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Simultaneous removal of strontium and refractory organic compounds from electrodialysis effluents by modified bovine bone char

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ABSTRACT

The presence of residual organic compounds has been harmful to salts crystallization processes. In addition, elements like strontium can damage industrial systems due to incrustation formation. This paper aims at evaluating the simultaneous removal of refractory organic compounds and strontium from industrial reverse electrodialysis wastewater of an oil refinery by adsorption onto bone char, in its fresh and modified surface forms, which constitutes the innovation of this work. The removal of 41% of chemical oxygen demand (COD) was obtained at the equilibrium time of 4 h whereas Sr removal of 37% required 24 h. The kinetics model of pseudo-second order described appropriately the system for both, COD and Sr removals. The strontium removal by bone char was better described by the Freundlich isotherm. The maximum removal of COD (54%) was attained by sulfamic acid pre-treated bone char and the maximum removal of strontium (61%) was obtained using nitric acid treated bone char. Regarding the organics removal, the Redlich-Peterson model better described the systems for untreated bone char and aluminum hydroxide modified bone char, whereas the Freundlich model fitted to aluminum sulfate modified bone char results. A moderate improvement of the organic compounds removal by aluminum sulfate modified bone char (ALBC) compared to untreated bone char (UTBC) from 18.43 to 22.31mg/L was obtained, respectively, using a solid liquid ratio of 60 g bone char/L wastewater.

Keywords: Bone char; Surface modification; Strontium; Organic compounds; Oil refinery wastewater

1. Introduction

The increasing needs on availability of water due to required quality and the progressively restrictive environmental laws force the development and establishment of additional wastewater treatments and water reuse technologies in industry [1]. Nowadays, associated to advanced industrialization, petroleum products and their derivatives become one of the major sources of environmental pollution and several effluents may be released due to transportation, distribution and storage of crude oil [2–4].

According to Alva-Argáez et al. [5], the petroleum industry consumes an average of 246–340 L(water)/day crude oil barrel. In addition, this process generates an effluent amount between 0.4–1.6 times of the processed oil volume [5,6], which, according to Nonato et al. [7], may exceed 10 times the volume of oil produced. This wastewater amount is quite high to be discharged in the scene of water scarcity, thus stimulating the recovery of water contained in this stream. This requires specific treatment processes, to change the effluent characteristics in order to comply with operational specifications of the process or to meet the standards of environmental regulations for final discharge [8,9].

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According to Gontijo et al. [1] 68% of water may be recovered through conventional wastewater treatment generated by an oil refinery. The tertiary treatment, such as by membrane separation processes, for example, may increase the water recovery to 80% or more. However, if zero liquid discharge (ZLD) is pursued, quaternary steps may be demanded, aiming at increasing water recovery [8].

Electrodialysis is usually chosen as the tertiary wastewater treatment in oil industries and produces high quality permeate for reuse and a residual brine stream, contaminated with dissolved inorganic and organic substances [8]. The organic content in wastewaters cause the depletion of dissolved oxygen and may create serious consequences for the biota [10]. Additionally, as stated by Mesquita et al. [6], they may bring corrosion, toxicity and carcinogenicity to streams. Organic contaminants, such as long-chain hydrocarbons, aromatic compounds (such as benzene and phenolic ones), amines and amides, have been identified in an industrial concentrate from electrodialysis unit [6,8,11]. These toxic compounds are not easily degraded by conventional treatments and advanced techniques are required to remove them from the refinery wastewaters [12].

Several kinds of treatments have been proposed in this regard, including advanced oxidation process (AOP) [13], flotation [14], coagulation [15], ultrafiltration [16], electrochemical process [17] and adsorption [6]. However, each treatment process shows advantages and limitations [12].

The inorganic content in the concentrate under investigation can interfere negatively in the process due to the scaling formation derived from precipitation of low solubility compounds, basically strontium and calcium salts. In addition, element such as barium, that besides the formation of incrustation also exhibit potential toxicity, must also be removed.

Strontium is naturally found in the earth's crust in the range of 0.02–0.03% in minerals such as celestite (strontium sulfate) and strontianite (strontium carbonate) [18,19]. Additionally, this element can occur as radioactive isotopes (^{90}Sr half-life of 28.8 years), which is particularly worrisome due to its high fission, yielding 5–6% wastage, strong water solubility and beta radiation emission [18,20]. Precipitation, ion exchange, membrane separation and adsorption have been used to treat wastewater containing toxic metal ions, including radionuclides, such as ^{137}Cs and ^{90}Sr [18,21–23].

Since the 1990s, literature reports an increased interest in the adsorption process since water quality may be increased by the reduction of the metals concentrations at very low levels [18,24,25]. On the other hand, evaporative crystallization was proven to be an effective method for the removal of salts from reverse electrodialysis concentrate [8]. However, the presence of organic contaminants and salts of low solubility affected negatively the crystallization process [8,26,27]. Therefore, the previously detected precipitation of strontium and barium compounds has to be prevented, to allow a better performance of the crystallization unit.

Several authors report the substitution of Sr^{2+} by Ca^{2+} ions in the structure of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] [28–30]. Their chemical similarities favour the accumulation of Sr in the human body by replacing of the calcium ions in the hydroxyapatite structure of bone tissue [23]. On the other hand, since bone char is mainly composed of calcium phosphate (70–75%) as hydroxyapatite phase within the carbonaceous matrix, this similarity between Sr and Ca may be particularly interesting for the Sr removal by adsorption onto bovine bone char, which was reported by Smiciklas et al. [28]. Indeed, bone char has been used in various applications based on ions exchange, outstanding its fluoride removal application from underground water and distinct wastewaters [31–35].

Adsorption is a process of easy implementation, usually cheaper, if compared to other methods. The simple operating system associated to a low-cost adsorbent can make adsorption implantation attractive [32,36–40]. The adsorption capacity for a given adsorbent-adsorbate system may be enhanced by changes on the adsorbents surface, attained through pre-treatments with different compounds. However, as the process involves mass-transfer phenomena and surface interactions, chemical modifications may strongly increase the adsorption capacity for a given adsorbent-adsorbate system, which has been performed in several studies,as shown in Table 1 [32,41–44].

Nevertheless, despite the numerous studies observed in literature for adsorbents surface modification, none of them was dedicated to bone char simultaneous removal of refractory organics and strontium from industrial electrodialysis streams, which is a relevant contribution of this work. Additionally, efficient removal of both compounds would lead to relevant process and feasibility gains, as it would contribute to enhance the efficiency of the crystallization of salts contained in electrodialysis concentrate, aiming at maximizing the water recovery in an oil refinery. Additionally, the results may be extended to similar wastewaters.

2. Experimental

Samples of a real electrodialysis concentrate stream (C-EDR) were collected from a unique batch in flasks of 20 L and kept frozen to preserve its characteristics along the experiments.

Bone char particles (0.5–1.4 mm), supplied by Bonechar-Carvão Ativado do Brasil, Maringá-Paraná, Brazil, were previously washed four times with distilled water (2 L water/500 g of bone char) to remove tiny particles adhered to the solid surface and, then, dried at 60°C for 24 h.

Adsorption tests were carried out in an orbital shaker using erlenmeyers of 250 mL filled with 50 mL of C-EDR. The kinetics tests were performed with 10 g/L solid-liquid ratio, at 25°C and pH constantly monitored. The sorption isotherms were obtained from tests with solid/liquid ratio range from 0.5 to 60 g/L, at constant temperature of 25°C and monitored pH.

2.1. Modification of bone char

Aiming at improving the adsorption capacity of bovine bone char, surface modifications with diverse chemicals, using methodologies reported in the literature (Table 1), were carried out as depicted in Table 2.

2.2. Solids and solutions characterization

The content of dissolved organic compounds was quantified indirectly by chemical oxygen demand (COD) deter-

Table 1
Surface modification in different sorbent materials

	Material	Modifying agent	Goal
[45]	Human osteosarcoma cells	poly(e-caprolactone) (PCL), oleic acid and hydroxyapatite	Bone composition
[46]	Hydroxyapatite nanoparticles	Oleic acid	Docetaxel (Dtxl) encapsulation
[47]	Coal tar pitch	Oleic acid	Improvement of surfactant properties
[48]	Hematite nanoparticles	Oleic acid	Surface modification of hematite nanoparticles
[49]	Nanoparticles of SiO_2	Oleic acid	Increased dispersion in organic solvents
[42]	Bone char	Sodium dodecyl sulfate	Sequestration of triaryl methane dyes
[50]	Zeolites	Sodium dodecyl sulfate	Removal of organic matter
[51]	Coconut-based activated carbons	Sodium dodecyl sulfate	Lead removal
[52]	Activated carbon	Sodium dodecyl sulfate	Copper removal (VI)
[44]	Granular activated charcoal	Citric acid	Copper removal
[41]	Bone char	Citric acid	Removal of formaldehyde in air
[53]	Polymers: cationic, anionic and non-ionic	Aluminum sulfate	Removal of organic compounds from oily sands
[43]	Bone char	Aluminum sulfate	Removal of fluoride
[54]	Activated carbon	Phosphoric acid	Removal of 2,4-dichlorophenol
[55]	Bentonite, diatomite and vermiculite	Carnauba wax	Removal of organic compounds
[56]	Activated carbon	Nitric acid	Removal of benzene and toluene
[57]	Corncob-based activated carbon	Nitric acid	Removal of phenol, p-nitrophenol, methylene blue and lead
[58]	Activated carbon from waste bamboo	Hydrochloric acid	Removal of organic contaminants
[59]	Activated carbon of bark of Morindatinctoria	Aluminum hydroxide	Removal of fluoride
[28]	Bone char	Hydrogen peroxide	Removal of strontium
[60]	Coconut shell	Sodium hydroxide and sulfuric, nitric and phosphoric acids	VOC removal

mination in closed reflux colorimetric method for low COD range [61]. An analytical standard curve was built with potassium biphthalate solution (10, 20, 30, 40, 50, 60 and 70 mg/L), previously filtered using 0.22 mm membrane (Millipore Millex GV, hydrophilic PVDF), and the absorbance was measured in a HACH DR 2800 spectrophotometer at a wavelength of 420 nm. Table 3 presents the analytical methods for aqueous solutions characterization.

Bone char was characterized regarding (i) its functional groups, by Fourier-transform infrared spectroscopy (FTIR) (Bruker Alpha, attenuated total reflectance – ATR, diffuse reflectance accessory – DRIFT), (ii) chemical elements, by energy dispersive X-ray fluorescence (EDX) in S2 RANGER – BRUKER with pellets preparation in Hoechst wax C micropowder, (iii) morphology, by transmission electron microscopy (TEM) coupled to EDX analysis. Images of CNW whiskers were taken using a FEI Tecnai G2-Spirit with 120 kV acceleration voltage and (iv) zeta potential was measured by a ZM3-D-G meter, Zeta Meter system 3.0+, with direct video imaging.

3. Results and discussion

The C-EDR salinity of 2,454 mg/L (Table 4) hinders its direct discharge into watercourses. The high concentration of chlorides (>1,100 mg/L), sodium (>450 mg/L), sulfates (>330 mg/L) and calcium (>250 mg/L) are compatible with concentrates from membrane separation process. Additionally, the COD of approximately 54 mgO_2/L is due to presence of refractory organic compounds as pointed out by Mesquita et al. [62]. Both strontium and barium concentration are very low, respectively 10 mg/L and<1 mg/L.

3.1. Kinetics of adsorption

Fig. 1 shows the removal of organic compounds (expressed as COD), and strontium, by unmodified bone char at 25±1ºC and pH 8.0±0.5. The maximum removal of organics (41%) was reached in 4 h of contact, when no further COD retention was observed. On the other hand, the removal of strontium showed slower kinetic, requiring at least 24 h for equilibrium to be reached. These results agreed with those reported by Mesquita et al. [62] and Smiciklas et al. [28,34].

Mathematical models of pseudo-first order [63] and pseudo-second order have been used by many researchers to evaluate the kinetics of adsorption [64]. The pseudo-first order velocity can be written as Eqs. (1) and (2) (the integrated form) [65].

$$\frac{dq_t}{d_t} = k_1\left(q_e - q_t\right) \tag{1}$$

Table 2
Methodologies for chemical pretreatment of bone char (BC)

Reagent	Modification methodology
Oleic acid	2 g of BC and 0.67 mL of oleic acid in 50 mL of chloroform in ultrasound for 1 h. Washing* (1 $mol_{(oleic\ acid)}/kg_{(bone\ char)}$).
Sodium dodecyl sulfate	50 g/L of BC in 0.02 mol/L of sodium dodecyl sulfate solution, stirring at 150 rpm for 24 h. Washing* (0.5 $mol_{(sodium\ dodeciyls.)}/kg_{(bone\ char)}$).
Nitric acid	100 g/L of BC in 0.25 mol/L of nitric acid and placed in the ultrasound for 1 h. Washing* (2.5 $mol_{(nitric\ acid)}/kg_{(bone\ char)}$).
Phosphoric acid	100 g/L of BC in 1 mol/L of phosphoric acid placed in the ultrasound for 1 h. Washing* (10 $mol_{(phosphoric\ acid)}/kg_{(bone\ char)}$).
Hydrogen peroxide	200 g/L of BC in the H_2O_2 (35%, AG). The process ended when the bubbling stopped. Washing* (7.3 $kg_{(hydrogen\ peroxide)}/kg_{(bone\ char)}$).
Carnauba wax	3 g of carnauba wax + 20 mL of ethanol and heated up to boiling temperature. 30 g of BC was added to the solution and placed under gentle agitation. Washing* (0.1 $kg_{(Carnauba\ w.)}/kg_{(bone\ char)}$).
Citric acid	160 g/L of BC in 1 mol/L of citric acid and placed in ultrasound for 1 h. Washing* (6.2 $mol_{(citric\ acid)}$ $/kg_{(bone\ char)}$).
Acetic acid	60 g/L of BC in 1 mol/L of acetic acid placed on ultrasound for 1 h and dried at 120°C for 2 h. Washing* (16.7 $mol_{(acetic\ acid)}$ $/kg_{(bone\ char)}$).
Aluminum sulfate	34 g/L of BC in 0.1 mol/L of $Al_2(SO_4)_3$′ stirring at 150 rpm for 6 h. Washing* (2.9 $mol_{(aluminum\ sulfate)}$ $/kg_{(bone\ char)}$).
Aluminum hydroxide	34g/L of BC in 0.1 mol/L of $Al(OH)_3$, stirring at 150 rpm for 6 h. Washing* (2.9 $mol_{(aluminum\ hydroxide)}$ $/kg_{(bone\ char)}$).
Hydrochloric acid	100 g/L of BC in 1 mol/L of HCl placed on ultrasound for 1 h. Washing* (10 $mol_{(Hydrochloric\ acid)}$ $/kg_{(bone\ char)}$).
Sulfuric acid	100 g/L of BC in 1 mol/L of H_2SO_4 solution placed on ultrasound for 1 h. Washing* (10 $mol_{(sulfuric\ acid)}/kg_{(bone\ char)}$).
Sulfamic acid	34 g/L of BC in 0.1 mol/L of sulfamic acid on radial stirring at 90 rpm for 4 h. Washing* (2.9 $mol_{(sulfamic\ acid)}/kg_{(bone\ char)}$).

* Washing with distilled water and dried at 60°C for 24 h

Table 3
Methods of analysis used to characterize the C-EDR effluent

Parameters	Analysis method
Sr, Ca, Na, Mg, K e Ba	GBC Atomic Absorption Spectrophotometer, model AVANTA
Bicarbonate Alkalinity, Chlorides	Titimetry [61]
Total organic carbon (TOC), Inorganic Carbon (IC) and Total Carbon (TC)	TOC-V CSN Shimadzu chromatograph, by Oxidation associated with catalytic combustion
Chemical oxygen demand (COD)	Closed reflux colorimetric method [61]
Sulfates	Turbidimetry [61]
pH, conductivity, salinity	Instrumental [61]
Total Phosphorus and nitrate	Colorimetric [61]
Total dissolved solids (TDS)	Evaporation [61]
Total Nitrogen	TOC-V CSN Shimadzu chromatograph, by Oxidation associated with catalytic combustion

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{2}$$

In these equations, k_1 is the adsorption constant, q_t is the amount of adsorbate adsorbed per mass unit of adsorbent as a function of time (t) and q_e is the amount of adsorbate adsorbed per mass unit of the adsorbent at equilibrium.

The kinetic model of pseudo-second order can be expressed by Eq. (3) that, thought integration, gives Eq. (4) [65,66].

$$\frac{dq_t}{d_t} = k_2\left(q_e - q_t\right)^2 \tag{3}$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad or \quad q_t = \frac{(q_e^2 k_2 t)}{(1 + q_e k_2 t)} \tag{4}$$

where k_2 is the pseudo-second order velocity constant.

Table 4
Characterization of the C-EDR effluent

Parameter	Value
Strontium (mg/L)	10.00
Calcium (mg/L)	272.82
Sodium (mg/L)	468.00
Magnesium (mg/L)	25.70
Potassium (mg/L)	21.00
Barium (mg/L)	< 1
Alkalinity Bicarbonate (mg/L)	227.00
Chlorides (mg/L)	1154.30
TOC (mg/L)	18.59
TC (mg/L)	58.60
IC (mg/L)	40.02
Sulfates (mg/L)	339.90
pH	7.85
Total phosphorus (mg/L)	0.31
Total dissolved solids (mg/L)	2,805.33
Nitric nitrogen (mg/L)	40.38
Total nitrogen (mg/L)	67.60
Electrical conductivity (S/cm)	4.884
Salinity (mg/L)	2,454
COD (mg(O_2)/L)	54

[61].

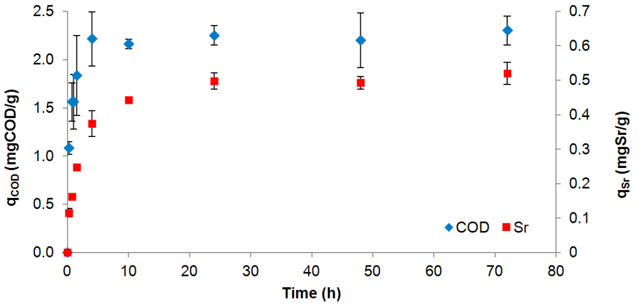

Fig. 1. COD and strontium removals from C-EDR by 10 g/L of unmodified bone char at 25ºC and pH 8.0± 0.5. Initial COD: 54 mg(O_2)/L and Initial [Sr] = 10 mg/L.

The kinetics models of pseudo-first order and pseudo-second order for COD and Sr were fitted to the experimental data. The results are presented in Fig. 2 and all parameters obtained are shown in Table 5. The pseudo-second order model described more appropriately the system bone char – solute in both cases (R^2 = 0.9876, for COD and R^2 = 0.9907, for Sr), that is an indication of a chemical adsorption mechanism.

3.2. *Solutes removals by surface modified bone char*

Fig. 3 shows the residual COD (a) and Sr concentration (b), after 4 h of contact with bone char, chemically modified

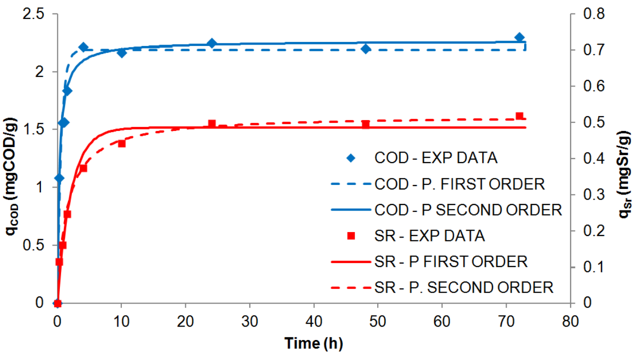

Fig. 2. Pseudo-first order and pseudo-second order model fit for simultaneous removal of COD and Sr from C-EDR by unmodified bone char at 25ºC and pH 8.0± 0.5. Initial COD: 54 mg(O_2)/L and [Sr] = 10 mg/L.

by several reagents. The dashed line shown is a reference performance for non-modified bone char.

Non-modified bone char removed 41% of COD, similar to what was reported by Mesquita et al. [62] and 37% of strontium. Nevertheless, it is worth to remind that the strontium removal equilibrium time was 24 h.

Surfactant reagents, such as sodium dodecyl sulfate (SDS) and oleic acid were expected to raise the removal capacity of COD due to the interaction between the polar groups and the surface of bone char, thus changing the surface character and favoring the subsequent interaction with organic compounds. Wabaidur et al. [42], successfully used SDS modified bone char for adsorption of cationic dyes and Mahvi et al. [50], also succeeded with SDS modified zeolites to improve the removal organic compounds. However, in this study, bone char modified by SDS and oleic acid did not present any gain on COD removal; instead, these chemicals were released to the solution, as it was observed an increase in the final COD concentration.

Similar result was observed to strontium removal by SDS modified bone char, strontium removal reduced from 37% to 33%. Chaudhari and Wanjari [52] and Song et al. [51], who evaluated the modification of activated charcoal to enhance metals removal, achieved positive results, but working at lower pH values of 2 and 5, respectively. However, in this work, bone char modified by oleic acid marginally increased the strontium removal from 37% to 44%.

It was expected that bone char surface hydrophobization using carnauba wax would also raise the COD removal, but this harmed the removal of organics as well as of strontium (Fig. 3). The surface treatment with hydrogen peroxide showed a moderately worse performance in the adsorption capacity, reaching 34% of removal for both solutes whereas phosphoric acid did not bring any gains.

Bone char treated by aluminum sulfate presented one of the three best results for organics removal (52%), a fact that may be related to its ability to coagulate and remove organic matter, as reported by Pourrezaei et al. [53]. However, the strontium removal was not affected (35%). Alternatively, bone char modified by aluminum hydroxide (Fig. 3) did not respond positively for organics but raised the strontium removal from 35 to 48%. This increase in the strontium removal may be associated with the increase of solution pH (7.8) provided in the treatment with aluminum hydroxide

Table 5
Kinetic parameters for organics and strontium adsorption by bone char

ORGANICS (COD)										
Pseudo-first order					Pseudo-second order					q_{exp}
k_1	$k_{1\,error}$	q_e	$q_{e\,error}$	R^2	k_2	$k_{2\,error}$	q_e	$q_{e\,error}$	R^2	
1.6422	0.2383	2.1882	0.0701	0.9508	1.3442	0.1618	2.2657	0.0391	0.9876	2.3493
STRONTIUM										
Pseudo-first order					Pseudo-second order					q_{exp}
k_1	$k_{1\,error}$	q_e	$q_{e\,error}$	R^2	k_2	$k_{2\,error}$	q_e	$q_{e\,error}$	R^2	
0.4674	0.0712	0.4854	0.0173	0.9676	1.2589	0.1517	0.5195	0.0112	0.9907	0.5197

The units for q_{exp}, q_e: mg/g; k_1: L/h; k_2: mg/(gh); Solid/Liquid ratio: 10 g/L; temperature: 25±1°C; Initial COD and strontium concentration. 54 mg(O_2)/L and 10 mg/L, respectively.

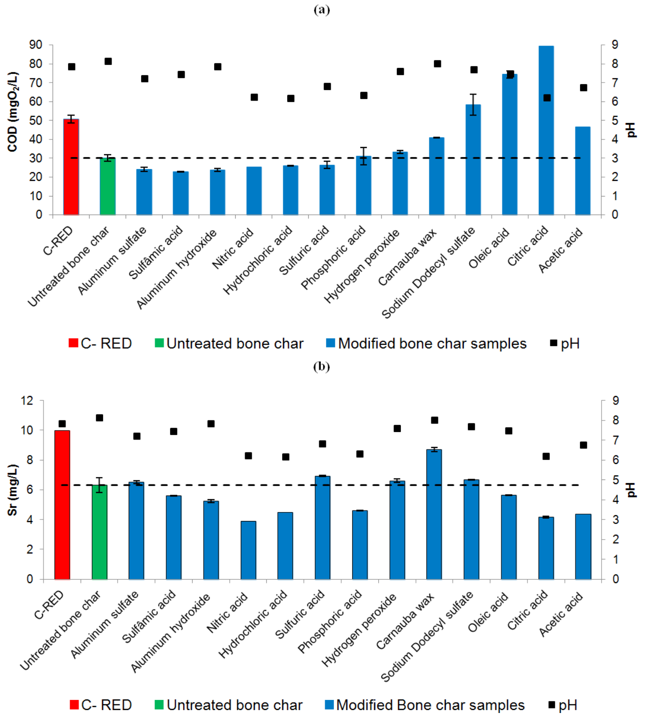

Fig. 3. Residual COD (a) and Sr concentration (b) in the effluent after adsorption with different pretreated bone chars at 25°C. Initial COD: 54 mg(O_2)/L and [Sr] = 10 mg/L. Solid/liquid ratio: 10 g/L; contact time 4 h; pH error ± 0.5.

compared to aluminum sulfate (7.2), a positive effect that was also pointed out by Smiciklas et al. [34].

Nitric acid increased both, organics and strontium removal, in 50% and 61%, respectively, giving the largest removals capacity found for strontium. However, it is noteworthy that bone char had a substantial modification of its structure, the content of minerals reduced, due to a loss of 65% in its mass. Hydrochloric and sulfuric acids exhibited equivalent behavior (49% and 48%) whereas for the strontium removal they acted considerably different from each other (55% and 31%).

The use of citric acid showed the worst result for organic compounds removal (Fig. 3). In fact, there was a release of citric acid from the treated bone char into the solution, as observed for SDS and oleic acid. On the other hand, the treatment was effective for strontium removal (Fig. 4, 58% removal), which is in agreement with the work of Chen et al. [44], that modified conventional coal for copper adsorption.

The modification of bone char using acetic acid (1 mol/L in 60 g of bone char) decreased the COD removal but increased the strontium removal to 56%. On the other hand, bone char modified by sulfamic acid provided the best removal of organic compounds (55%) and the strontium removal increased from 35% to 44%. Nevertheless, it is noteworthy that a mass loss of approximately 25% occurred during the bone char treatment.

3.3. Adsorption isotherms

Adsorption isotherm, a curve built correlating the amount of solute adsorbed per mass of the adsorbent and the solute concentration at equilibrium, at constant pressure and temperature [67] is useful to predict the adsorption capacity of the adsorbent, one of the main parameters necessary for designing of an adsorption system [68,69]. It can be obtained in distinct conditions. The concentration of solids is an important variable that also affects the system hydrodynamics. Bone char adsorption capacity for COD removal, in distinct solid-liquid ratios, for untreated bone char (UTBC), bone char modified by aluminum sulfate (ALBC), bone char modified by sulfamic acid (SABC) and bone char modified by aluminum hydroxide (AHBC) were evaluated as shown in Fig. 4.

UTBC, ALBC, SABC and AHBC treated bone chars presented similar COD removal (Fig. 4). A small improvement of COD removal by ALBC (22.31 mg(O_2)/L) compared to UTBC (18.43 mg(O_2)/L) was observed at 60 g/L solid-liquid ratio. In addition, the pre-treatments with aluminum hydroxide (AHBC) and sulfamic acid (SABC) did not upgrade the COD removal. The reductions in pH observed during the adsorption experiments with ALBC and SABC samples, 5.2 and 6.1 ± 0.5, were higher than the unexpressive change observed for UTBC bone char (pH at 7.8± 0.5for 60 g/L solid-liquid ratio).

Table 6 presents the equations of the Freundlich, Langmuir, Redlich-Peterson, Sips and Temkin models in their general form, which were used to evaluate the results in this work.

Fig. 5 shows the best fit models for organic removal from C-EDR obtained by UTBC, ALBC, SABC and AHBC bone

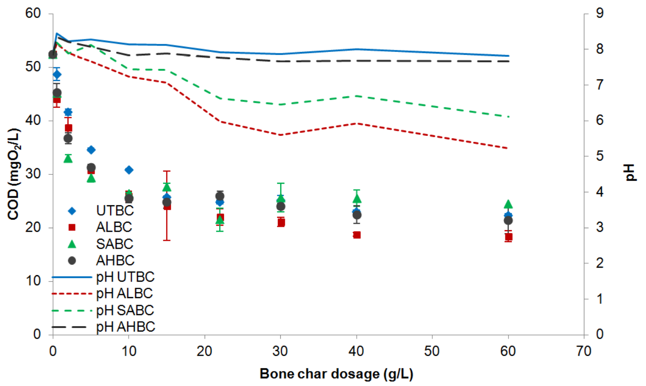

Fig. 4. COD variation as a function of adsorbent dosage at 25±1ºC; solid-liquid ratio: 0–60 g/L; 4 h; pH error ± 0.5. UTBC – Untreated bone char; ALBC – Bone char modified by aluminum sulfate; SABC – Bone char modified by sulfamic acid; AHBC – Bone char modified by aluminum hydroxide.

Table 6
Isotherm equation of Freundlich, Langmuir, Redlich-Peterson, Sips and Temkin models

Model	Equation	Ref.
Freundlich	$q_e = K_F C_e^{1/n}$	[70]
Langmuir	$q_e = \dfrac{q_m K_L C_e}{1 + K_L C_e}$	[71]
Redlich-Peterson	$q_e = \dfrac{K_{RP} C_e}{1 + a_{RP} C_e^{\beta}}$	[72]
Sips	$q_e = \dfrac{q_{ms} K_s C_e^{ms}}{1 + K_s C_e^{ms}}$	[73]
Temkin	$q_e = \dfrac{RT}{b} \ln\left(k_T C_e\right)$	[74]

where q_e Amount of solute adsorbed per mass of adsorbent (mg/g); K_F Freundlich constant related to the adsorption capacity (mg/g) (L/mg)$^{1/n}$; C_e Solute equilibrium concentration (mg/L); $1/n$ Experimental constant representing the intensity of adsorption; q_m Mass of solute adsorbed required to complete a monolayer on the adsorbent (mg/g); K_L Langmuir constant linked to the adsorption capacity (L/mg); K_{RP} Redlich-Peterson constant (L/g); a_{RP} Redlich-Peterson constant (L/mg); β Exponent that lies between 0 and 1; q_{ms} Sips maximum adsorption capacity (mg/g); K_s Sips equilibrium constant (L/mg)^{ms}; m_s Sips model exponent; R Universal ideal gas constant (8.314 J/(K·mol)); T Absolute temperature (K); b Heat of adsorption; k_T Equilibrium binding constant (L/mg).

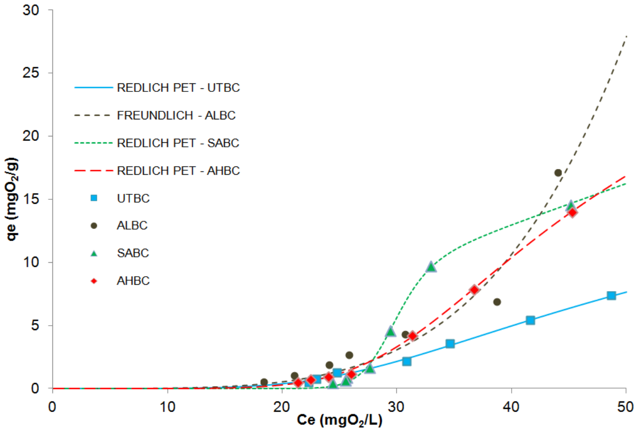

Fig. 5. Best fitting models for organics removal from C-EDR. Temperature: 25±1ºC; solid-liquid ratio: 0–60 g/L and 4 h. UTBC – Untreated bone char; ALBC – Bone char modified by aluminum sulfate; SABC – Bone char modified by sulfamic acid; AHBC – Bone char modified by aluminum hydroxide.

chars. All Freundlich, Langmuir, Redlich-Peterson, Sips and Temkin adsorptive parameters are presented in Table 7.

The Redlich-Peterson model was the best model to represent the results obtained with UTBC, SABC and AHBC, with determination coefficients of 0.9945, 0.9968 and 0.9987, respectively (Table 7). However, for bone char treated with aluminum sulfate, the Freundlich model fitted better (R^2 = 0.9461 against 0.9326, the same value for Sips model fit). The Redlich-Peterson model is a three-parameter empirical model consisting of Langmuir and Freundlich isotherm models, providing versatility for its application in homogeneous and heterogeneous approaches [75]. Negative values of β for UTBC, SABC and AHBC of –4.2171, –19.3900 and –5.7639, outside the range between 0 and 1, indicate a non-favorable adsorption [75]. Likewise, Freundlich model fitted to organics removal by ALBC and the n parameter of 0.2318, outside the common range 1–10, indicated an unfavorable condition of adsorption [76]. Similarly, it could be observed that K_{RP} and a_{RP}, the constants of the Redlich-Peterson model to experiments with ALBC, are greater than 1 (unit value), thus indicating that there is an approximation to Freundlich model [75,77]. This is confirmed by similar determination coefficients of the adsorption isotherm models (Freundlich: 0.9461 and Redlich-Peterson: 0.9326).

The Sips isotherm equation derives from the limiting behavior of Langmuir and Freundlich isotherms [78], characterized by the inclusion of the dimensionless heterogeneity factor, m_s, situated between 0 and 1. When m_s is equal to 1, the Sips equation is reduced to the Langmuir equation, implying a certain degree of homogeneity in the adsorption, which was not observed in the present study [79]. The Sips model fit presented determination coefficients of 0.9943, 0.9326 and 0.9985 for UTBC, ALBC and AHBC, respectively (Table 7). Furthermore, it is important to note that the adsorption curves are limited to the value of COD presented by the real C-EDR.

The enthalpy change of adsorption of COD by bone char at 20ºC was determined by Mesquita et al. [62], equal to 54.3 kJ/mol, in the middle of the range of enthalpy change (ΔH) values for physisorption and chemisorption, 0–20 kJ/mol and 80–400 kJ/mol, respectively [80]. This suggests that the mechanism of COD removal by bone char may be a combination of chemical and physical processes.

The adsorption isotherms for strontium removal by UTBC, ALBC, SABC and AHBC modified bone chars, for dosage of 60 g/L, depicted in Fig. 6, reveal similar Sr concentrations of 2.00±0.06, 2.65±0.05 and 1.43±0.19 mg/L,

Table 7
Adsorption parameters for COD removal by modified bone chars at 25±1ºC; solid/liquid ratio: 0–60 g/L and 4 h

Organic compounds								
UTBC								
Langmuir	q_m	106017.2891	K_L	9.9751E-7			$R^2_{Adj.}$	0.5446
Freundlich	K_F	2.7872E-4	n	0.3802			$R^2_{Adj.}$	0.9765
Temkin	K_T	0.0461	b	0.1187			$R^2_{Adj.}$	0.9634
Redlich-Peterson	K_{RP}	0.1806	a_{RP}	2.5423E6	β	–4.2171	$R^2_{Adj.}$	0.9945
Sips	q_{ms}	11.0147	K_s	8.1403E-8	m_s	4.3789	$R^2_{Adj.}$	0.9943
ALBC								
Langmuir	q_m	268973.2361	K_L	7.5372E-7			$R^2_{Adj.}$	0.3589
Freundlich	K_F	1.3026E-6	n	0.2318			$R^2_{Adj.}$	0.9461
Temkin	K_T	0.0490	b	0.0624			$R^2_{Adj.}$	0.7254
Redlich-Peterson	K_{RP}	32424.7835	a_{RP}	2.4980E10	β	–3.3156	$R^2_{Adj.}$	0.9326
Sips	q_{ms}	153989.332	K_s	8.2028E-12	m_s	4.3228	$R^2_{Adj.}$	0.9326
SABC								
Langmuir	q_m	247028.9456	K_L	7.3647E-7			$R^2_{Adj.}$	0.2557
Freundlich	K_F	6.3004E-5	n	0.3073			$R^2_{Adj.}$	0.8071
Temkin	K_T	0.0409	b	0.0399			$R^2_{Adj.}$	0.9458
Redlich-Peterson	K_{RP}	0.3247	a_{RP}	3.1832E28	β	–19.3900	$R^2_{Adj.}$	0.9968
Sips	q_{ms}	2.3622	K_s	0.1425	m_s	4.8655	$R^2_{Adj.}$	–0.8063
AHBC								
Langmuir	q_m	256167.7098	K_L	6.7423E-7			$R^2_{Adj.}$	0.3571
Freundlich	K_F	1.7239E-5	n	0.2796			$R^2_{Adj.}$	0.9793
Temkin	K_T	0.0445	b	0.0568			$R^2_{Adj.}$	0.9188
Redlich-Peterson	K_{RP}	0.3803	a_{RP}	7.9916E8	β	–5.7639	$R^2_{Adj.}$	0.9987
Sips	q_{ms}	19.9120	K_s	2.0773E-10	m_s	6.0743	$R^2_{Adj.}$	0.9985

UTBC – Untreated bone char; ALBC – Bone char modified by aluminum sulfate; SABC – Bone char modified by sulfamic acid; AHBC – Bone char modified by aluminum hydroxide

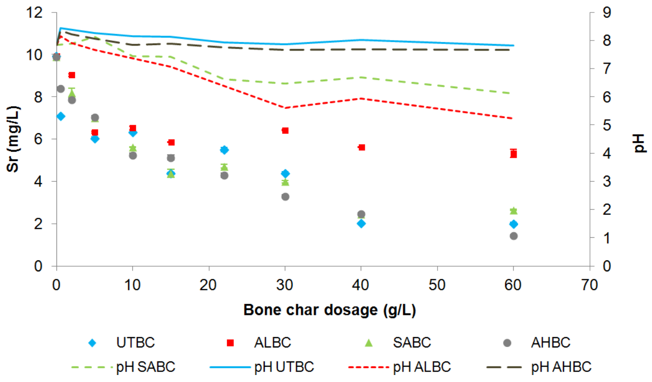

Fig. 6. Removal of strontium from C-EDR effluent as a function of bone char dosage at 25±1ºC; 4 h; pH error ± 0.5. UTBC – Untreated bone char; ALBC – Bone char modified by aluminum sulfate; SABC – Bone char modified by sulfamic acid; AHBC – Bone char modified by aluminum hydroxide.

respectively. Therefore, the surface treatment did not improve the strontium removal.

The lowest removal of strontium was obtained by aluminum sulfate (ALBC) with a residual strontium concentration of 5.32 mg/L (46% of removal).The pH changed from 7.85 to 5.23, at 60 g/L, in agreement with Dimovic et al. [35], who observed an increase of Sr adsorbed onto bone char with the increase of pH. Freundlich model described the system more adequately (Fig. 7) and the equation parameters are presented in Table 8. The results are in accordance with the work of Smiciklas et al. [28]. However, parameter $n < 1$ (Freundlich model) indicated an unfavorable adsorption condition. Nevertheless, the strontium concentration in the C-EDR is restricted to about 10 mg/L, which limits the extension of the adsorption curves. In spite of the kinetic study suggested a chemical mechanism, the adsorption model of Freundlich indicated a multilayer removal of strontium by bone char, with non-favorable patterns, suggesting physical mechanism. Future kinetic studies at different temperatures are suggested to assess the thermodynamic parameters and the evaluation of the energy involved in the process, in order to clarify the mechanism of strontium adsorption by bone char.

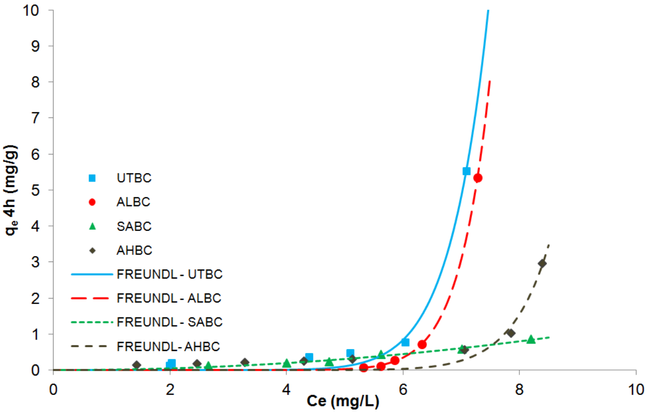

Fig. 7. Best fitting models for strontium removal from C-EDR at 25±1ºC; solid-liquid ratio: 0–60 g/L; 4 h. UTBC – Untreated bone char; ALBC – Bone char modified by aluminum sulfate; SABC – Bone char modified by sulfamic acid; AHBC – Bone char modified by aluminum hydroxide.

3.4 Characterization of bone char

The EDX analysis (qualitative) was performed for UTBC – Untreated bone char, ALBC – Bone char modified by aluminum sulfate, SABC – Bone char modified by sulfamic acid and AHBC – Bone char modified by aluminum, before and after adsorption, at 25°C, solid-liquid ratio of 10 g/L, 50 mL of C-EDR and 4 h of contact time. The results corroborate the removal of Sr from C-EDR through the increasing of Sr grade in all samples after the adsorption. Likewise, it was also observed an increase in the chloride concentration, thus indicating the simultaneous removal of this element. The sulfur content also increased after the adsorption, excluded for systems with bone char treated with aluminum sulfate (ALBC), suggesting the sulfate release to solution. A small change was observed for calcium concentration, but without any tendency. Therefore, no relation for calcium and strontium exchange in the hydroxyapatite structure of bone char could be established, what was previously expected, based on the findings of Smiciklas et al. [28].

The bone char surface is positively charged when the pH of the solution is below the isoelectric point (IEP) and negatively charged at pH above the isoelectric point. The IEP was determined by zeta potential measurements as equal to pH 8.1, similar to the value found by Medellin-Castillo et al. [81]. Since the adsorption experiments were carried out in

Table 8
Parameters determined for the adsorption models fit of strontium removal by various pre-treated bone chars at 25±1ºC; solid/liquid ratio: 0–60 g/L and 4 h

Strontium								
UTBC								
Langmuir	q_m	84584.4395	K_L	4.0994E-6			$R^2_{Adj.}$	0.1729
Freundlich	K_F	1.1996E-9	n	0.0880			$R^2_{Adj.}$	0.9822
Temkin	K_T	0.4435	b	0.4341			$R^2_{Adj.}$	0.1998
Redlich-Peterson	K_{RP}	21929.7684	a_{RP}	1.7779E18	β	–10.3624	$R^2_{Adj.}$	0.9762
Sips	q_{ms}	1879.7564	K_s	6.1511E-13	m_s	11.3820	$R^2_{Adj.}$	0.9762
ALBC								
Langmuir	q_m	54815.1858	K_L	4.4923E-6			$R^2_{Adj.}$	–0.1501
Freundlich	K_F	3.1497E-12	n	0.0705			$R^2_{Adj.}$	0.9999
Temkin	K_T	0.1789	b	0.0594			$R^2_{Adj.}$	0.7578
Redlich-Peterson	K_{RP}	86.9020	a_{RP}	2.9945E13	β	–13.2299	$R^2_{Adj.}$	0.9998
Sips	q_{ms}	360.0653	K_s	7.5509E-15	m_s	14.2661	$R^2_{Adj.}$	0.9998
SABC								
Langmuir	q_m	34278.0847	K_L	2.3849E-6			$R^2_{Adj.}$	0.7261
Freundlich	K_F	0.0117	n	0.4916			$R^2_{Adj.}$	0.9821
Temkin	K_T	0.3769	b	1.5777			$R^2_{Adj.}$	0.8086
Redlich-Peterson	K_{RP}	2068.6715	a_{RP}	176329.6823	β	–1.0344	$R^2_{Adj.}$	0.9761
Sips	q_{ms}	0.0141	K_s	1.0083E-4	m_s	54.4451	$R^2_{Adj.}$	–4.5558
AHBC								
Langmuir	q_m	35718.5622	K_L	4.6889E-6			$R^2_{Adj.}$	0.3504
Freundlich	K_F	1.5741E-12	n	0.0753			$R^2_{Adj.}$	0.9303
Temkin	K_T	0.4824	b	1.0275			$R^2_{Adj.}$	0.2963
Redlich-Peterson	K_{RP}	28608.7208	a_{RP}	1.8204E16	β	–12.2807	$R^2_{Adj.}$	0.9164
Sips	q_{ms}	1306.3373	K_s	1.1836E-15	m_s	13.2893	$R^2_{Adj.}$	0.9163

UTBC – Untreated bone char; ALBC – Bone char modified by aluminum sulfate; SABC – Bone char modified by sulfamic acid; AHBC – Bone char modified by aluminum hydroxide

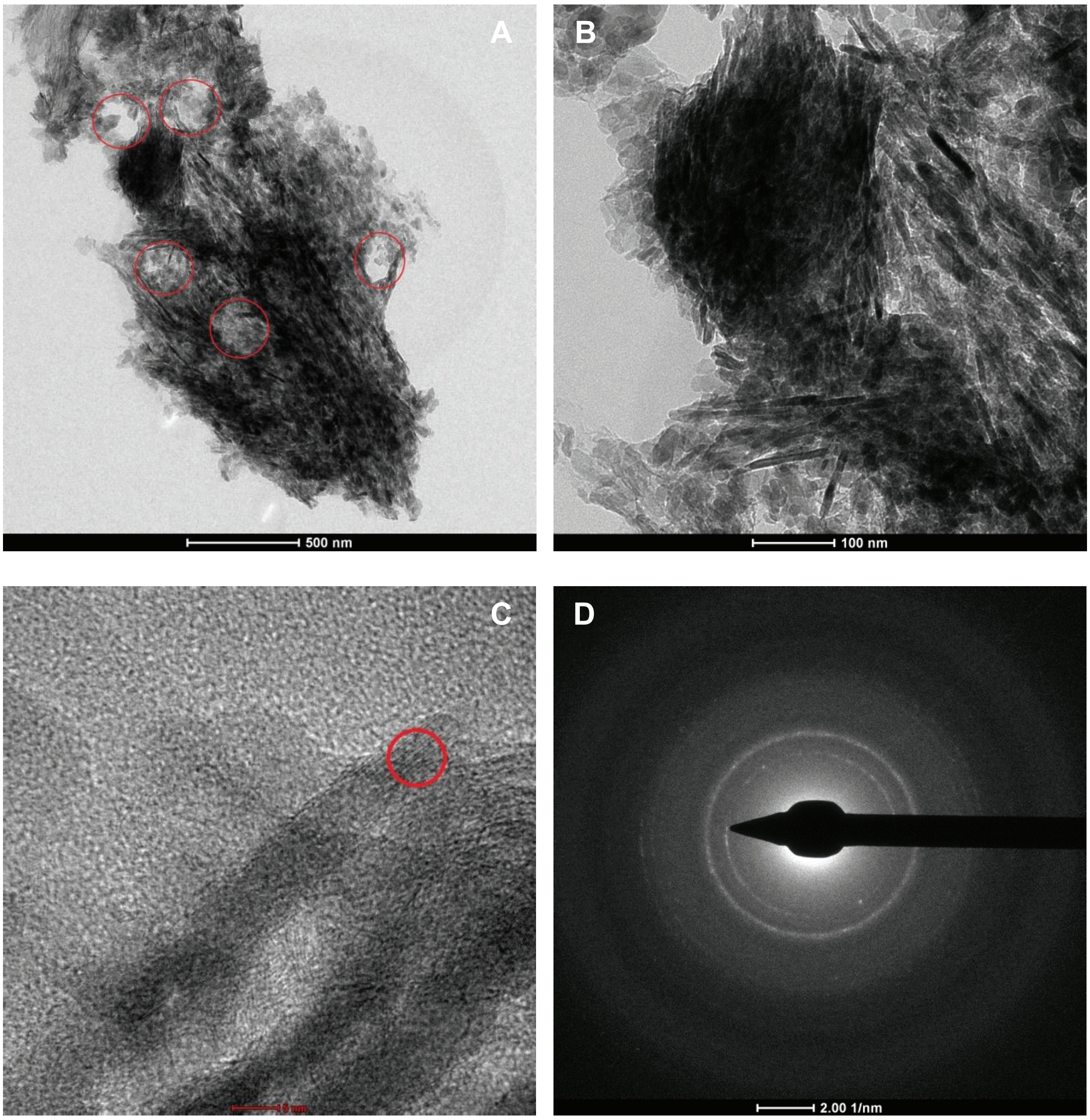

Fig. 8. Transmission electron microscope images for untreated bone char sample: (A) 500 nm scale image, (B) 100 nm scale image, (C) 5 nm scale image and (D) SAED standard.

pH near the bone char IEP pH, this may have affected the strontium adsorption.

Micrographs of untreated bone char (UTBC) are presented in Fig. 8. The image in Fig. 8A shows a porous structure through bone char particles (highlighted). Fig. 8B displays needle-shaped particles as reported by Patel et al.[82], showing the growth variation of hydroxyapatite nanocrystals due to the carbonization temperature of bovine bones. In certain regions, hydroxyapatite crystals have a preferred (highlighted) orientation, as shown in Fig. 8C. Finally, Fig. 8D presents the diffraction pattern for the untreated bone char sample. The EDX spectra for elemental analysis of the untreated bone char confirms the presence of Ca, P and O, the elements in the structure of hydroxyapatite.

Fig. 9 shows the FTIR spectra for UTBC, ALBC, SABC and AHBC before and after adsorption (AA). According to Rojas-Mayorga et al. [42], the groups corresponding to the bands are: C=C (1455 cm^{-1}), PO_4^{3-} (1409 and 600 cm^{-1}), CO_3^{2-} (870 and 1409 cm^{-1}) and Ca (560 cm^{-1}) and according to Thompson et al. [83], CO_3^{2-} (870, 1409 cm^{-1}), PO_4^{3-} (560, 600 and 1019 cm^{-1}). Thompson et al. [83], also evaluated the carbonyl (C=O at 1455 cm^{-1}) and carbonate (CO_3^{2-} at 1409 cm^{-1}) bands, which indicate the presence of organic compounds on bone char surface. A decrease in the intensity of these bands with the increase in temperature are due to the decomposition reactions suffered by the organic compounds. In the present study, no variation has been observed between the carbonyl and carbonate bands; however, an increase in their intensities, evidenced the removal of organic compounds, except for SABC bone char.

An increase in the intensity of bands 469, 560, 600, 870, 960, 1019, 1090, 1409 and 1455 cm^{-1}, are consistent with the observations of Nigri et al. [36], that reported 560, 600 and 636 cm^{-1} bands (typical for hydroxyapatite in bone char) and Tianyuan et al. [84], who reported the bands of 1090, 1019, 960, 600, 560, 469 cm^{-1} from PO_4^{3-} group, contained in hydroxyap-

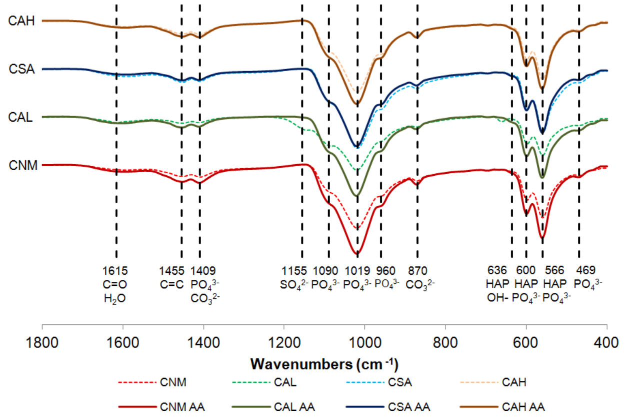

Fig. 9. FTIR analysis for modified bone chars, before and after adsorption. Initial COD concentration: 50 mg(O_2)/L; solid/liquid ratio: 10 g/L; temperature: 25±1ºC and 4 h. UTBC – Untreated bone char; ALBC – Bone char modified by aluminum sulfate; SABC – Bone char modified by sulfamic acid; AHBC – Bone char modified by aluminum; AA – After adsorption.

atite nanorods. Dimović et al. [85] also identified the bands at 1090, 960, 600, 560 cm^{-1} as PO_4^{3-} group and 1160 cm^{-1} band as due to HPO_4^{2-} group. The lines 870 and 664 cm^{-1} may be assigned to the CO_3^{2-} group and at 636 cm^{-1}to the OH^- radical. The band at 1615 cm^{-1} can be attributed to water or aromatics bonds, C=C [62]; and at 1155 cm^{-1} [86], due to SO_4^{2-} group [87].

4. Conclusions

The simultaneous removal of refractory organic compounds and strontium from an industrial electrodialysis concentrate (C-EDR) was evaluated through adsorption with bone char pre-treated by several reagents, aiming at enhancing the efficiency of the process. The equilibrium time for removal of COD from C-EDR by non-modified bone char was reached in 4 h, whereas the strontium removal required 24 h to achieve equilibrium. Pseudo-second order kinetic model represented the removal of organic compounds and strontium from C-EDR effluent, suggesting possible chemical adsorption mechanism. However, the adsorption models indicated the multilayer removal of refractory organic compounds and strontium by bone char, with non-favorable patterns, suggesting the presence of physical mechanism in heterogeneous active sites. Future kinetic studies at different temperatures are suggested to assess the thermodynamic parameters and to evaluate the energy involved in the process for Sr, in order to clarify the adsorption mechanism.

A moderate improvement of COD removal by aluminum sulfate modified bone char (ALBC) compared to untreated bone char (UTBC) (from 18.43 to 22.31 mg(O_2)/L, respectively) was obtained, for 60 g/L bone char dosage. On the other hand, this pre-treatment did not affect strontium removal, and an insignificant improvement was observed with UTBC, ALBC and SABC, that led to similar final strontium concentrations of 2.00, 2.65 and 1.43 mg/L, respectively. Conversely, citric acid modified bone char has shown a promising increase for the strontium adsorption, resulting in 58% removal vs. 37% for unmodified bone char. In addition, chlorides and sulfates concentration were only slightly affected.

The Redlich-Peterson model fitted better for organic compounds removal performed by UTBC, SABC and AHBC, while the Freundlich model better described the adsorption data obtained with ALBC. The Freundlich model also fitted better to results for strontium removal. However, the initial strontium and organic compounds concentration limited the extent of adsorption curves, being isothermal models applied to restricted conditions of solid liquid ratio.

The results obtained from the characterization of the adsorbent corroborate the removal of Sr from C-EDR through the increase of Sr grade after the adsorption process in UTBC, ALBC, SABC and AHBC samples. It was also observed an increase in the chloride content in all the samples, after the adsorption process, indicating the simultaneous removal of this element.

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Symbols

$1/n$ — Experimental constant representing the intensity of adsorption;
a_{RP} — Redlich-Peterson constant (L/mg);
b — Heat of adsorption;
C_e — Solute equilibrium concentration (mg/L);
k_1 — Adsorption constant (L/mg);
k_2 — Pseudo-second order velocity constant (mg/gh);
K_F — Freundlich constant related to the adsorption capacity (mg/g)(L/mg)$^{1/n}$;
K_L — Langmuir constant linked to the adsorption capacity (L/mg);
K_{RP} — Redlich-Peterson constant (L/g);
K_s — Sips equilibrium constant (L/mg)^{ms};
k_T — Equilibrium binding constant (L/mg);
m_s — Sips model exponent;
q_e — Amount of solute adsorbed per mass of adsorbent (mg/g);
q_m — Mass of solute adsorbed required to complete a monolayer on the adsorbent (mg/g);
q_{ms} — Sips maximum adsorption capacity (mg/g);
q_t — Amount of adsorbate adsorbed per mass unit of adsorbent as a function of time (mg/g);
R — Universal ideal gas constant (8.314 J/(K·mol));
T — Temperature (K);
β — Exponent that lies between 0 and 1;

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