodium silicate (Na₂SiO₃) until a pH of 2.0 was reached. The mixture was then mechanically agitated continuously for 15 min. The pH was gradually increased to 7.0 by the addition of 6% Na₂SiO₃. The resultant polymeric gel was washed several times with deionized water, until no sulfate was detected

(using the BaCl₂ test, with formation of BaSO₄ precipitate). The polymer was placed on a tray and dried overnight at 60 °C, then ground using a pestle and mortar. Finally, the material was passed through a 20–40 mesh sieve to obtain a uniform particle size. de la Rosa et al. [18] reported that the immobilization process did not alter the physical properties (size and specific area) of the material.

2.4. Sample characterization

2.4.1. Thermal gravimetric analysis (TGA)

Portions (~8 mg) of *in natura* or immobilized humin were ground using a pestle and mortar, and then passed through a 100 mesh sieve in order to obtain a consistent particle size. The samples were placed in alumina crucibles and heated continuously from 25 to 1000 °C at a heating rate of 10 °C min⁻¹ in an atmosphere of synthetic air (99.999%, 20% O₂ and 80% N₂) provided at a flow rate of 100 mL min⁻¹. TGA curves were recorded using a Shimadzu TGA 50 instrument.

2.4.2. Specific surface area (BET method)

Nitrogen physisorption experiments were performed at 77 K using a NOVA 1200e analytical system (Quantachrome Corp., USA). The specific surface area (*S*_{BET}) was calculated using the Brunauer–Emmett–Teller (BET) method for *P*/*P*₀, and ranged between 0.05 and 0.30.

2.4.3. FTIR

Infrared spectra were obtained using tablets prepared by mixing dry KBr with humin, and analyzed using the transmission method with a resolution of 4 cm⁻¹, accumulating 16 spectra. The measurements were made with a Perkin Elmer spectrometer (in the range 400–4000 cm⁻¹).

2.5. Batch experiments

2.5.1. Comparative tests using *in natura* and immobilized humin

Since the fixed bed column experiments involved humin immobilized on sodium silicate, experiments were performed to determine whether the immobilization influenced adsorption of the THM. These tests were performed using both humin immobilized on sodium silicate and *in natura* humin. 0.1 g of humin and 10 mL of a 250 μg L⁻¹ solution of THM were placed in amber flasks, which were maintained at 25 ± 0.2 °C under constant agitation (150 rpm) for 240 min. The samples were then filtered through a 0.45 μm syringe filter (Millipore), and the concentrations of the individual THM compounds were determined using a gas chromatograph (Varian, USA) fitted with an electron capture detector (ECD) and coupled to a purge-and-trap system (Mason, USA) (GC-ECD/PT). An internal standard was added at the time of injection in order to avoid any losses. The control solution was prepared in the absence of the humic material, and all experiments were performed in triplicate.

2.5.2. Capacity of humin to adsorb chlorine

Experiments to assess the capacity of humin to adsorb chlorine were conducted in order to confirm that the adsorbent material did not consume chlorine, which in WTS could result in contamination of the water distribution network. These tests were undertaken using *in natura* humin, humin immobilized on sodium silicate, and commercial activated charcoal, following the same procedure described above (Section 2.5.1). Solutions of sodium hypochlorite were prepared at concentrations in the range 1.0–4.0 mg L⁻¹. Aliquots were removed after 240 min of agitation, and the chlorine content was quantified using the DPD-based method 4500-D of the American Public Health Association [17]. The control solution

was prepared in the absence of the adsorbents, and all experiments were performed in triplicate.

The results were expressed in terms of removal percentages, calculated according to: % removal = $(C_i - C_f)/C_i \times 100$, where C_i and C_f are the initial and final chlorine concentrations, respectively.

2.6. Use of a fixed bed column with humin immobilized on sodium silicate

2.6.1. Preparation of THM solutions for percolation through the column

It was not economically viable to use THM analytical standards in the fixed bed column experiments, due to the large volumes of solution required. A solution containing THM was therefore produced by reaction of water naturally rich in organic matter (23 mg L^{-1} dissolved organic carbon (DOC)) with a solution containing a known concentration of chlorine together with a measured amount of potassium bromide. The prepared solutions were stored under refrigeration at $\pm 4^\circ\text{C}$, in glass flasks without any headspace, for a maximum period of 72 h. The concentrations of the THMs were determined before the start of each experiment.

The individual THM concentrations determined using the GC-ECD/PT system were $225 \text{ }\mu\text{g L}^{-1}$ (chloroform), $45.6 \text{ }\mu\text{g L}^{-1}$ (dichlorobromomethane), $57.4 \text{ }\mu\text{g L}^{-1}$ (dibromochloromethane), and $102 \text{ }\mu\text{g L}^{-1}$ (bromoform). The TTHM concentration was $429 \text{ }\mu\text{g L}^{-1}$.

2.6.2. Packing of humin in the column

Humin immobilized on sodium silicate was packed into a glass column ($20 \text{ cm} \times 2.0 \text{ cm}$ i.d.), through which the THM solution (described in Section 2.6.1) was percolated in descending flow using a peristaltic pump (Gilson Miniplus 3). Breakthrough curves (C/C_0 vs. time, where C is the concentration exiting the column, and C_0 is the initial concentration) were obtained under the optimized conditions described by Cunha et al. [6], using a bed depth of 4 cm and a flow rate of 2 mL min^{-1} . Aliquots were collected in amber flasks after different time intervals (up to 600 min) during the course of five complete cycles. The concentrations of THM remaining in the solution exiting the column, and in the solution at the end of the experiment (used to identify possible losses by volatilization) were determined by GC-ECD/PT.

2.7. Desorption and column recycling

2.7.1. Validation of the thermal desorption system

A thermal desorption system (Fig. 1) was developed since the compounds investigated are volatile. This technique was favored in order to avoid generation of residues that might be even more toxic than the THM, which could result from using organic solvents for desorption. A further advantage is that the THM could be recovered and used in industrial processes. For example, chloroform is used for the extraction and purification of a very wide range of substances, including drugs, vitamins, oils, resins, adhesives, and rubber.

The influence of temperature was investigated first, using temperatures of 40, 60 and 80°C . 20 mL of $100 \text{ }\mu\text{g L}^{-1}$ chloroform solution was added to flask 1, and 10 mL portions of deionized water were added to flasks 2 and 3. Flask 1 was then heated for 10 min at 40°C , after which the sample contained in all the flasks was collected and the THM concentration was determined by GC-ECD/PT. The same procedure was repeated at the other temperatures. Once the optimum temperature had been identified, further tests investigated the influence of different heating times (10, 15, and 30 min) and chloroform concentrations (25 , 50 , and $200 \text{ }\mu\text{g L}^{-1}$). The experiments were repeated for the other THM, using the same time and temperature that had been optimized for chloroform.

The results were interpreted using the following expression:

$$p = C_{v1} - C_{v2} - C_{v3}$$

where C_{v1} , C_{v2} , and C_{v3} are the concentrations of THM in flasks 1, 2, and 3, respectively, and p is the amount lost, since the system was not hermetically sealed. Measurement of the amount lost is essential for determination of the efficiency of the system. The losses can be expressed as percentages, using the following expression:

$$\%p = \frac{C_{v1} - (C_{v2} + C_{v3})}{C_{v1}} \times 100$$

2.7.2. Thermal desorption

The solution of THM containing concentrations of 225, 45.6, 57.4, 102, and $429 \text{ }\mu\text{g L}^{-1}$ of chloroform, dichlorobromomethane, dibromochloromethane, bromoform, and TTHM, respectively, was percolated through the column packed with humin immobilized on sodium silicate for 10 h under optimized conditions (using a flow rate of 2 mL min^{-1} and a bed depth of 4 cm). The thermal desorption procedure was then started. The remaining solution was removed, and the column was unpacked. The humin was transferred to flask 1, and heated in a water bath for 10 min at the previously optimized temperature of 60°C (Section 2.7.1). The concentration of THM extracted from the column was determined by GC-ECD/PT analysis of the solutions contained in flasks 2 and 3, and interpreted using the equation described above (Section 2.7.1). The column was then repacked, and the THM solution again percolated through it. Five cycles were performed, reusing the same column in order to determine the ability to regenerate the humin for subsequent THM adsorption.

2.8. Determination of trihalomethanes

Sample analysis was performed using a CP-3800 gas chromatograph (Varian, CA, USA), fitted with an electron capture detector (ECD) and a split/splitless capillary injection system, and coupled to a purge and trap system. The separation column was a CP 7709 (CP-Sil 5 CB, length 25 m, external diameter 0.25 mm and $0.4 \text{ }\mu\text{m}$ film thickness). The oven temperature program was 50°C for 3.0 min, followed by a ramp to 80°C at $10^\circ\text{C min}^{-1}$, a hold for 7 min, a ramp to 200°C at $50^\circ\text{C min}^{-1}$, and a final hold for 2 min. The injector and detector temperatures were set at 200°C and 250°C , respectively. Nitrogen was used as the carrier gas, at a flow rate of 1 mL min^{-1} , and injections were made in split mode with a ratio of 1:100. Under these conditions, the retention times for chloroform, dichlorobromomethane, dibromochloromethane, bromoform, and p-fluorobromobenzene (internal standard) were 1.17, 1.63, 2.56, 4.10, and 5.02 min, respectively. Correlation coefficients of 0.997, 0.998, 0.996, and 0.995 were obtained for the calibration curves of chloroform, dichlorobromomethane, dibromochloromethane, and bromoform, respectively. The calibration curves were constructed in the concentration range $1\text{--}250 \text{ }\mu\text{g L}^{-1}$ for all the analytes. All measurements were performed in triplicate.

The analyses employed a Tekmar 3100 Purge and Trap concentrator (Dohrmann, Cincinnati, OH, USA), coupled to the Varian gas chromatograph. Samples were purged and the analytes were transferred to the GC using ultrapure nitrogen. Compounds were adsorbed on a trap containing VOCARBTM 4000 (Supelco, Bellefonte, USA). During the desorption step, the trap was initially preheated (without gas flow) to 230°C , after which the temperature was increased to 250°C (with gas flow), transferring the retained compounds to the injector of the chromatograph through a transfer line heated to 150°C . A glass syringe (SGE, Australia) was used to introduce the samples into the PT system.

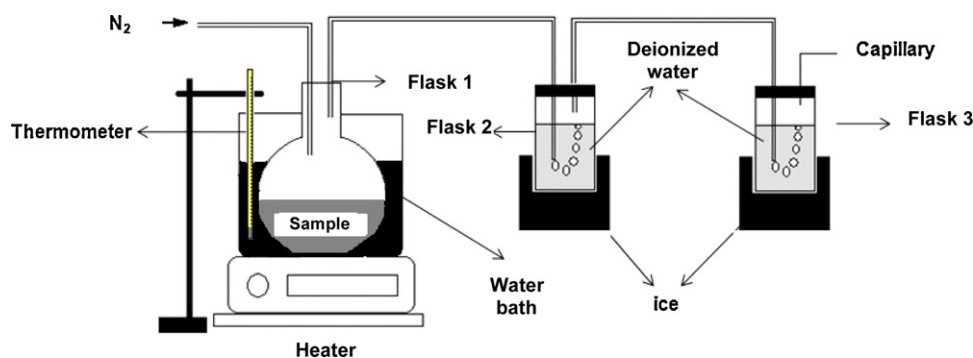


Fig. 1. Schematic of the thermal desorption system.

2.9. Statistical analysis

The normality of the data was investigated using the Shapiro–Wilk test (XLSTAT-Pro statistical package). The influences of concentration and time on adsorption of THM by the fixed bed column of humin were assessed using either the parametric Pearson or the non-parametric Spearman correlation tests, as required. Significant differences between the dependent variables were identified using one-way or two-way Student's and ANOVA parametric tests, followed by the Bonferroni post hoc test and the non-parametric Mann–Whitney test, as necessary. The significance level adopted throughout was $p < 0.05$.

3. Results and discussion

3.1. Characterization of the samples

3.1.1. Thermal gravimetric analyses (TGA)

The thermograms obtained for *in natura* humin and humin immobilized on sodium silicate are shown in Fig. 2a and b, respectively. At around 100 °C there were losses of mass of approximately 5% and 7%, respectively, due to sample dehydration. There was therefore no possibility of structural changes of the humin under the conditions employed, since the temperature used for

desorption was lower than that at which loss of water occurred. These results were in agreement with the findings of Romão et al. [14], who analyzed the peat from which the humin used in the present work was extracted, and identified an endothermic peak accompanied by a weight loss of 5% due to dehydration of the sample. It was also shown from weight loss curves that the decomposition of soil organic matter (SOM) increased at 300 °C and was essentially complete at 600 °C.

3.1.2. Specific surface area

Application of the BET technique showed that the *in natura* humin possessed a surface area of $14.97 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $0.0067 \text{ cm}^3 \text{ g}^{-1}$, while the corresponding values for the immobilized humin were $84.75 \text{ m}^2 \text{ g}^{-1}$ and $0.045 \text{ cm}^3 \text{ g}^{-1}$, respectively. Blockage of the bed occurred when *in natura* humin was used. Under the conditions employed, this material could therefore only be used in batch experiments, and not under dynamic flow conditions with a fixed bed column, which is the most practical procedure for use in large-scale systems.

The immobilization process resulted in a material with a surface area six times greater than that of *in natura* humin, which favored the percolation of the THM in solution through the fixed bed column without causing any blockage of the filter bed. The larger particle size following immobilization also facilitated regeneration of

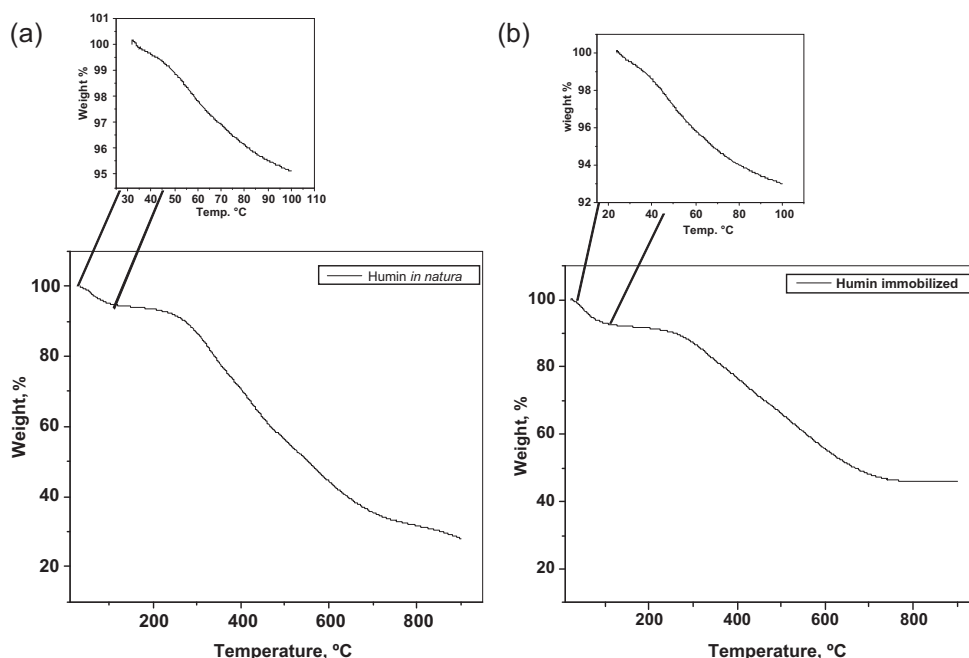


Fig. 2. Thermal gravimetric analyses (TGA) of (a) *in natura* humin, and (b) immobilized humin.

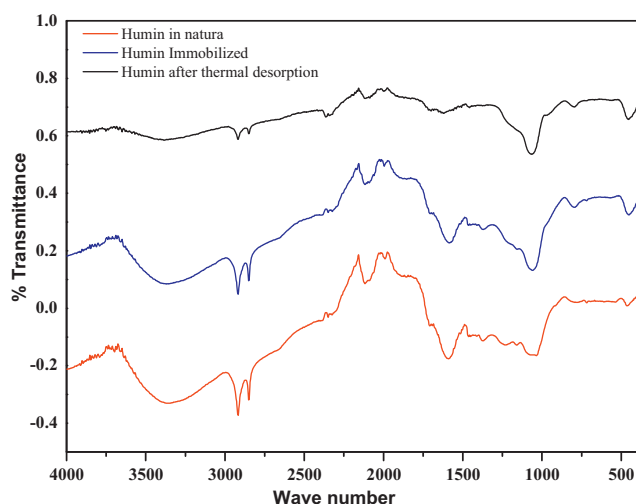


Fig. 3. Infrared spectra of humin, *in natura* and immobilized on sodium silicate.

the bed after each cycle, in agreement with Koopal et al. [19], who found that the small size of humic particles complicated regeneration. An advantage of using silica particles is that silica is often found together with humic fractions (including humin) in natural environments. Moreover, silica and its derivatives have been used extensively in chromatography because of their excellent mechanical strength, well-controlled structural parameters (such as surface area, pore size, and particle shape and size) and chemical stability.

3.1.3. Infrared absorption spectra

According to de la Rosa et al. [18], silica is used as a polymerization agent. Further information about the chemical bonding is provided in Fig. 3, which shows the infrared absorption spectra of humin (*in natura*, immobilized on sodium silicate, and after thermal desorption). The absorption band near 1622 cm^{-1} is indicative of the existence of carboxylate groups, with stretching of CH bonds observed near 2926 cm^{-1} . For *in natura* humin, the contribution of the absorption band from around 830 to 1110 cm^{-1} , associated with Si–O stretching, is less than for humin immobilized on silicate, showing that there was interaction between humin and sodium silicate. A marked reduction in the absorption bands around 2926 and 1622 cm^{-1} , which are related to the presence of carboxylate groups, was also observed, indicative of interaction between silica and these groups [6].

3.2. Batch experiments

3.2.1. Influence of immobilization of humin

The results of the batch experiments showed that there were no significant differences ($p > 0.05$) in adsorption of the THM, using either *in natura* or immobilized humin (Table 1). The immobilization of humin therefore provided physical advantages, in terms of avoidance of bed blockage and improved percolation of solutions

Table 1

Influence of the immobilization of humin on sodium silicate on adsorption of THM. Initial THM concentration, $250.0\text{ }\mu\text{g L}^{-1}$; mass of humin, 0.1 g ; temperature, $25 \pm 0.1\text{ }^\circ\text{C}$; contact time, 240 min .

Trihalomethane	% Removal	
	<i>Humina in natura</i>	Immobilized humin
Bromoform	83.2	84.8
Dibromochloromethane	78.0	79.2
Dichlorobromomethane	77.0	78.2
Chloroform	74.6	76.1

containing THM, without diminishing the effectiveness of humin as an adsorbent.

3.2.2. Capacity of humin for adsorption of chlorine

The activated charcoal commonly used in WTS showed a statistically significant greater affinity for chlorine. For chlorine concentrations in the range 1.00 – 4.00 mg L^{-1} , the removal percentage using activated charcoal was 45.0 – 58.0% , while for *in natura* and immobilized humin the values were 4.75 – 15.0% and 3.32 – 16.0% , respectively. Nonetheless, in all experiments the chlorine concentration remained within the acceptable limits for potable water required by current Brazilian legislation (0.2 – 5.0 mg L^{-1} , with a maximum recommended value of 2.0 mg L^{-1}). The humin (*in natura* or immobilized) showed low affinity for chlorine, indicating that it could be employed in WTS using the same equipment as that required for activated charcoal. For the same reason it should also be suitable for the manufacture of domestic water filters.

3.3. Desorption and column recycling

3.3.1. Validation of the thermal desorption system

Recovery of the THM using the thermal desorption system operated at different temperatures and heating times was investigated for the individual compounds at concentrations of $100\text{ }\mu\text{g L}^{-1}$ (Table 2). These experiments were used to optimize the working conditions and evaluate the precision and efficiency of the technique for desorption of the THM adsorbed on the humin.

The best results were obtained using a temperature of $60\text{ }^\circ\text{C}$ and a heating time of 10 min (Table 2). At lower temperatures, recoveries were poorer, even with longer heating times, since the boiling points of the compounds are higher than $60\text{ }^\circ\text{C}$. At higher temperatures there was a significant reduction ($p < 0.05$) in recoveries, which can also be explained by the boiling points of the compounds since the concentrations obtained in the second flask were greater, increasing losses through the capillary designed to avoid build-up of pressure and possible explosion of the system. There was therefore a loss of the compounds to the environment, which increased when higher temperatures and/or heating times were used.

The influence of THM concentration on the efficiency of the thermal desorption system (Table 3) was determined following optimization of the temperature and heating time. There was no significant influence ($p > 0.05$) of THM concentration on the

Table 2

Recoveries of THM using the thermal desorption system and THM concentrations of $100\text{ }\mu\text{g L}^{-1}$.

Trihalomethane	CF ^a	% Recovery								
		10 min			15 min			30 min		
		40 °C	60 °C	80 °C	40 °C	60 °C	80 °C	40 °C	60 °C	80 °C
Bromoform	99.8	79.4	95.3	80.1	76.8	70.5	65.1	60.1	55.9	47.1
Dibromochloromethane	101.1	80.3	96.9	77.6	72.5	68.1	60.1	65.3	50.5	42.2
Dichlorobromomethane	106.6	82.2	98.4	65.1	61.9	59.3	50.0	54.4	43.4	35.5
Chloroform	98.8	81.8	97.6	74.9	70.1	63.5	59.1	62.1	40.1	39.8

^a Concentration found ($\mu\text{g L}^{-1}$).

Table 3

Recoveries obtained for different concentrations of THM, using the thermal desorption system operated at a temperature of 60 °C and with a heating time of 10 min.

THM	% Recovery		
	Concentration ($\mu\text{g L}^{-1}$)		
	25	200	600
Bromoform	96.9	95.3	96.8
Dibromochloromethane	97.3	96.8	97.1
Dichlorobromomethane	99.2	98.8	98.0
Chloroform	98.5	97.9	98.5

recoveries obtained using the thermal desorption system, which remained within acceptable levels at all concentrations. The technique should therefore be potentially suitable for large-scale recovery of compounds such as chloroform, which could be used in other industrial processes.

In addition to the potential for losses and reduced recoveries (Table 3), the use of temperatures higher than 60 °C and heating times longer than 15 min was considered to be undesirable from the perspective of energy consumption. For most of the individual trihalomethanes the desorption efficiency was better than 90%, while for total trihalomethanes it was greater than 94%. Given these high efficiencies, it was considered unnecessary to conduct further experiments using higher temperatures.

3.3.2. Adsorption/desorption using a fixed bed column

3.3.2.1. Adsorption. Various different factors can influence adsorption, and can usually be best evaluated using batch laboratory experiments. However, the objective of the present work was to study adsorption in a dynamic system, since this should better reflect the behavior of the process employed during large-scale water treatment. The aim was to mirror as closely as possible the operational and adsorption characteristics of a WTS system, and therefore to determine the efficiency of our adsorbent for the adsorption and desorption of trihalomethanes under the most realistic possible conditions. The experiments were only performed following a theoretical evaluation of the factors governing adsorption (time, concentration, and pH). The influence of these parameters was described in our earlier paper [6], and it was found that the adsorption of THM by humin could be described by pseudo-second order kinetics and isothermally according to the Freundlich model.

Investigation of adsorption using dynamic systems can provide improved characterization of the processes occurring in large-scale operations involving liquid flow and complex mass transfer. The dynamic behavior is determined by both the physical dimensions of the column and the time-dependent saturation of sites along it [20]. This type of experiment can also be used to measure the ability to recycle columns packed with biomass (or other materials).

Due to the high adsorption capacity of humin for the THM (especially the brominated compounds), breakthrough experiments were continued until the concentration of chloroform leaving the column reached approximately 50% of the input concentration. Determination of the total saturation time ($C/C_0 = 1$) for each of the THM compounds would require the adsorption to be monitored for very long periods.

The results for adsorption of the THM on immobilized humin using the continuous system are presented as breakthrough curves, for all five column reuse cycles (Fig. 4). The ratio between the final (C) and initial (C_0) concentrations was calculated as a function of time (C/C_0 vs. t) [19].

There was no observed saturation of the fixed bed column after 10 h of percolation of the THM solution, in any of the five

Table 4
Thermal desorption results for the five cycles.

Cycles	Bromoform			Dibromochloromethane			Dichlorobromomethane			Chloroform			TTHM			
	Mass Ret. (μg)	Effic. of Ret.	Mass Des.	Mass Ret. (μg)	Effic. of Ret.	Mass Des.	Mass Ret. (μg)	Effic. of Ret.	Mass Des.	Mass Ret. (μg)	Effic. of Ret.	Mass Des.	Mass Ret. (μg)	Effic. of Ret.	Mass Des.	
1	88.96	71.23	90.85	46.98	68.27	52.90	31.43	57.47	43.29	94.99	124.67	45.88	223.17	99.25	223.17	99.25
2	106.07	76.77	101.08	57.76	77.93	55.79	36.14	62.45	44.84	93.71	137.75	50.30	224.39	99.05	224.39	99.05
3	121.96	81.78	110.33	68.58	83.24	60.71	45.96	70.03	45.99	90.43	147.96	54.46	225.65	98.68	225.65	98.68
4	140.39	85.22	123.31	72.17	79.68	66.71	47.18	74.70	48.64	87.26	160.28	57.27	227.58	98.22	227.58	98.22
5	163.16	90.11	135.59	88.01	86.36	65.14	60.29	81.63	54.60	86.90	188.05	66.03	228.51	97.80	228.51	97.80

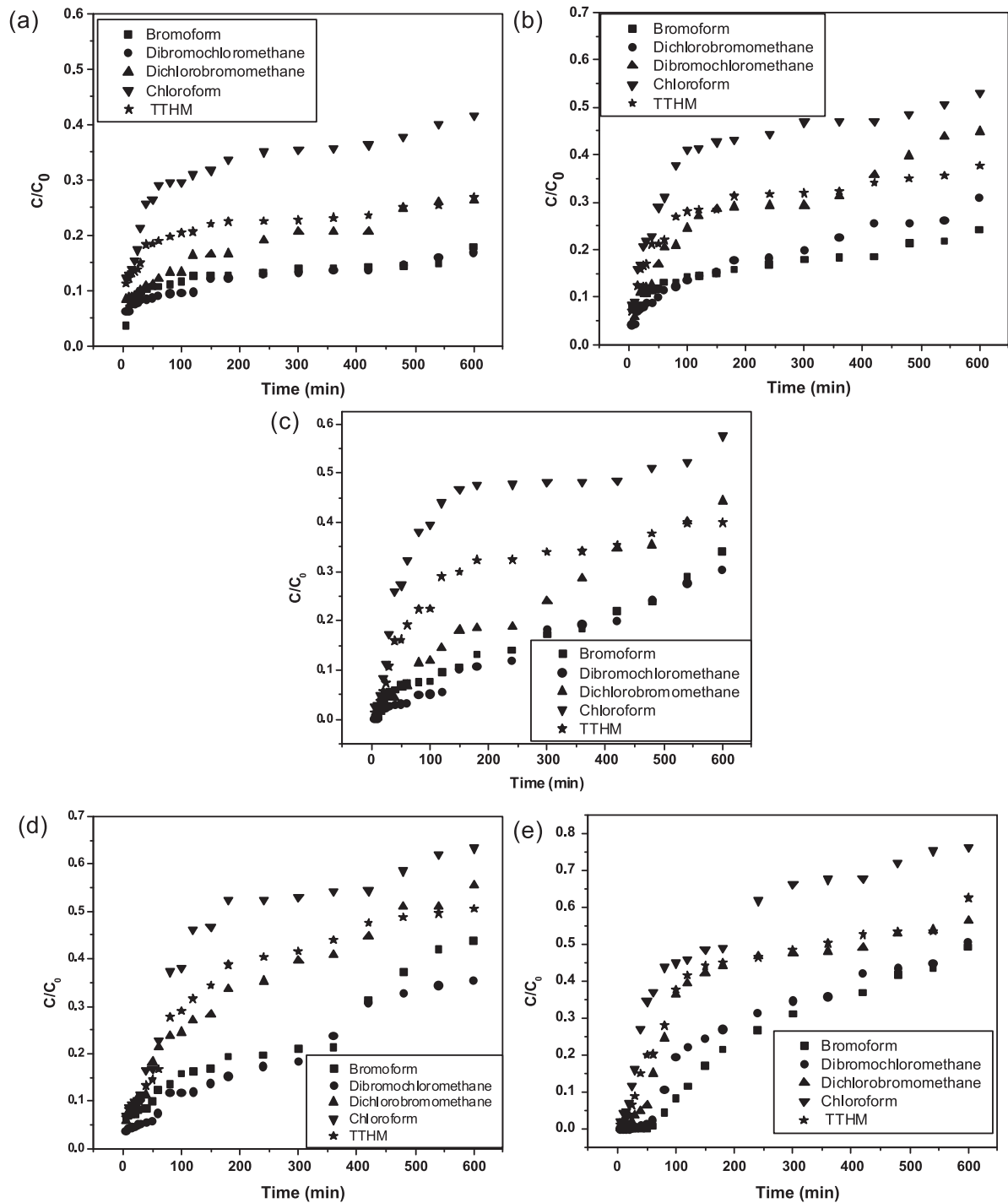


Fig. 4. Adsorption curves of THM on humin immobilized on sodium silicate: (a) first cycle; (b) second cycle; (c) third cycle; (d) fourth cycle; (e) fifth cycle. Flow rate, 2 mL min^{-1} ; bed depth, 4 cm; temperature, $25 \pm 0.1 \text{ }^\circ\text{C}$.

experimental cycles. However, there was a significant increase ($p < 0.05$) of the adsorptive capacity of the humin during the course of the cycles of reuse. The selectivity of the humin was significantly different for the different THM, and followed the order $\text{CHBr}_3 > \text{CHBr}_2\text{Cl} > \text{CHBrCl}_2 > \text{CHCl}_3$. Similar results were obtained by Lu et al. [21] for the adsorption of THM by powdered activated charcoal in batch experiments, as well as by Morawski and Inagaki [22], who studied the adsorptive capacity of carbon spheres for THM using batch experiments, and by Cunha et al. [6], who applied batch and fixed bed column procedures to the adsorption of THM by humin.

3.3.2.2. Thermal desorption. The breakthrough curves obtained in the THM adsorption experiments were used to determine the masses of the compounds retained by numerical integration, and hence enable calculation of the efficiency of desorption of the THM from humin immobilized on sodium silicate.

The retention was calculated according to Eq. (1), and is presented in the form of a plot of retained mass against time (Fig. 5).

$$\mathcal{M} = \frac{dm}{dt} = Q(C_0 - C) \quad (1)$$

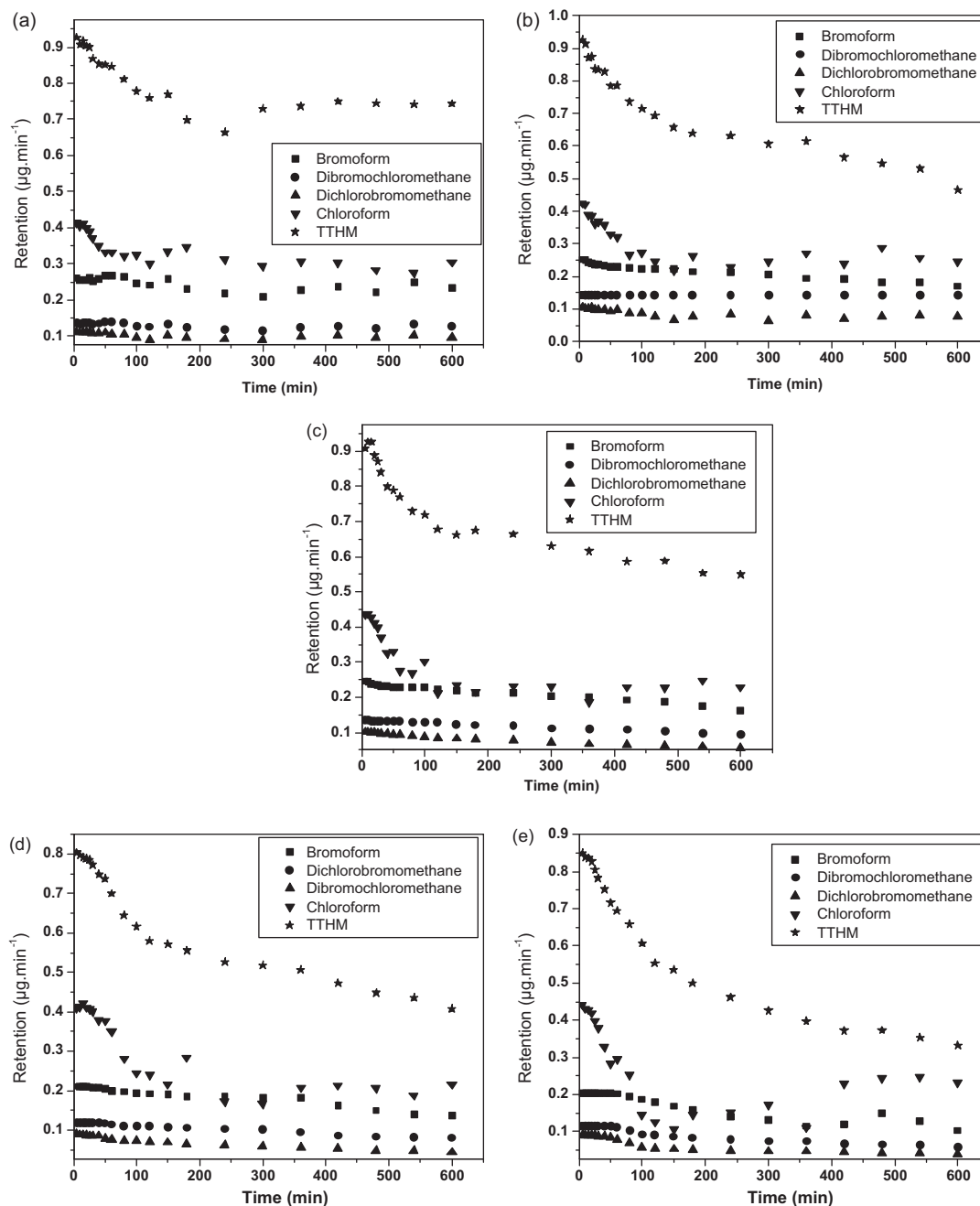


Fig. 5. Retention, according to time, of THM on the column of humin immobilized on sodium silicate: (a) first cycle; (b) second cycle; (c) third cycle; (d) fourth cycle; (e) fifth cycle. Bed depth, 4 cm; flow rate, $2 \text{ mL}\cdot\text{min}^{-1}$.

where \dot{M} is the retained mass; Q is the liquid flow rate ($\text{mL}\cdot\text{min}^{-1}$); C_0 is the initial THM concentration ($\mu\text{g}\cdot\text{L}^{-1}$); C is the concentration of THM exiting the column ($\mu\text{g}\cdot\text{L}^{-1}$).

Eq. (1) expresses mass per unit time, so that the integration of retention in relation to time provides the retained mass. Since the algebraic function describing this was unknown, numerical methods were employed to resolve the integral. The most appropriate of the commonly used approximations is the trapezium rule, which only requires known data points. This was used to calculate the mass retained on the column by numerical integration, obtaining the following expression describing the retained mass:

$$M_{\text{retained}} = \int_0^t \dot{M} \times dt \approx \frac{1}{2} \sum [\dot{M}_k + \dot{M}_{k+1}] \Delta t_k \quad (2)$$

where \dot{M}_k is the retention at time t_k ; Δt_k is the time interval $t_{k+1} - t_k$.

The retention efficiency is given by the ratio between the retained and total masses. The total mass is described by:

$$M_{\text{total}} = C_0 \times Q \times \Delta t \quad (3)$$

Eq. (1) was applied to the experimental data of retention as a function of time for each cycle (Fig. 5). Using Eq. (2), values of 89.0, 46.9, 31.4, 125, and $296 \mu\text{g}$ were obtained for bromoform, dibromochloromethane, dichlorobromomethane, chloroform, and TTHM, respectively, retained in the first cycle, giving efficiencies of 88.9, 68.3, 57.5, 45.9, and 55.8%, respectively. The values obtained for the other experimental cycles are provided in Table 4.

The procedure described previously (Section 2.5.2) was used in the desorption experiments. Knowledge of the retained and desorbed masses then enabled calculation of desorption efficiencies of the system for TTHM and the individual THM, in all five cycles (Table 4).

The total mass removed was given by the sum of the concentrations measured in each of the three flasks. Using the calculation scheme described above, in the first desorption cycle the total masses removed were 90.8, 52.9, 43.3, 223, and 410 μg of bromoform, dibromochloromethane, dichlorobromomethane, chloroform, and TTHM, respectively, giving column regeneration efficiencies of 90.0, 92.2, 94.9, 95.5, and 96.0%, respectively. The residual THM (the fraction that was not desorbed) remained adsorbed on the humin, since the silicate material only provided the improved granulometric characteristics required to enable use of the adsorbent in a fixed bed column. In terms of adsorption, *in natura* humin and immobilized humin provided very similar results (Table 1). The regeneration efficiencies for the remaining cycles and the total masses removed in each test are listed in Table 4. The desorption efficiencies of the individual compounds were significantly different ($p < 0.05$), and followed the order $\text{CHCl}_3 > \text{CHBrCl}_2 > \text{CHBr}_2\text{Cl} > \text{CHBr}_3$, which was the opposite of that obtained for adsorption and could also be explained by consideration of the boiling points of the different compounds, with those having lower affinity for the humin being desorbed first. In addition, the hydrophobic nature of humin results in it binding more strongly with the less polar compounds.

Repeated application of the thermal desorption procedure significantly increased the adsorption capacity of the humin, except for dibromochloromethane, which showed a slight reduction in the fourth cycle followed by another increase in the fifth. A similar observation was made by Li et al. [23], who studied the efficiency of activated charcoal for removal of THM and found a significant increase of the adsorptive capacity of the charcoal in the summer. The higher temperature could have activated additional adsorption sites by volatilization of compounds already present on the material. The thermal analyses indicated that no structural alterations of the material occurred under the conditions employed in this work. The increase in adsorption capacity of the adsorbent for the THM could therefore be a result of water loss, since at close to 100 °C a weight loss of 7% was observed due to dehydration, which should increase the availability of adsorption sites. Another explanation is that the surface structures of humin become more hydrophobic during thermal desorption (by elimination of polar species such as carboxylic and phenolic hydroxyl groups). This can be observed in the FTIR spectra of immobilized humin and humin. After sample thermal desorption, there was a marked reduction in the absorption bands around 2923 and 1593 cm^{-1} , which are related to the presence of carboxylate groups (Fig. 3).

4. Conclusions

The immobilization of humin on sodium silicate avoids problems related to blockage of the filtration bed, so the technique developed here could be readily scaled-up and used in water treatment plants for the efficient removal of trihalomethanes. Adsorption efficiencies were in the range 45.9–90.1%, and the order of selectivity was $\text{CHBr}_3 > \text{CHBr}_2\text{Cl} > \text{CHBrCl}_2 > \text{CHCl}_3$. The humin-based adsorbent could be recycled many times using thermal desorption. In large-scale deployment, the THM recovered could be used in other industrial processes. Of special interest is that the adsorptive capacity of the adsorbent increased over the course

of several experimental cycles. The technique therefore offers enhanced adsorption performance, and reduced material costs and waste generation.

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