

Original Research

## Chemical Regeneration of Activated Carbon Used in A Water Treatment System for Medical Services

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### Abstract

The chemical regeneration of exhausted granular activated carbon (GAC) from a water treatment plant to produce dialysis water used in hemodialysis treatments for chronic renal disease patients from a general Hospital of Ciego de Avila province, Cuba, was investigated. Activated carbon (AC) exhausted mainly by inorganics (Ca (Ca-chelates), Mg and Na) was



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regenerated using hydrochloric acid and acetic acid (one regeneration cycle). Solutions of 5%, 10%, 15% and 20%(v/v) as well as four contact times (2 h, 4 h, 6 h and 48 h) for hydrochloric acid and three contact times (2 h, 4 h and 6 h) for acetic acid at 25°C and 1 atm in a dosage of 1 g GAC/10 mL were used. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), thermogravimetric analysis (TGA), X-ray absorption technique (XRA) and Scanning Electronic Microscopy (SEM) were used to evaluate the effect of the regeneration on exhausted GAC. Batch and scaled column experiments were developed. Breakthrough curves were obtained to assess the AC's performances after chemical regeneration. The removal/adsorption capacity towards free chlorine (as disinfection agent) and hardness ions (expressed in mg CaCO<sub>3</sub>/L) was estimated using the area under the breakthrough curves from scaled columns experiments. The hydrochloric acid arises as the best acidic regenerator; using a concentration of 20%(v/v), regenerated GACs using hydrochloric acid showed the highest desorption rate of inorganics as well as a free chlorine removal performance of around 30% concerning the virgin GAC sample. A new GAC management scheme is proposed for GACs used in the medical industry to improve the sustainability and economics of the water treatment process.

### Keywords

Activated carbon; water treatment; sustainability; chemical regeneration; GAC management

## 1. Introduction

Because of its special pore structure and surface characteristics, activated carbon (AC) adsorption has been widely used to remove organic and inorganic pollutants from waters and wastewaters. These properties promoted the use of AC in all kinds of industries such as: food, chemical processes, metallurgy, energy, water treatment and medical services [1, 2]. In Cuba, granular activated carbon (GAC) is commonly used in hospitals for HClO, ClO<sup>-</sup>(forming free chlorine) and/or chloramines removal after the addition of chlorinated compounds to the water city supply for water disinfection [3, 4]. As many accidents have been reported caused by these contaminants towards patient exposure [3, 5, 6] the GAC is thus essential in hemodialysis.

However, the GAC used in the water treatment plants for hemodialysis in Cuban hospitals is unavailable for national production. Therefore, it must be imported from European countries. The economic competitiveness of the GAC adsorption process depends upon the reusability of exhausted GAC. In this regard GAC regeneration has an important role in its correct management for the hospitals. Correct management of GAC constitutes four main steps: (1) Characterization, (2) Exploitation, (3) Regeneration and (4) Reuse [2, 3]. Therefore, the regeneration of the GAC cannot only preserve the natural resources and reduce secondary pollution, but can also bring economic profit [2].

Four main regeneration methods for carbonaceous adsorbents are used: thermal, chemical and microbiological regeneration, with a new group defined as vacuum regeneration [7-10]. The most common regeneration technique for removing volatile organics is thermal regeneration. This technique has the disadvantage that the spent GAC commonly needs to be transported to an off-

site specialized facility and the increased costs due to the frequency of regeneration cycles [2]. In this regard chemical regeneration arises as a suitable method for *in situ* regeneration of GAC adsorbers used in hospitals for dialysis water production.

The GAC removes the residual free chlorine, commonly used for water disinfection in the water treatment plant for dialysis water production. The removal of free chlorine cannot be explained using the traditional adsorption concept.

The hydrolysis of the molecular chlorine results in the formation of HClO and/or ClO<sup>-</sup> depending on the pH of the solution [3]. The formed HClO/ClO<sup>-</sup> in the treated water is reduced by the GAC into a non-oxidative chloride ion (Cl<sup>-</sup>) resulting in a GAC matrix deterioration (with possible removal of some organic fraction) as a result of the *in situ* formation of oxygenated carbon functionalities (hydroxyl, carbonyl and carboxyl groups) in the carbonaceous matrix [3].

These oxygenated carbon functionalities have the potential to act as complexing sites at the GAC surface with the inorganic ions present in the used water [3]. Recently, formed complexes (Ca-carboxylates) have been reported in GAC adsorbers used in hospitals [3]. The formation of these complexes at the GAC surface together with the GAC matrix degradation due to HClO oxidation initiates an exhaustion process of this GAC, reducing its adsorption capacity towards inorganic ions [3] and decreasing its dechlorinating capacity (redox reactions), and thus affecting the reliability of the water treatment system and therefore the hemodialysis therapy itself.

Although chemical regeneration has been widely used for GAC regeneration in water treatment plants for multiple purposes depending on the type of adsorbate, its use in water treatment plants in hospitals for dialysis water production has not been widely explored. Considering the characteristics of the adsorbed compounds (inorganic species such as calcium, sodium and magnesium, [3]) on the GAC, acid washing arises as a suitable regeneration option, offering a high potential for remediation of accumulated metal ions.

Additionally, it has been demonstrated that the GAC adsorber used in the water treatment plant for hemodialysis removes Ca, Na and Mg ions without indications of detectable amounts of organic compounds [3]. Recent studies point to HCl as an excellent alternative agent for efficiently regenerating GAC adsorbers exhausted with the mentioned ions [11]. The rapid small-scale column test (RSSCT) has been used to study its breakthrough behavior. Additionally, acid-leached sample tests prove that much of the calcium is removed via acid washing, resulting in a lower calcium and ash content [2, 7, 12-14].

Two different acidic solutions (hydrochloric acid and acetic acid) were selected, taking into account their availability in the hemodialysis services of the hospital in the Ciego de Avila province, Cuba. They were subsequently used to regenerate GAC adsorber previously declared exhausted by conductivity measurements (above 20  $\mu\text{S}/\text{cm}$ ) [3]. Additionally, these acids were chosen because the target ions to be removed were Ca, Na and Mg, and no significant amount of adsorbed organics were found in the GAC surface [3]. These ions can be easily substituted by hydrogen ions delivered by both acids. As the functional groups on the surface of the GAC act as weak bases, present as Ca, Na and Mg salts, they are protonated by both acids and liberating Ca, Mg and Na ions. From the other side, acetic acid is used as a complexing agent for Ca and Mg ions and removes these ions from the exhausted GAC as complexes, soluble in water. Basic regenerating agents are therefore not relevant.

The performance of both acids for regeneration has been compared using different analytical techniques such as TGA and ICP-AES, SEM and RSSCT (for obtaining breakthrough curves), as well as a new X-ray absorption method (XRA) [3, 15-17].

The performance of the regenerated GACs towards free chlorine removal has been assessed using small-scale dynamic adsorption tests by the virgin GAC material performance as a reference. The recovery of the original performance of the GAC matrix concerning free chlorine removal is rather limited, inducing only an indirect effect (removal of inorganic ions such as  $\text{Ca}^{2+}$ ) which could eventually positively affect redox reactions for free chlorine removal.

Additionally, when dealing with water treatment adsorbers used in hospitals, some difficulties regarding correctly managing the GAC adsorber commonly arise. The GAC adsorbers' dimensions vary between 1.5 m to 2 m in length and between 50 cm to 70 cm diameter, their volume can vary between 0.3 m<sup>3</sup> and 0.8 m<sup>3</sup>, and they require between 115 kg and 300 kg of GAC, respectively for a correct operation. Although the operation of the adsorbers is relatively straightforward, getting access to its main opening usually is not easy, making the GAC replacement operations demanding and time consuming.

On the other hand, the operations of regeneration/replacement of the GAC used for renal replacement therapies in the hospital must be accomplished within 24 hours, usually on Sundays, without disrupting the dialysis schedule of the patients under renal replacement therapy.

The management strategy used in water treatment plants for dialysis water production does not include a characterization, regeneration or reuse of this material. Once the material is declared exhausted the adsorber is usually landfilled and replaced by fresh GAC. In order to overcome the shortcomings mentioned above, a new flowchart of GAC management is proposed. Information regarding grey intensity obtained from the application of XRA at two halves (GAC-Top halve and GAC-Bottom halve) in the GAC adsorber will be used in order to apply the best possible management strategy; which ultimately could help to overcome (as far as possible) the problems related with GAC management in the hospital.

## 2. Materials and Methods

### 2.1 Materials and Reagents

GAC (CG-900, from Merck) was obtained from an adsorber (previously declared “out of operation” based on conductivity measurements) used in a water purification system to produce dialysis water [3], at a general hospital of Ciego de Avila province, Cuba. Figure S1 depicts the schematic diagram of the water treatment filter used for obtaining dialysis water for hemodialysis treatments as well as the location of samples at different layers in the GAC bed. The characterization of the GAC according to the manufacturer is presented in Table 1.

**Table 1** CG-900 GAC technical characteristics according to the manufacturer.

Sample	Ash	Iodine value	Surface Area	Moisture	Apparent density
GAC(CG-900)	3 wt.% max	>900 mg/g	>900 m <sup>2</sup> /g	4 wt.%	500(±20) kg/m <sup>3</sup>

GAC samples from the first 20 cm of the adsorber (GAC-Top) were selected for the regeneration, considering the large amount of adsorbed inorganics found at the upper layers in the adsorber

compared with a virgin GAC sample [3]. Samples were collected using the procedure described in [3, 15, 16]. The GAC-Top sample was selected using GAC samples between 0 cm and the first 20 cm of the GAC bed (see Figure S1). Prior to the regeneration, the samples were pulverized and sieved using multiple sieves of 63 to 500  $\mu\text{m}$  in order to increase as much as possible the contact area of the GAC prior to the regeneration.

The target contaminants to be removed from the exhausted sample were Ca and Mg ions (present as carboxylate-type complexes) and Na ions [3]. The selected regeneration concentrations were obtained from mixing deionized water with the commercial acids (HCl 37%, Merck and  $\text{CH}_3\text{COOH}$  100%, Merck). A sodium hypochlorite ( $\text{NaClO}$ , 14%  $\text{Cl}_2$ ) from Merck was used to prepare a stock solution of  $\text{NaClO}$  at a concentration of 10 mg  $\text{Cl}_2/\text{L}$ .

A further dilution using 200 mL of this solution with 300 mL of deionized (MQ) water resulted in a  $\text{NaClO}$  solution of 4 mg  $\text{Cl}_2/\text{L}$ . N, N-Diethyl-p-phenylenediamine sulfate salt (DPD) from Merck was used as a colorimetric agent for spectrophotometric determinations of free chlorine at 516 nm during the column removal experiments [18]. Synthetic water for hardness adsorption experiments was produced according to the Standard Operating Procedure for preparing hard water and other diluents for antimicrobial products [19].

This work used synthetic water with a total hardness of around 500 mg/L (expressed in mg  $\text{CaCO}_3/\text{L}$ ) to evaluate regenerated GAC's ability towards inorganic salts adsorption. Hard water concentration was selected considering the real hardness of Cuba's Ciego de Avila aquifers (see Table S1) [3].

## **2.2 Detection and Quantification of the Target Contaminants**

Silver nitrate ( $\text{AgNO}_3$ , 99%) from Merck, at a concentration of 2%(w/v) was used to monitor the presence of chloride in washing solutions after the regeneration using HCl. Iron chloride ( $\text{FeCl}_3$ , 98%) from Merck, at a concentration of 1%(w/v) was used to monitor the calcium acetate presence in wash solutions after the  $\text{CH}_3\text{COOH}$  treatment. Washing solutions were concentrated by evaporation to 150 mL and 15 mL of each solution was delivered for ICP-AES metal ions detection, with 10 mL of the initial HCl and  $\text{CH}_3\text{COOH}$  solutions as a blank to perform the analysis.

## **2.3 Characterization**

Several analytical techniques assessed the characteristics of the exhausted, regenerated and virgin GAC before and after the regeneration. ICP-AES was used to quantify the concentration of metal ions in the solutions after the regeneration. TGA, SEM and XRA analyses were used to study the composition and morphology of the regenerated, exhausted and virgin GAC samples.

### **2.3.1 Thermogravimetry (TGA).**

A TA Hi-Res 2950 Thermogravimetric Analyzer was used to obtain thermogravimetric curves. About 15 mg of sample is heated under approximately 35 mL/min  $\text{N}_2$  gas flow at a heating rate of 20°C/min from room temperature to 600°C, then the gas flow is switched to  $\text{O}_2$  and heating is prolonged until 920°C at the same heating rate.

### 2.3.2 Scanning Electron Microscopy (SEM)

A TM3000 electron microscope was used to observe the morphological characteristics of the GAC samples. An acceleration voltage of 15 kV, an emission current of approximately 46  $\mu$ A and a filament current of 1.85 mA was applied for all analyzed samples. Standard experimental conditions and a magnification of  $\times 60$ (1 mm) and  $\times 200$ (500  $\mu$ m) were used to study the morphological characteristics of exhausted GAC before and after the regeneration. (See section 3.2).

### 2.3.3 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

A Perkin-Elmer Optima 8300DV ICP-AES(USA) was used to determine eight elements(see section 3.1) in regeneration solutions after the batch desorption experiments, taking as a reference the inlet water composition(Table S1) [3]. A RF power of 1400 W, a nebulizer, and an auxiliary gas flow of 0.75 L/min and 0.2 L/min were used, respectively. The integration time ranged between 1 s(min) to 5 s(max).

### 2.3.4 X-Ray Absorption Experiments (XRA)

XRA method [3, 15-17] uses digital image processing on digital X-Ray radiography. X-ray radiography experiments were conducted using a TOSHIBA Mamorez-mgu 100d X-ray equipment used for mammography studies in manual mode, according to [16]. The mathematical analysis of the digital X-Ray radiographic images and obtaining the image's histograms and frequency spectra were performed using dedicated software developed in MATLAB<sup>®</sup> specifically for this application [3, 15-17].

## 2.4 Batch Desorption Tests

Batch desorption experiments of the target contaminants were conducted using HCl solutions of 5%, 10%, 15% and 20%(v/v) from a commercial HCl solution at an initial concentration of 37%. Four contact times were used: 2 h, 4 h, 6 h and 48 h. After the treatment, the GAC was washed using MQ water until no residual chloride was detected (no precipitate of AgCl after AgNO<sub>3</sub> addition).

Batch desorption tests using CH<sub>3</sub>COOH were developed using solutions of 5%, 10%, 15% and 20%(v/v) respectively of a commercial CH<sub>3</sub>COOH solution at an initial concentration of 100%. Three contact times were used: 2 h, 4 h and 6 h. After the treatment, GAC was washed using MQ water until the calcium acetate (product of the reaction between the CH<sub>3</sub>COOH and Ca<sup>2+</sup> ions) concentration was small enough to finish the wash.

GAC was regenerated with stirring at 25°C and 1 atm in a 1 g GAC/10 mL dosage for each concentration of the acidic solutions during the selected contact times. This dosage was used to shorten the equilibration time as much as possible [20, 21] and to increase the adsorption probability of the solute (acid solutions) aiming for enhanced desorption of adsorbed inorganics. Once the concentration and contact time were found with the optimal desorption effect between analyzed samples, lower dosages were used for dynamic removal/adsorption experiments.

No batch experiments were developed for the free chlorine removal considering the limited amount of samples. Therefore, only the dynamic removal experiments using scaled columns were carried out. For these experiments, 10 mg of powder AC (63  $\mu$ m) was used to remove free chlorine from the inlet solution with a concentration of 4 mg/L during 330 min for the virgin GAC at a

constant flow of around 1 mL each 15 min. Using previous information, it is possible to estimate that after 330 min the amount of GAC used was capable of processing around 22 mL of the inlet solution, which gives an approximated dosage of 0.5 mg/mL for the dynamic removal of free chlorine using scaled columns. This dosage aligns with recent works where dosages between 0.3 and 0.5 mg GAC per mL of solute are used [22].

Virgin GAC samples were also submitted to leaching experiments using the regeneration mentioned above conditions.

## **2.5 Column Tests**

In addition to the batch desorption regeneration tests, column tests for free chlorine (removal) and hardness (adsorption) were carried out using a glass column (2.5 cm diameter, 5 cm height) filled with approximately 10 g powder AC (0.063 mm). The scaling down of the GAC adsorber for column laboratory experiments was done following the scaling down rules for commercial GAC adsorbers according to [2]. Briefly, the ratio between the diameter and the length of the industrial and the lab scale adsorber was kept constant. The length of the experimental column as well as the mass of powder GAC (0.063 mm fraction of GC-900 GAC) used for the experiments were obtained following this rule [2].

Regeneration experiments were conducted using the set-up and the methodology described in [2]. On the other hand, free chlorine removal tests on scaled columns were carried out using a modification of the experimental setup depicted in [2]. The stock free chlorine solution was pumped through the experimental column using a peristaltic pump Heidolph Pump drive 5001 (tubing size: 1.5 mm), the effluent was collected and the free chlorine concentration was measured at fixed intervals (15 min). The effluent's concentration in free chlorine was determined using a Spectrophotometer Ultrospec® 7000 and the methodology described in [18].

Virgin, exhausted and regenerated GACs from the hospital water treatment plant were used for free chlorine/hard water removal/adsorption tests. The procedure for obtaining the breakthrough curves was applied according to [2]. The breakthrough curve concept is supported as a predominant factor for a successful design/evaluation for upscaling to an industrial column. The flow rate of the acidic solutions, free chlorine solutions and hard water was 0.1 mL/min, being small enough for a potential intra-particle diffusion process [2].

In order to obtain the breakthrough curves for the regeneration, pH was monitored until the column reached a constant ( $H^+$ ) concentration (equal to the initial HCl or  $CH_3COOH$  solution). The breakthrough curves for removal of free chlorine were conducted until the column delivered a constant concentration of free chlorine in the effluent (Absorbance values of the effluent equal to the absorbance values of the initial  $NaClO$  solution) using colorimetric determination of free chlorine ( $HClO$  and/or  $ClO^-$ ) in water according to Standard Method 4500-Cl G for free chlorine [18, 23, 24].

Hardness adsorption breakthrough curves were conducted by measuring the outlet conductivity of the column at 20 min intervals and using a conductivity meter Inolab Cond 7110; 1 mL solution was sampled and transferred to a measurement beaker and diluted (1:50) until the output conductivity was within the 5% range of the inlet conductivity values.

### 2.5.1 Breakthrough Curves

The methodology carried out for the construction of the breakthrough curves used for the evaluation of the regeneration effectiveness as well as the free chlorine removal capacity and hardness adsorption, is described in the supplementary information of this work.

The dechlorinating capacity, as well as the adsorption capacity for hardness ions of the GAC was calculated and quantified considering the removed free chlorine and hardness ions from the inlet water by the adsorber and the time during which the adsorber is capable of maintaining its removal/adsorption capacity concerning the virgin material. In our case, breakthrough time ( $t_p$ ) was determined as the time for reaching the equilibrium at which the derivative of the ratio ( $C_e/C_o$ ) to the time reaches its maximum, and the breakthrough curve gets an inflection point. At this point, the removal/adsorption capacity of the GAC towards free chlorine and hardness ions can be estimated using equation 1. It could be used as an indicator of regeneration efficiency in regenerated samples.

$$CA = \frac{\int_0^{t_{p(i)}} \left[ 1 - \left( \frac{1}{C_o} \cdot C_{e_i}(x) \right) \right] dx}{\int_0^{t_{p(virgin)}} \left[ 1 - \left( \frac{1}{C_o} \cdot C_{e(virgin)}(x) \right) \right] dx} \cdot 100 \quad (1)$$

Where:

$CA$ : Removal/adsorption capacity towards the adsorbate (in percent);

$t_{p_i}$ : Breakthrough time of the sample  $i$  for adsorbate removal/adsorption (in min);

$t_{p(virgin)}$ : Breakthrough time virgin GAC sample for adsorbate removal/adsorption (in min);

$C_{e_i}$ : Adsorbate concentration of the effluent for sample  $i$  (in mg/L);

$C_{e(virgin)}$ : Adsorbate concentration of the effluent for the virgin GAC sample (in mg/L);

$C_o$ : Adsorbate concentration at the inlet of the column (in mg/L).

Equation 1 calculates the ratio between the area under the curve from obtained breakthrough curves for each analyzed GAC sample and the virgin GAC sample; giving the result as a percent concerning the adsorbate removal capacity of the virgin GAC sample.

The use of equation 1 allows taking into account the complete shape of the breakthrough curve (changes in the effluent concentration as well as the breakthrough time) for the estimation of the sample removal/adsorption capacity, which could ultimately be used as a regeneration efficiency indicator for regenerated samples. The calculation for numerical estimation of the area under the curve for each analyzed sample was done using the software packages Origin® and MATLAB®.

## 3. Results and Discussion

### 3.1 Characterization

#### 3.1.1 ICP-AES

Eight elements were detected in the regeneration solutions using the ICP-AES analysis (see Tables S2 and S3) for HCl and CH<sub>3</sub>COOH respectively. Concentrations depicted in Table 2 and Table 3 for detected elements using HCl and CH<sub>3</sub>COOH at 20%(v/v) 2 h and 15%(v/v) 4 h, respectively are



calculated concerning the virgin sample leaching solutions (see Tables S4 and S5). The concentration of detected elements in the blank solutions was depicted in Table S6 and Table S7.

**Table 2** Detected elements in acid solutions after batch regeneration experiments using HCl.

	Al	Ca	Fe	K	Mg	Mn	Na	Zn
HCL	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
20%(v/v) 2 h	0.360	442.09	1.061	1.748	19.79	0.176	66.32	7.417
Blank	<0.050	<0.05	<0.050	<0.050	<0.005	<0.005	<0.10	<0.050

**Table 3** Detected elements in acid solutions after batch regeneration experiments using CH<sub>3</sub>COOH.

	Al	Ca	Fe	K	Mg	Mn	Na	Zn
CH <sub>3</sub> COOH	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
15%(v/v) 4 h	0.043	67.13	<0.050	0.822	4.729	0.046	33.21	0.864
Blank	<0.050	<0.05	<0.050	<0.050	<0.005	<0.005	<0.10	<0.050

Based on the ICP-AES results, it is possible to state that Ca, Mg and Na are the major desorbed ions during the batch regeneration using both acidic solutions, which is by the adsorbed ions in exhausted GAC for the production of dialysis water [3] as well as with recent work dealing with the regeneration of exhausted GACs used in power plants [2] where increased adsorption of inorganics (mainly CaCO<sub>3</sub>) is reported. The feed water composition for the water treatment plant is presented in Table S1 [3].

From a comparison between the two acidic regeneration solutions used, it is possible that HCl can remove a higher amount of adsorbed inorganic ions than CH<sub>3</sub>COOH for all the combinations of contact time and acid concentrations.

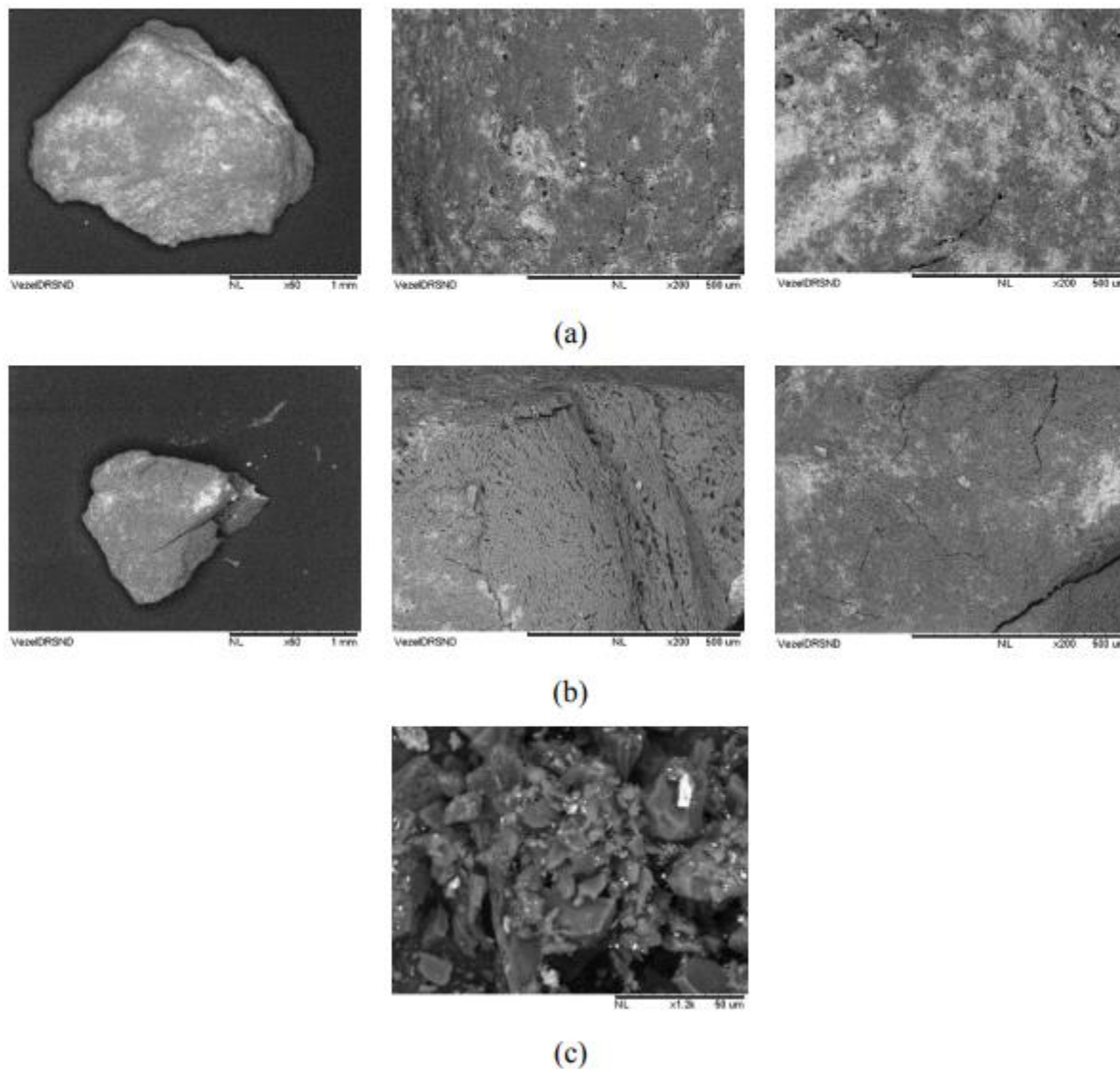
From Table 2 and Table 3 we can observe that, on average, the higher desorption rates towards Ca, Mg and Na are achieved using 20%(v/v) HCl and 2 h contact time, reaching values around 442 mg/L, 20 mg/L and 66 mg/L respectively. On the other hand, the desorption rates of inorganics (including Ca, Mg and Na) using CH<sub>3</sub>COOH are significantly lower than HCl. The highest desorption for CH<sub>3</sub>COOH was obtained using a concentration of 15%(v/v) and 4 h of contact time with values around 67 mg/L, 5 mg/L and 33 mg/L for Ca, Mg and Na respectively.

According to Tables S2 and S3 increasing the contact time beyond 6 h does not significantly impact the regeneration of the GAC, depicting very similar values for desorbed inorganics. On the contrary, an excessive increase of the contact time could cause a re-adsorption process between the GAC and released inorganics, as can be observed in Table S2 for HCl when the contact time is increased on purpose up to 48 h.

### 3.1.2 SEM

Figure 1(a), (b) and (c) depicts the SEM images of exhausted GAC before (Figure 1 (a)) and after (Figure 1 (b)) the batch regeneration test using HCl 20%(v/v) and 2 h contact time and the virgin GAC (Figure 1 (c)). Recently higher values in the SEM grey-scale images (increases in brightness)

have been related to higher surface deterioration and, thus, an indicator of the exhaustion degree of the GAC [3].



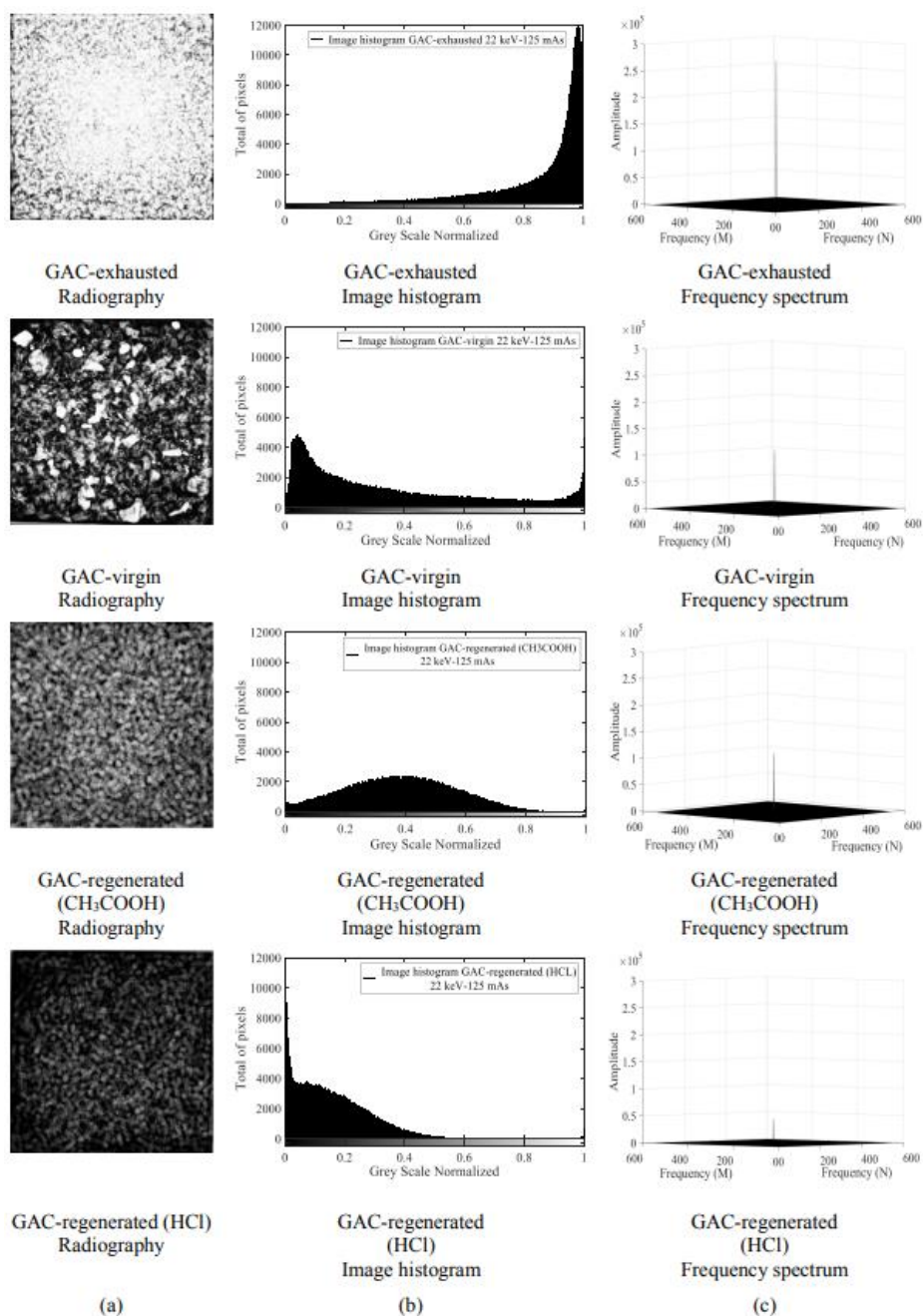
**Figure 1** a) SEM image GAC exhausted, b) SEM image GAC exhausted after regeneration using HCl 20%(v/v) and 2 h contact time and c) Virgin GAC.

On the other hand, lower values in the grey scale (darker images) have been related to previous work with a less deteriorated GAC surface [3]. Figure 1 (a) depicts a smooth coated surface with inorganic material ( $\text{Ca}^{2+}$  complexes) [3]. Figure 1 (b) depicts a less covered surface with deeper cracks in the GAC surface and a reduction of the surface coverage; indicating the removal of inorganics due to the acid treatment as confirmed by ICP-AES analysis.

Although indications of an improvement in surface characteristics can be observed in SEM images (Figure 1 (b)), it is also possible to see some morphological changes when comparing Figure 1 (a) and Figure 1 (b), mainly related to the stirring during the regeneration process.

### 3.1.3 XRA

XRA takes advantage of the different attenuation levels of X-ray radiation by materials with different densities [3, 15-17]. Figure 2 depicts the original X-ray radiographic images(a), the image histograms(b) and the frequency spectra(c) of the exhausted GAC before and after the regeneration using HCl 20%(v/v) and 2 h contact time and CH<sub>3</sub>COOH 15%(v/v) and 4 h contact time as well as the virgin GAC sample. The differences in brightness in the grey-scale radiographic images are noticeable. The digital images obtained with this method show a grey-scale image where the more exhausted samples are closer to one in the normalized grey-scale (whiter zones). On the other hand, the less exhausted samples are closer to zero in the normalized grey scale (darker zones) [3, 15-17].



**Figure 2** a) Digital radiographic images, b) Image histograms and c) Image frequency spectra of different samples and the virgin GAC.

The GAC-exhausted sample presents clearer zones than GAC-virgin and regenerated GAC samples, showing a histogram peak completely displaced to the right (“one”) in the normalized grey scale. The GAC-virgin sample shows quite different behaviour in the acquired histograms concerning the histograms of the regenerated and exhausted sample. The peak of the histogram (Figure 2 (b)) is displaced to the left in the normalized grey scale (closer to zero). Obtained results for GAC-virgin and GAC-exhausted are in line with the reported results in [3, 16, 17] from the application of XRA. On the other hand, depicted displacements on XRA image histograms from regenerated GACs indicate reduced ash content in the samples after the chemical treatment, which has also been reported in [2, 3].

As GAC-virgin has not been used in the filtration system, its photonic absorption is lower than the other used samples, thus producing a darker image, the origin of the different white spots present in GAC-virgin has been described in depth in [16].

The peak observed in the frequency spectra (Figure 2 (c)) is the direct component ( $D_C$ ) of the digital radiographic image and represents the sum of intensity levels of each pixel for the entire image; this is a result of the spatial frequency equal to zero [3, 16]. The direct component of the (Figure 2 (c)) of GAC-virgin’s frequency spectrum is significantly lower than the direct component of the frequency spectrum from the GAC-exhausted.

Regenerated samples show a different pattern (see Figure 2 (b)) where the distribution peak for the GAC sample regenerated with  $CH_3COOH$  is mainly centrally distributed around 0.4 in the normalized grey scale. The histogram’s regenerated sample using HCl depicts a shift to the left , where the distribution peak is displaced to zero (“0”). Significant differences between peak amplitude can be observed between the exhausted GAC and regenerated samples, being more abrupt between the GAC-exhausted and GAC-regenerated using HCl, having the lowest peak amplitude value of all analyzed samples. On the other hand, GAC-virgin and GAC-regenerated using  $CH_3COOH$  present a similar peak amplitude.

Table 4 depicts the frequency spectrum peak amplitude (DC component) for each digital image obtained from each studied sample.

**Table 4** Frequency spectrum peak amplitude for exhausted, regenerated and virgin GACs.

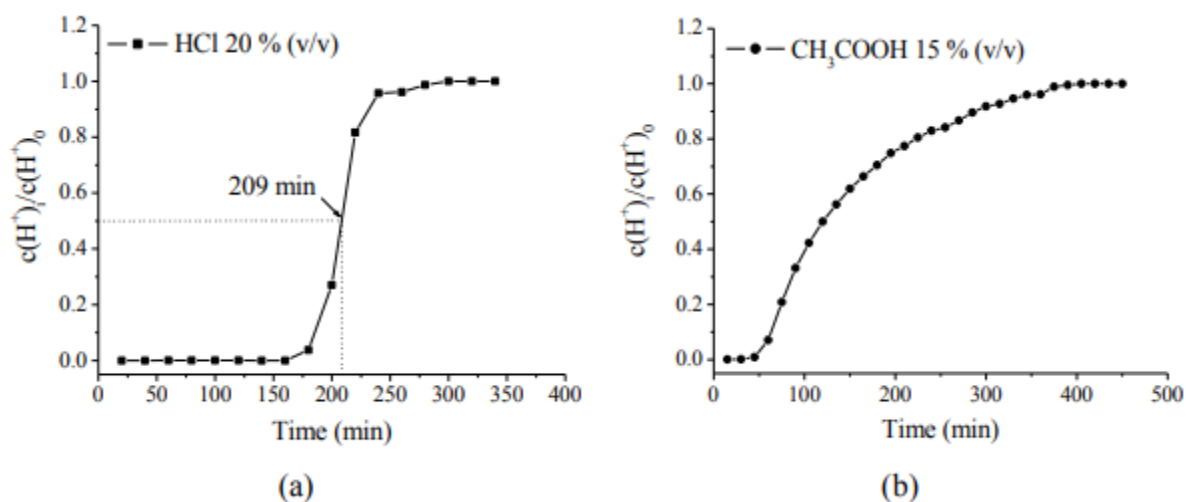
GAC-sample	GAC-exhausted	GAC-virgin	GAC-regenerated( $CH_3COOH$ )	GAC-regenerated(HCl)
$D_C(0.0)$	260000	100000	110000	45000
$\sigma(D_C)$	2702	1074	1088	1023

$D_C$ : mean of the peak amplitude values for five independent experiments for spatial frequencies equal to zero ( $x = y = 0$ ) and  $\sigma(D_C)$ : standard deviation.

The differences in the peak amplitude values presented in Table 4 confirm the observations from Figure 2. The peak amplitude of the GAC-exhausted is significantly higher than the other samples. GAC-virgin and GAC-regenerated using  $CH_3COOH$  depict a similar peak amplitude value slightly superior for the regenerated sample. Finally, the GAC-regenerated sample using HCl depicts all studied samples' lowest peak amplitude values.

### 3.2 Dynamic Regeneration

Dynamic regeneration experiments were developed using the scaling rules for scaling down the hospital GAC adsorber according to [2]. Figures 3 (a) and (b) depict the regeneration breakthrough curves for HCl 20%(v/v) and 2 h of contact time and CH<sub>3</sub>COOH 15%(v/v) and 4 h of contact time, respectively after applying the rapid small-scale column test. The breakthrough time was calculated as described in section 2.5.1.



**Figure 3** a) Breakthrough curve for HCl regeneration 20%(v/v) and 2 h contact time and (b) Breakthrough curve for CH<sub>3</sub>COOH regeneration 15%(v/v) and 4 h of contact time.

The breakthrough curve for HCl depicts a sharp and relatively fast transition during the regeneration, indicating a high desorption rate with a breakthrough time of approximately 209 min. Such behavior for HCl regeneration of GAC exhausted with inorganics (mainly Ca<sup>2+</sup>) has been previously reported in [2]. On the other hand, the breakthrough curve for CH<sub>3</sub>COOH depicts a different behavior, showing a prolonged transition during the regeneration, indicating a lower desorption rate during the chemical regeneration with no drastic breakthrough time. To reach a ratio  $c(H^+)_i/c(H^+)_0$  of almost 1, for HCl it takes 240 min and in the case of CH<sub>3</sub>COOH a much longer time of 360 min is required.

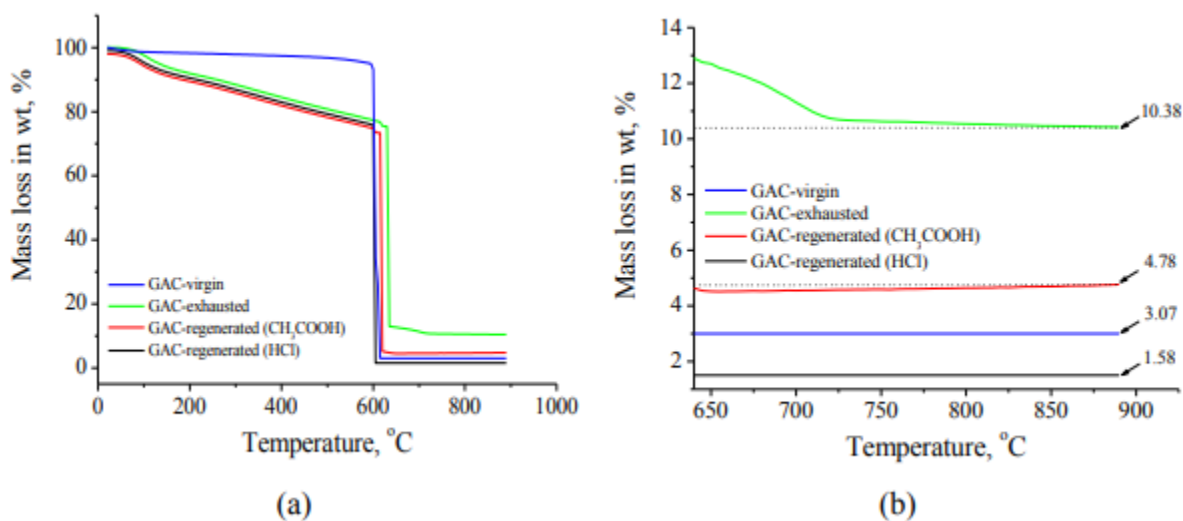
According to Figures 3 (a) and (b) HCl reacts with the adsorbed compounds on the GAC (mainly Ca<sup>2+</sup> ions) in a much faster way in comparison with CH<sub>3</sub>COOH, leading to faster regeneration of the GAC.

On the contrary, CH<sub>3</sub>COOH depicts a lower reactivity than HCl, leading to a slower and less efficient column regeneration. The HCl desorption capacity for Ca<sup>2+</sup> ions increases due to a faster desorption time leading to better regeneration. On the other hand, CH<sub>3</sub>COOH shows a very slow transition during the regeneration (Figure 3 (b)). As a result, the desorption capacity for Ca<sup>2+</sup> decreases, leading to a less efficient regeneration than HCl (confirmed by ICP-AES) due to a greater desorption time.

#### 3.2.1 TGA

The mass loss curves for the exhausted and virgin GACs as well as regenerated GACs using HCl 20%(v/v) and 2 h of contact time and CH<sub>3</sub>COOH 15%(v/v) and 4 h of contact time, are presented in

Figure 4 (a) and (b). Four stages of mass losses are observed: (1) A first mass loss between 125°C and 170°C consistent with moisture loss in the sample; (2) a gradual mass loss between 170°C to 600°C consistent with the release of CO<sub>2</sub> and H<sub>2</sub>O as the result of thermal degradation of the oxidized GAC surface [3]; (3) mass loss occurring at 600°C after switching to an oxidative(O<sub>2</sub>) atmosphere, without any further significant mass changes for the virgin GAC and regenerated GAC; leaving the residue(ash); (4) a mass loss between 620°C and 680°C for the exhausted GAC, related with the thermal degradation of the in-situ formed calcium carbonate(CaCO<sub>3</sub>) [3].



**Figure 4** Mass losses for analyzed GAC samples as a function of the temperature, (a) 25°C to 900°C and (b) 620°C to 900°C(O<sub>2</sub>).

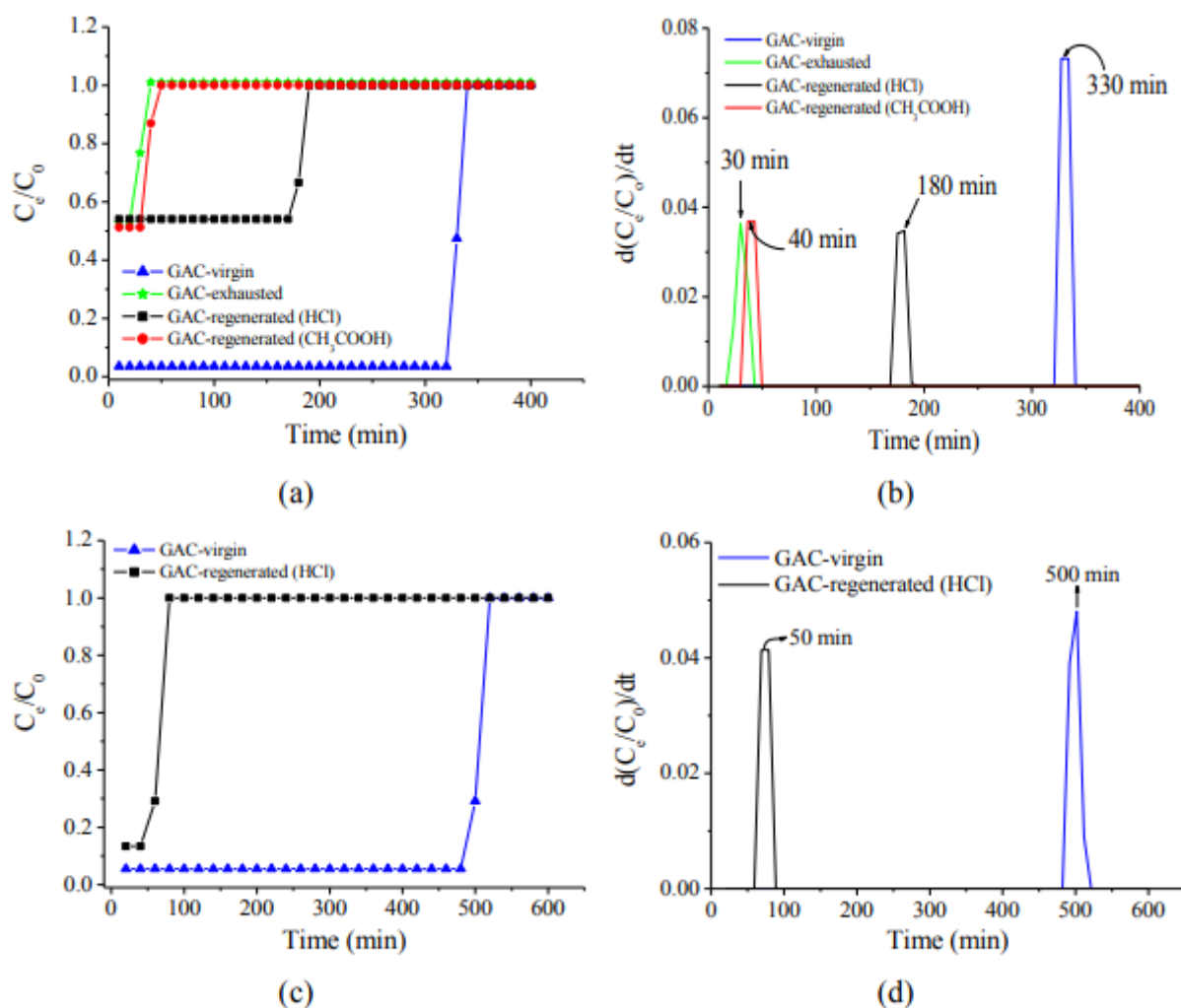
Based on Figure 4 (a) the mass loss for the virgin GAC sample presents a pattern completely different from the exhausted and regenerated GAC samples; being rather thermally stable. On the other hand, the samples from exhausted and regenerated GAC depict a very similar pattern between 25°C and 600°C to the patterns found in [3], where a mass loss of around 20 and 25% can be observed as the result of the thermal treatment on an already oxidized carbonaceous surface(due to reaction with HClO treated feed water) mainly related with the release of CO<sub>2</sub> and H<sub>2</sub>O [3].

According to Figure 4 (b) the ash content depicted for the GAC sample regenerated using HCl 20%(v/v) and 2 h of contact time is even lower than the ash content from the virgin GAC sample. HCl can remove inorganic material (ash soluble components) already present in the virgin material due to the deterioration of the virgin GAC and the presence of Ca<sup>2+</sup> species, which can act as a catalyst (as confirmed by ICP-AES results from leaching experiments on virgin GAC samples, see Tables S4 and S5). On the other hand, the acetic acid shows a slightly higher ash content value than the virgin GAC sample.

### 3.3 Free Chlorine and Hardness Ions Removal/Adsorption Tests in Scaled Columns

In order to evaluate the efficiency of the regeneration process towards free chlorine removal and hardness ions adsorption, dynamic experiments using scaled columns were developed and breakthrough curves were obtained for each studied sample. Figures 5 (a) and (c) depict the breakthrough curves for free chlorine removal and hardness ions adsorption for analyzed samples.

On the other hand, Figures 5 (b) and (d) depict the derivative of the ratio ( $C_e/C_0$ ) concerning to the regeneration time.



**Figure 5** Breakthrough curves for free chlorine removal (a) and hardness ions (c) adsorption in scaled columns and the derivative plots of the ratios  $C_e/C_0$  versus time (b), (d).

Figure 5 (a) depicts interesting trends for the four analyzed GAC samples. All studied GAC samples show a very abrupt transition zone during removal with different breakthrough times (Figure 5 (b)). The virgin GAC sample shows a completely different behavior than the other samples. According to Figure 5 (a) and (b) GAC-virgin presents the highest removal performance with a breakthrough time of around 330 min and a maximum (100%) removal capacity towards free chlorine (3.86 mg/L of free chlorine removed using 10 mg of GAC-virgin) using an inlet concentration ( $C_0$ ) of 4 mg free  $Cl_2/L$  (volume of the feed water around 30 mL).

The GAC-exhausted sample depicts the worst performance, showing a removal capacity for free chlorine around 3% concerning the virgin sample (1.8 mg/L of free chlorine removed using 10 mg of GAC-exhausted) with a breakthrough time of 30 min (volume of the feed water around 3 ml).

GAC-regenerated using HCl (20%(v/v) and 2 h of contact time) and GAC-regenerated using  $CH_3COOH$ (15%(v/v) and 4 h of contact time) depict significantly different values in removal capacity for free chlorine in comparison with GAC-exhausted with values around 27 and 2.5% (between 1.8

and 2 mg/L of free chlorine removed using 10 mg of exhausted AC) but with different breakthrough times; with 180 min and 40 min for HCl and CH<sub>3</sub>COOH respectively (volume of the feed water between 18 and 4 mL respectively). In Figure 5 (c) and (d), it is possible to observe the adsorption performance of the virgin and regenerated GAC towards hardness ions.

According to Figure 5 (a) the virgin GAC depicts an excellent adsorption capacity for hardness ions showing a breakthrough time of 500 min, approximately (485 mg/L of removed hardness ions using 10 mg of AC for a volume of feed water around 50 mL) for an inlet concentration (C<sub>0</sub>) of 500 mg/L.

On the other hand, regenerated GAC using HCl as regeneration acid (20%(v/v)) and 2 h of contact time depicts a drastic lower adsorption capacity towards hardness ions with values around 7% (465 mg/L of removed hardness ions using 10 mg of AC and a feed water volume around 5 mL) and a breakthrough time significantly lower in comparison with the virgin sample (around 50 min). Table 5 depicts the calculated values of area under the curve from breakthrough curves and the removal capacity towards free chlorine according to equation 1 (see section 2.5.1).

**Table 5** Area under breakthrough curves (A<sub>C</sub>) and free chlorine removal capacity (CA<sub>(HClO/ClO<sup>-</sup>)</sub>).

GAC-sample	GAC-exhausted	GAC-virgin	GAC-regenerated(CH <sub>3</sub> COOH)	GAC-regenerated(HCl)
A <sub>C</sub>	8.22	306	7.83	82.04
σ(A <sub>C</sub> )	0.08	3.55	0.06	0.74
CA <sub>(HClO/ClO<sup>-</sup>)</sub> (%)	2.68	100	2.55	26.76
σ(CA <sub>(HClO/ClO<sup>-</sup>)</sub> )	0.02	1.52	0.03	0.33

A<sub>C</sub>: mean of the area under the curve for five independent experiments and CA<sub>(HClO/ClO<sup>-</sup>)</sub>: mean of the removal capacity values for five independent experiments with σ(i): standard deviation.

According to Table 5 it is possible to state that the free chlorine removal capacity of GAC-exhausted in comparison with GAC-virgin is around 3%; indicating that this GAC has lost almost all its dechlorinating capacity, as shown in Figure 5 (a).

At this point, the GAC-exhausted can keep the concentrations of free chlorine in the effluent around 2 mg/L for only 30 min. The GAC-regenerated using HCl(20%(v/v)) and 2 h of contact time depicts a free chlorine removal capacity of around 27% concerning GAC-virgin. This indicates that the chemical treatment impacted its dechlorinating capacity, being capable of maintaining the concentration of free chlorine in the effluent at around 2 mg/L for 180 min. Although the dechlorinating capacity of this GAC has been reduced to 70% approximately, it is still capable of eliminating around 2 mg/L of free chlorine from an inlet concentration of 4 mg/L.

The GAC-regenerated using CH<sub>3</sub>COOH depicts a behavior very similar to GAC-exhausted, showing a free chlorine removal capacity of around 2.55% with a breakthrough time of 40 min, only 10 min more in comparison with the exhausted sample. Even though some removal of inorganics from the GAC surface has been achieved using acetic acid (see ICP-AES, TGA and XRA results), its dechlorinating capacity does not show significant improvements compared with GAC-exhausted. Table 6 depicts the calculated values of area under the curve from breakthrough curves and the adsorption capacity of the virgin and regenerated GAC samples towards hardness ions.



**Table 6** Area under breakthrough curves ( $A_C$ ) and hardness ions adsorption capacity ( $CA_{(mg\ CaCO_3/L)}$ ).

GAC-sample	GAC-virgin	GAC-regenerated(HCl)
$A_C$	473	33.1
$\sigma(A_C)$	2.4	0.8
$CA_{(mg\ CaCO_3/L)}(\%)$	100	7.3
$\sigma(CA_{(mg\ CaCO_3/L)})$	1.1	0.2

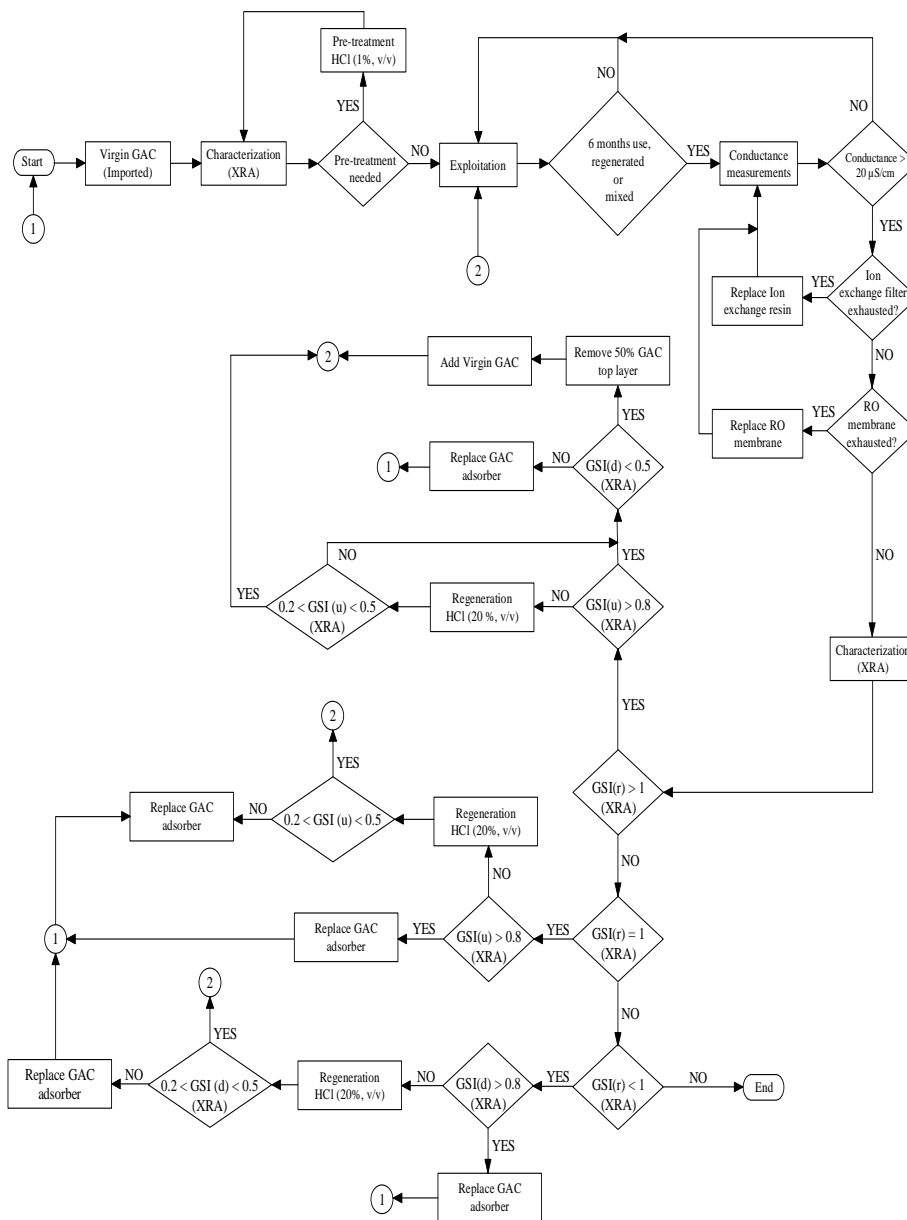
$A_C$ : mean of the area under the curve for five independent experiments and  $CA_{(mg\ CaCO_3/L)}$ : mean of the adsorption capacity values for five independent experiments with  $\sigma(i)$ : standard deviation.

According to Table 6, it is possible to state that the adsorption capacity towards hardness ions of the regenerated GAC in comparison with the virgin GAC is around 7%, indicating that this GAC has lost almost all its ability to adsorb inorganic ions.

According to Table 6 and Figure 5 (c) the adsorption capacity of GAC-regenerated (HCl) is still quite significant (around 465 mg/L from an inlet solution at 500 mg/L) at the beginning of the process. However, it can only sustain that adsorption capacity a fraction (1/10) of the breakthrough time of the GAC-virgin.

### 3.4 Proposal of A GAC Management Flowchart for ACs Used in the Medical Industry

Figure 6 depicts the new proposal for the GAC management flowchart in the hospital. The GAC management scheme shown in Figure 6 estimates the exhaustion degree of the entire adsorber using the difference in brightness at different layers in the adsorber using XRA. With this information, it could be possible to assess which section of the adsorber is more exhausted concerning the other one and if regeneration or a replacement of the GAC should be applied.



**Figure 6** Proposed flow chart for a GAC management in medical industry. For  $GSI(r) = GSI(u)/GSI(d)$ ; with  $GSI(u)$ : grey scale level of GAC samples at the top half of the GAC bed and  $GSI(d)$ : grey scale levels of GAC samples at the bottom half of the GAC bed. Numbers “1” and “2” inside circles are the links between the same numbers at different locations in the flowchart considering the arrow direction. Using this methodology, the sampling process could be done only two times as a minimum: two samples (at top half and at bottom half) before the regeneration (if needed) and two samples after the regeneration, without removing the GAC from the adsorber, unless a complete GAC replacement is needed. In order to select the best strategy to follow, the performance of the entire filter must be evaluated. The GAC management flowchart evaluates the exhaustion degree of both halves in the adsorber (top and bottom half); being  $GSI(u)$ : the GSI level at the first top half of the adsorber and  $GSI(d)$ : the GSI level at the bottom half of the adsorber. The goal of the proposed GAC management scheme is to characterize the GAC before reaching a significant exhaustion degree, with the aim of applying the regeneration at the right moment and therefore, allowing extended use of this material.

According to Figure 6 after evaluating the ion exchange filter and the reverse osmosis (RO) membrane, a characterization using XRA is proposed. After this first characterization the parameter  $GSI_{(r)}$  is evaluated.  $GSI_{(r)}$  can adopt three possible values:

- (a)  $GSI_{(r)} = \frac{GSI_{(u)}}{GSI_{(d)}} = 1$  Homogenous exhaustion degree in the complete GAC adsorber.
- (b)  $GSI_{(r)} = \frac{GSI_{(u)}}{GSI_{(d)}} > 1$  Top layer in the adsorber is more exhausted in comparison with bottom layer (rather common).
- (c)  $GSI_{(r)} = \frac{GSI_{(u)}}{GSI_{(d)}} < 1$  Bottom layer in the adsorber is more exhausted in comparison with top layer (rather uncommon) [2, 3, 15-17].

Case(a) indicates that the exhaustion degree at the bottom layer and the top layer in the entire adsorber is similar/equal ( $GSI_{(u)} = GSI_{(d)}$ ). If the exhaustion degree is too high, regeneration is not recommended. If the value of  $GSI_{(u)}$  is higher than 0.8, the recommendation is to replace the entire adsorber since regeneration will only recover a 27% free chlorine removal capacity.

On the contrary, if the  $GSI_{(u)}$  value is lower than 0.8, regeneration of the entire adsorber using HCL 20%(v/v) is recommended. This regeneration should allow extended use of this material. However, before continuing with the exploitation of the adsorber the effectiveness of the regeneration must be tested.

If after the regeneration, the value of  $GSI_{(u)}$  is between 0.2 and 0.5 the adsorber has recovered at least a 50% of its dechlorinating capacity, and it is recommended to continue the exploitation of this GAC. If this is not the case ( $GSI_{(u)}$  value above 0.5), replacing the entire GAC adsorber is recommended.

Case(b) indicates that the exhaustion level at the top half layer is higher than the bottom half layer (which is a common situation). Here the same strategy for case(a) is recommended. If the  $GSI_{(u)}$  level is below 0.8, the same logic sequence should be applied as in case(a). If  $GSI_{(d)}$  is lower than 0.5, the bottom half of the adsorber retains a minimum of 50% of its original capacity for free chlorine removal and can thus be used in the process.

Then the replacement of the top half is recommended using virgin GAC if the  $GSI_{(u)}$  level is higher than 0.8. On the contrary, if  $GSI_{(d)}$  is higher than 0.5, the bottom half has already lost more than the 50% of its capacity for free chlorine removal and therefore, both layers should be replaced by virgin GAC.

Case(c) can only result from extended use of the adsorber, a previous replacement of top layers in the adsorber or poor GAC management. For case(c), a complete replacement of the GAC adsorber with virgin GAC is recommended if  $GSI_{(d)} > 0.8$ , otherwise, a regeneration of the adsorber is recommended with the subsequent re-evaluation using XRA (see Figure 6). Although regenerated GAC using HCl (20%(v/v)) only shows around a 27% recovery of its original free chlorine removal capacity, it is necessary to take into account that dynamic regeneration experiments conducted in this work were developed using exhausted GAC from the Top layer of an adsorber with more than two years of exploitation, being an extreme case of exhaustion (worst case scenario).

The water treatment adsorber for dialysis water production used as a case study for this work is a clear example of case(b). This adsorber has been exploited for over two years without GAC replacement or regeneration. The top layer of the filter has been extensively exhausted (GSI = 1, see Figure 2 (a) and (b) section 3.1.3) in comparison with the bottom layers (GSI values ranging between 0.4 to 0.5 in the normalized grey scale [3]). Considering that GSI values at the top layers are above 0.8 and at the bottom layers are between 0.4 and 0.5 a replacement of the first half of the adsorber using virgin GAC is recommended.

Although regeneration has been applied to extreme exhaustion scenarios, the dechlorinating capacity of regenerated GAC is still considerable (around 2 mg/L for an inlet solution at a concentration of 4 mg/L), which may allow using this GAC, as long as the inlet concentration of free chlorine is below 2 mg/L. On the other hand, modifications in the total volume of treated water by regenerated GACs could be another alternative if modifications in the flow rate are not a problem. Besides, exhausted GAC could always be used in a parallel adsorber system connected after the first one. Using this alternative, the effective area of the GAC bed for mass transfer could be virtually extended, allowing still an extended use of this material.

#### 4. Conclusions

This work evaluates using two acids (HCl and CH<sub>3</sub>COOH) to restore the performance of exhausted GACs from a GAC adsorber used in a hospital. Higher desorption rates of inorganics (Ca, Mg and Na) and a significant decrease in the ash content are found from ICP-AES and TGA using HCl 20%(v/v), arising as a good option for the chemical regeneration of GAC adsorbers for dialysis water production.

An increase of approximately 24% in the removal capacity towards free chlorine in GAC-regenerated (HCl) concerning the exhausted GAC has been obtained from breakthrough curves and the free chlorine removal RSSCT experiments when using HCl as a chemical agent. However, this GAC-regenerated free chlorine elimination is two times lower than the GAC-virgin removal capacity.

Exhausted GAC using HCl (20%(v/v) and 2 h of contact time) revealed a lower ash content (TGA) after regeneration (1.58%) as well as a lower adsorption capacity towards hardness ions with values around 7%. Although the initial adsorption capacity of this GAC-regenerated is significantly high (around 465 mg/L from a 500 mg/L solution of synthetic hard water), it can only sustain this performance as a fraction (1/10) of the GAC-virgin adsorption time.

The free chlorine removal capacity of the GAC regenerated using this acid was around 27% with respect to GAC-virgin.

The use of CH<sub>3</sub>COOH as a regeneration agent achieved a free chlorine removal capacity of around 2.55% concerning GAC-Virgin. However, the ash content (TGA) after regeneration using CH<sub>3</sub>COOH was significantly lower (4.78%) compared to HCl.

The proposed GAC management scheme succeeds in classifying the type of exhaustion present in the adsorber, allowing one to choose a proper management strategy considering the information obtained from XRA. The proposed scheme, successfully integrates XRA data as an alternative evaluation criterion to conventional methods to select the best regeneration strategy for the extended use of the adsorber.

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## Author Contributions

Conceptualization: J.P.T. and H.C.S.; methodology: J.P.T., H.C.S., J.Y. and R.C.; formal analysis: J.P.T., H.C.S., J.Y., R.C., G.C., G.R., P.S., D.V., and P.A.; Language Editing: J.Y., R.C., and D.V.; investigation: J.P.T., H.C.S. and T.M.P.; resources: J.Y., Á.B.S. and P.A.; data curation: J.P.T. and H.C.S.; writing original draft preparation: J.P.T. and H.C.S.; writing—review and editing: J.P.T., H.C.S., J.Y., R.C., D.V., and Á.B.S.; visualization: J.P.T. and H.C.S.; supervision: J.Y., H.C.S., Á.B.S., R.C., D.V. and P.A.; Project administration: H.C.S. and J.Y. All authors have read and agreed to the published version of the manuscript.

## Competing Interests

The authors have declared that no competing interests exist.

## Additional Materials

The following additional materials are uploaded to the page of this paper.

1. Figure S1: Schematic diagram of the water treatment filter used for obtaining dialysis water for hemodialysis treatments and the location of samples at different layers in the GAC bed (a) and schematic diagram of the sampling process developed (b).
2. Figure S2: Calibration curve of absorbance (A) as a function of different NaClO concentrations (in mg free Cl<sub>2</sub>/L) (a) and calibration curve of conductivity (μS/cm) vs. hardness of synthetic water solutions, in mg CaCO<sub>3</sub>/L(b).
3. Table S1: Ionic composition in mg/L reported in Ciego de Avila aquifers.
4. Table S2: Detected elements in acid solutions after batch regeneration experiments using HCl.
5. Table S3: Detected elements in acid solutions after batch regeneration experiments using CH<sub>3</sub>COOH.
6. Table S4: Detected elements in acid solutions after leaching experiments using HCl virgin GAC samples.
7. Table S5: Detected elements in acid solutions after batch regeneration experiments using CH<sub>3</sub>COOH on virgin GAC samples.
8. Table S6: Detected elements in blank HCl solutions.
9. Table S7: Detected elements in blank CH<sub>3</sub>COOH solutions.

## References

1. Danish M, Ahmad T. A review on utilization of wood biomass as a sustainable precursor for activated carbon production and application. *Renew Sust Energ Rev.* 2018; 87: 1-21.

2. Mariño Peacock T, Crespo Sariol H, Puente Torres J, Yperman J, Sánchez Roca Á, Carleer R, et al. Mathematical tool based on breakthrough curves to evaluate the economic advantages of chemical regeneration of activated carbon in power plants: A comparative study. *Appl Sci*. 2021; 11: 11786.
3. Torres JP, Sariol HC, Yperman J, Adriaensens P, Carleer R, Peacock TM, et al. X-ray absorption as an alternative method to determine the exhausting degree of activated carbon layers in water treatment system for medical services. *Talanta*. 2019; 205: 120058.
4. Yin R, Shang C. Removal of micropollutants in drinking water using UV-LED/chlorine advanced oxidation process followed by activated carbon adsorption. *Water Res*. 2020; 185: 116297.
5. Mabel A, Jihad M, Walid A. Ultrapure water in haemodialysis: A step towards better quality in Lebanon. *East Mediterr Health J*. 2018; 25: 134-141.
6. Janudin N, Kasim NA, Knight VF, Halim NA, Noor SA, Ong KK, et al. Sensing techniques on determination of chlorine gas and free chlorine in water. *J Sensors*. 2022; 2022: 1898417.
7. Larasati A, Fowler GD, Graham NJ. Chemical regeneration of granular activated carbon: Preliminary evaluation of alternative regenerant solutions. *Environ Sci*. 2020; 6: 2043-2056.
8. de Carvalho Costa LR, de Moraes Ribeiro L, Hidalgo GE, Féris LA. Evaluation of efficiency and capacity of thermal, chemical and ultrasonic regeneration of tetracycline exhausted activated carbon. *Environ Technol*. 2022; 43: 907-917.
9. Ma Y, Zhang X, Wen J. Study on the harm of waste activated carbon and novel regeneration technology of it. *IOP Conf Ser*. 2021; 769: 022047.
10. Nguyen TN, Chen Z, Zeraati AS, Shiran HS, Sadaf SM, Kibria MG, et al. Catalyst regeneration via chemical oxidation enables long-term electrochemical carbon dioxide reduction. *J Am Chem Soc*. 2022; 144: 13254-13265.
11. Wan D, Wu L, Liu Y, Chen J, Zhao H, Xiao S. Enhanced adsorption of aqueous tetracycline hydrochloride on renewable porous clay-carbon adsorbent derived from spent bleaching earth via pyrolysis. *Langmuir*. 2019; 35: 3925-3936.
12. Kamran U, Heo YJ, Lee JW, Park SJ. Chemically modified activated carbon decorated with MnO<sub>2</sub> nanocomposites for improving lithium adsorption and recovery from aqueous media. *J Alloys Compd*. 2019; 794: 425-434.
13. Patel H. Batch and continuous fixed bed adsorption of heavy metals removal using activated charcoal from neem (*Azadirachta indica*) leaf powder. *Sci Rep*. 2020; 10: 16895.
14. Mirzaee SA, Bayati B, Valizadeh MR, Gomes HT, Noorimotlagh Z. Adsorption of diclofenac on mesoporous activated carbons: Physical and chemical activation, modeling with genetic programming and molecular dynamic simulation. *Chem Eng Res Des*. 2021; 167: 116-128.
15. Puente Torres J, Crespo Sariol H, Mariño Peacock T, Yperman J, Adriaensens P, Carleer R, et al. X-ray absorption (XRA): A new technique for the characterization of granular activated carbons. *Materials*. 2020; 14: 91.
16. Puente Torres J, Crespo Sariol H, Yperman J, Brito Sauvanell Á, Carleer R, Navarro Campa J. A novel X-ray radiography approach for the characterization of granular activated carbons used in the rum production. *J Anal Sci Technol*. 2018; 9: 1.
17. Torres JP, Codorniu RT, Baracaldo RL, Sariol HC, Peacock TM, Yperman J, et al. A convolutional neural networks approach using X-ray absorption images for studying granular activated carbon. *SN Appl Sci*. 2020; 2: 2088.

18. Harp DL. Current Technology of Chlorine Analysis for water and wastewater, Technical information series-Booklet No. 17. USA: Hach Company; 1995.
19. US environmental protection agency office of pesticide programs. Standard operating procedure for preparation of hard water and other diluents for preparation of antimicrobial products. Ft. Meade, MD: Office of pesticide programs microbiology laboratory environmental science center; 2019.
20. Narbaitz RM, McEwen J. Electrochemical regeneration of field spent GAC from two water treatment plants. *Water Res.* 2012; 46: 4852-4860.
21. Genç N, Durna E, Erkişi E. Optimization of the adsorption of diclofenac by activated carbon and the acidic regeneration of spent activated carbon. *Water Sci Technol.* 2021; 83: 396-408.
22. Lu PJ, Lin HC, Yu WT, Chern JM. Chemical regeneration of activated carbon used for dye adsorption. *J Taiwan Inst Chem Eng.* 2011; 42: 305-311.
23. Palin AT. The determination of free and combined chlorine in water by the use of diethyl-p-phenylene diamine. *Am Water Works Assoc.* 1957; 49: 873-880.
24. Rice EW, Bridgewater L, American Public Health Association. Standard methods for the examination of water and wastewater. Washington, DC: American public health association; 2012.