



## Biosorption of Cr(III) using *in natura* and chemically treated tropical peats

A.P.S. Batista<sup>a</sup>, L.P.C. Romão<sup>a,\*</sup>, M.L.P.M. Arguelho<sup>a</sup>, C.A.B. Garcia<sup>a</sup>, J.P.H. Alves<sup>a</sup>, E.A. Passos<sup>a,b</sup>, A.H. Rosa<sup>c</sup>

<sup>a</sup> Departamento de Química, Universidade Federal de Sergipe, 49100-000 São Cristóvão, SE, Brazil

<sup>b</sup> Instituto de Química, Universidade Federal da Bahia, 40170-115 Salvador, BA, Brazil

<sup>c</sup> Departamento de Engenharia Ambiental, Universidade Estadual Paulista, 18087-180 Sorocaba, SP, Brazil

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### ABSTRACT

The physicochemical characteristics of three Brazilian peats were investigated using elemental analysis, scanning electron microscopy (SEM), X-ray diffractometry (XRD) and studies of Cr(III) biosorption based on adsorption isotherms. Adsorption of Cr(III) by *in natura* peat from Santo Amaro das Brotas (Sergipe State) was much greater than by peats from either Ribeirão Preto (São Paulo State) or Itabaiana (Sergipe State), with adsorption capacities ( $q$ ) of  $4.90 \pm 0.01$ ,  $1.70 \pm 0.01$  and  $1.40 \pm 0.01$  mg g<sup>-1</sup>, respectively. Pre-treatments with HCl and NaOH + HCl reduced adsorption by the Santo Amaro das Brotas peat, showing that adsorption efficiency was associated with the amount of organic matter present. Conversely, increase in the mineral content following pre-treatment increased adsorption of Cr(III) by the Ribeirão Preto and Itabaiana peats. Highest adsorption (retention >95.0%) was achieved at equilibrium pH 4.0 using the Santo Amaro das Brotas peat. Experimental data for the adsorption of Cr(III) from aqueous solution onto this peat were fitted to the Langmuir equation, from which an equilibrium adsorption capacity,  $q_{\max}$ , of 5.60 mg g<sup>-1</sup> was obtained, which was close to the experimentally determined value.

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### 1. Introduction

Exponentially increasing human populations have resulted in higher inputs of metallic species into the environment. However, under pressure by the public and the media, governments are progressively introducing and enforcing stricter regulations concerning metal discharges, to avoid deterioration of surface water quality by industrial operations [1,2]. Cr(III) is a metal commonly found in wastewaters, and although thought to be an essential nutrient required for sugar and fat metabolism in organisms, long-term exposure has been linked to skin allergies and cancer. Moreover, the metal can be oxidized to the more carcinogenic and mutagenic Cr(VI), which is toxic to human body tissue owing to its oxidizing potential and ability to permeate biological membranes [3]. Legal discharge limits for Cr(III) vary from 0.05 mg L<sup>-1</sup> (in surface waters) to 2.0 mg L<sup>-1</sup> (in sewers) according to country, the process concerned and wastewater treatment methods [4].

Increased attention is being focused on effective and inexpensive technologies capable of treating large quantities of wastewater rich in toxic metals, and biosorption has recently emerged as a viable technique for metal removal. Compared to conventional methods for removal of toxic metals from industrial effluents, biosorption offers advantages including low operating cost,

minimal generation of chemical or biological sludge, efficient detoxification of very dilute effluents, and no nutrient requirement [5]. Previous studies have shown that a variety of biosorbents can be used for this purpose [6–13].

Humic substances are the main component of the natural organic matter (NOM) present in biosorbent peat. These substances are a very important biomass because they serve as a major reservoir of organic carbon for the global carbon cycle and are thought to be one of the major mechanisms of metal ions transport in the environment [7,14]. Typical carbon and hydrogen contents of peat are in the ranges 40–60 and 4–6%, respectively [15]. High contents of carbon and organic matter are important characteristics, which influence the extent of metal uptake by the biosorbent.

Mohan and Pittman [16] reported that peat is a natural humic substance with recognized potential for wastewater treatment due to its ability to sequester metals. The abundance of alkyl-C functional groups plays an important role in complexation and ion exchange during metal ions fixation, although mechanisms of cation uptake can vary greatly depending on the type of peat used. Biosorption onto peat is a relatively inexpensive and widely available procedure, which has applicability for a variety of metals, and an important aspect is that peat can be modified to improve its sorption capacity [17].

Various low-cost chemical treatments can be used to modify the adsorption properties of peat, such as treatment with HCl or HCl + NaOH to improve removal of Cr by the mineral fraction. Hydrochloric acid is not an oxidizing agent, hence should not

\* Corresponding author. Tel.: +55 7921056649; fax: +55 7921056651.

E-mail addresses: [luciane@ufs.br](mailto:luciane@ufs.br), [lucianepcr@hotmail.com](mailto:lucianepcr@hotmail.com) (L.P.C. Romão).

oxidize the organic peat fraction; the combination of hydrochloric acid and sodium hydroxide should cover the surface of the solid phase with a mixture of oxides, at the same time dissolving a good part of the organic fraction. Alkaline extraction is recommended for extraction of humic substances by IHSS (International Humic Substances Society).

Our previous work [18] used a multi-method approach to show that the structures and properties of Sergipe and São Paulo peats differ, due to their different organic and inorganic compositions, while sorption efficiency can be manipulated by alteration of their physicochemical properties. Acid treatment has been reported to increase the cation exchange capacity of peat by 92%, relative to *in natura* peat [19].

Sergipe State, in northeast Brazil, possesses many tanning industries, which represent a pollution threat to regional watercourses. There are also extensive local supplies of peat, which can potentially be used as an economical material for treatment of Cr-containing wastes. For this reason, increased attention is being focused on peat-based technologies for waste treatment applications.

In the present paper we report on the physicochemical characterization of peats from different regions of Brazil, using elemental analysis, scanning electron microscopy (SEM) and X-ray diffractometry (XRD), as well as on studies of Cr(III) biosorption based on adsorption isotherms for *in natura*, and chemically pre-treated, peat samples.

## 2. Materials and methods

### 2.1. Preparation of biosorbent

Three peat samples were collected, from two different regions of Sergipe State, Itabaiana (ITA) and Santo Amaro das Brotas (SAO), and from Ribeirão Preto in São Paulo State (SAP), Brazil. The raw peat was air-dried at room temperature as recommended in the literature [15], and the material was then sieved through a nine-mesh grid.

### 2.2. Characterization of peat samples

A Carlo Erber 1110 elemental analyzer was used to determine the elemental compositions of the peat samples. The proportion of dry ash was obtained after ignition at 750 °C for 4 h [20]. SEM measurements were performed using a JSM T330A SEM under ultra-high vacuum. Peat samples were placed onto clean electron microscopy support stubs, and coated with gold in an Emscope SC 500 sputter coater. Detailed mineralogical studies of peat samples were carried out using X-ray diffraction (Siemens D-5000), with step time 1 s, step size 0.05 dg and wavelength 1.54 Å. The experimental XRD patterns have been indexed using the international JCPDF (Joint Committee for Powder Diffraction Files) database, searchable by the position of the X-ray diffraction peaks.

### 2.3. Chemical pre-treatment

The three different peats were chemically pre-treated to explore the influence on Cr(III) sorption capacity. For the first chemical treatment 10 g of peat was treated with 100 mL of 1.0 mol L<sup>-1</sup> HCl for 2 h, according to the procedure proposed by Gosset et al. [21]. The peat was then washed with deionized water until the pH of the filtrate reached 5.0, and subsequently dried at 80 °C for 2 h.

The second chemical treatment adopted to verify whether metal retention is due to interactions with mineral components of peat was based on the methodology described by Dahbi et al. [22]. 100 mL of 1.0 mol L<sup>-1</sup> HCl was added to 10 g of dried peat, with agitation for 1 h, followed by addition of 100 mL of 1.0 mol L<sup>-1</sup> NaOH, also

with agitation for 1 h. The peat was then washed with 2 L deionized water and dried at 80 °C for 2 h.

### 2.4. Adsorption experiment

Chromium stock solution (500 mg L<sup>-1</sup>) was prepared using Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (99.99%, Sigma–Aldrich). All solutions, including dilutions and standards, were prepared using deionized water (Millipore, Milli-Q Plus). Batch adsorption experiments were conducted in a constant temperature shaker bath at 25 ± 0.2 °C and 125 rpm. The adsorption process is dependent on the relationship between the masses of metal and adsorbent, and on the solution volume [23]. Hence fixed volumes of 50 mL aliquots of aqueous 10.0 mg L<sup>-1</sup> Cr(III) solution were added to 100 mg of peat in stoppered polyethylene flasks, adjusting the initial pH of solutions to a value of 5.0 (except for the pH study) with either 0.1 mol L<sup>-1</sup> HCl or 0.1 mol L<sup>-1</sup> NaOH solution. All experiments were conducted in triplicate. Each experiment corresponded to one datapoint, the sample being taken at predetermined time intervals up to a maximum of 72 h, without alteration of the final volume. A Millex-HV 0.45 µm syringe driven filter unit was used for removal of the supernatant for subsequent analysis. After filtration, a Shimadzu Model AA-6800 atomic absorption spectrometer was used for detection of Cr(III) concentrations in the supernatant solutions. The amounts of Cr(III) adsorbed onto the peat were then calculated from the difference between the initial and final concentrations of the solution, using the equation:

$$q = \frac{(c_0 - c)v}{m} \quad (1)$$

In this expression,  $q$  is the sorption capacity in mg of metal per g of dry peat,  $c_0$  the initial metal ion concentration in mg L<sup>-1</sup>,  $c$  the final metal ion concentration in mg L<sup>-1</sup>,  $v$  the volume of the liquid in L, and  $m$  the weight of the peat adsorbent (*in natura* and after treatment) in g [13]. After determining the time required for adsorption equilibration, the experiments were repeated at other initial pH values, in the range 3–7.

### 2.5. Adsorption isotherm

For the adsorption isotherm experiments, adsorbent (100 mg) was added to 50 mL of different concentrations of Cr(III) solution (4.0–60.0 mg L<sup>-1</sup>), at an equilibrium pH of 4.0. The bottles were shaken at 25 ± 0.2 °C for a predetermined equilibration time, after which the Cr(III) concentrations in the supernatants were determined by flame atomic absorption spectrometry. Metal removal data were used in the adsorption isotherm model that, according to Langmuir, is expressed as

$$q_e = \frac{q_{\max} b c_e}{1 + b c_e} \quad (2)$$

Or, in its linearised form:

$$\frac{c_e}{q_e} = \frac{c_e}{q_{\max}} + \frac{1}{q_{\max} b} \quad (3)$$

In this equation,  $q_{\max}$  is the maximum sorption capacity (mg g<sup>-1</sup>),  $q_e$  the amount of metal adsorbed at equilibrium (mg g<sup>-1</sup>) and  $c_e$  the solute concentration at equilibrium (mg L<sup>-1</sup>). Factor  $b$  is the equilibrium constant related to the energy of sorption, which quantitatively reflects the affinity between the sorbent and sorbate [1].

### 2.6. Statistical test

The average distribution of adsorption of Cr(III) by *in natura* and modified peats was assessed using analysis of variance (ANOVA).

**Table 1**

Adsorption<sup>a</sup> (*q*), elemental analysis and ash content results (mean ± S.D.) for peats collected from three different Brazilian municipalities

Peat	<i>q</i> (mg g <sup>-1</sup> )	C (%)	H (%)	Dry ash (%)
SAO <sup>b</sup>				
<i>In natura</i>	4.90 ± 0.01	53.1 ± 0.52	5.97 ± 0.25	9.40
HCl	3.30 ± 0.01	51.0 ± 4.47	4.88 ± 0.91	8.90
NaOH + HCl	3.40 ± 0.01	45.8 ± 0.83	5.37 ± 0.16	12.4
SAP <sup>c</sup>				
<i>In natura</i>	1.70 ± 0.01	6.23 ± 0.26	0.98 ± 0.02	80.9
HCl	1.70 ± 0.03	6.09 ± 1.00	0.93 ± 0.17	86.9
NaOH + HCl	2.20 ± 0.01	0.27 ± 0.02	n.d.	99.1
ITA <sup>d</sup>				
<i>In natura</i>	1.40 ± 0.01	5.12 ± 1.46	0.47 ± 0.15	87.8
HCl	1.70 ± 0.01	6.27 ± 0.43	0.56 ± 0.06	91.2
NaOH + HCl	1.90 ± 0.01	1.96 ± 0.01	0.12 ± 0.01	94.7

<sup>a</sup> Adsorption after 72 h using 100 mg of peat in contact with 50 mL of 10.0 mg L<sup>-1</sup> (initial concentration) Cr(III) solution.

<sup>b</sup> Santo Amaro das Brotas-SE.

<sup>c</sup> Ribeirão Preto-SP.

<sup>d</sup> Itabaiana-SE.

All data were analyzed using Tukey's multiple comparison test ( $P < 0.05$ ).

### 3. Results and discussion

#### 3.1. Characterization of peat samples

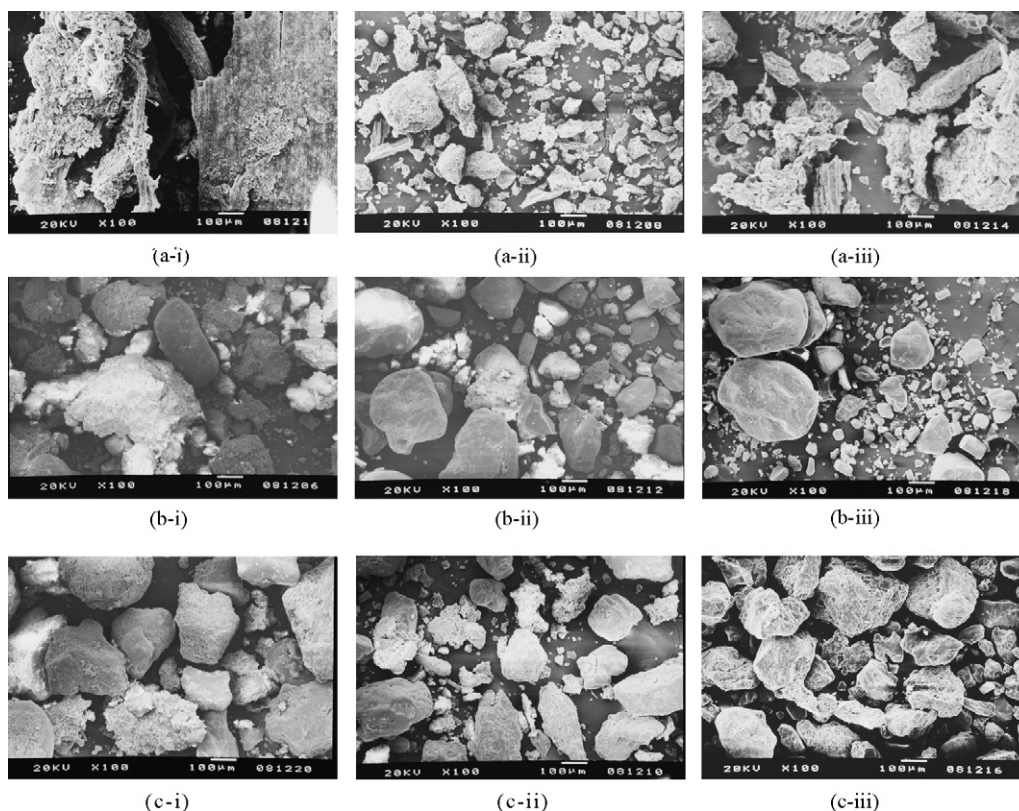
Elemental and dry ash contents are listed in Table 1. The *in natura* Santo Amaro peat (SAO) possessed higher carbon ( $53.1 \pm 0.52\%$ ) and hydrogen ( $5.97 \pm 0.25\%$ ) contents, and lower dry ash content (9.40%), than the *in natura* São Paulo (SAP) peat ( $6.23 \pm 0.26\%$  C,

$0.98 \pm 0.02\%$  H and 80.9% dry ash) and the *in natura* Itabaiana (ITA) peat ( $5.12 \pm 1.46\%$  C,  $0.47 \pm 0.15\%$  H and 87.8% dry ash).

Typical compositions of peat are in the range 40–60% C and 4–6% H [15]. The values from the elemental analysis of the *in natura* SAO peats studied here are in good agreement with those expected for this type of sample, which was not the case for the SAP and ITA *in natura* peats. In combination with XRD and SEM results, these data indicate that SAO peat possesses true peat characteristics.

Pre-treatments with 1.0 mol L<sup>-1</sup> HCl and 1.0 mol L<sup>-1</sup> NaOH + HCl reduced the amount of organic matter in the SAO peat and increased the dry ash contents of all the samples. SEM images are illustrated in Fig. 1. The untreated SAO sample showed characteristics typical of natural peat, with strands of plant material clearly visible (Fig. 1a). The ITA and SAP samples contained porous granules, as did the SAO sample, but (unlike the SAO sample) also contained a significant mineral phase (Fig. 1b and c). These observations are supported by the respective carbon and dry ash contents.

Detailed examination of the mineralogy of the peat samples, using XRD, is shown in Fig. 2. The XRD of the *in natura* SAO sample (Fig. 2a-i) was characteristic of amorphous matter, with a hump between 18° and 32°. After treatment with HCl (Fig. 2a-ii), the appearance of crystalline structures suggests that this inorganic phase had previously been covered by organic material. For the sample treated with HCl + NaOH, the diffractogram showed no difference relative to that obtained for the *in natura* sample (Fig. 2a-iii). The XRD analyses of SAP and ITA samples showed similarities for all treatments, with the presence of crystalline structures. From comparison with XRD standards stored in the JCPDF database of crystalline compounds (No. 85-0419), it was possible to conclude that these corresponded to the presence of mineral quartz. Hence, the SAO, SAP and ITA peats were very different in their inorganic and organic matter contents. The SEM and XRD analyses showed that only the SAO sample possessed true peat characteristics.



**Fig. 1.** Scanning electron microscopy of (a) SAO peat, (b) SAP peat and (c) ITA peat—(i) *in natura*, (ii) after HCl treatment and (iii) after HCl + NaOH treatment.

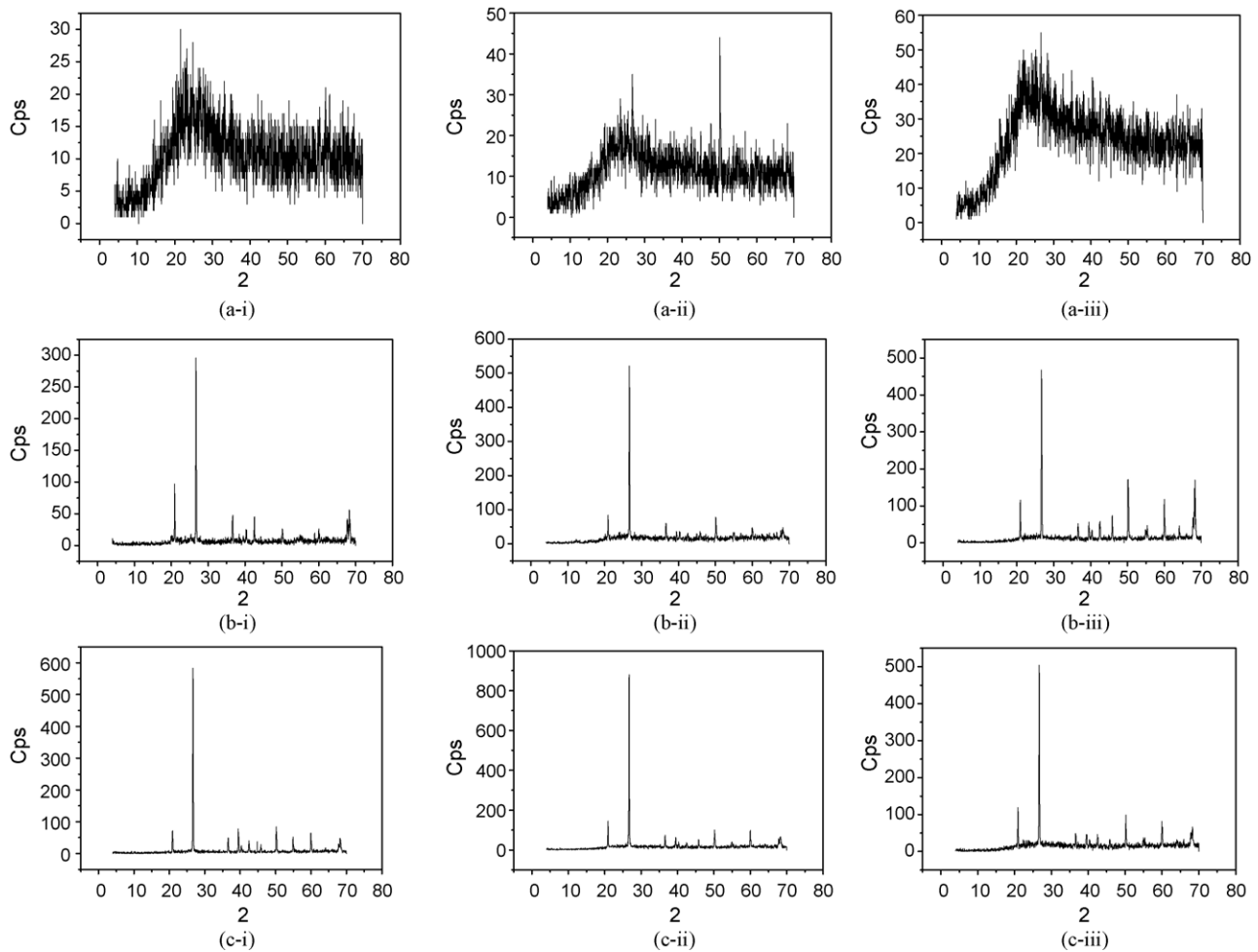


Fig. 2. X-ray diffractometry of peat samples: (a) SAO peat, (b) SAP peat and (c) ITA peat—(i) *in natura*, (ii) after HCl treatment and (iii) after HCl + NaOH treatment.

### 3.2. Adsorption capacity

Figs. 3–5 illustrate the Cr(III) adsorption capacity ( $q$ ) of the three peat samples, *in natura*, after pre-treatment with HCl and after pre-treatment with NaOH + HCl, respectively, up to 72 h.

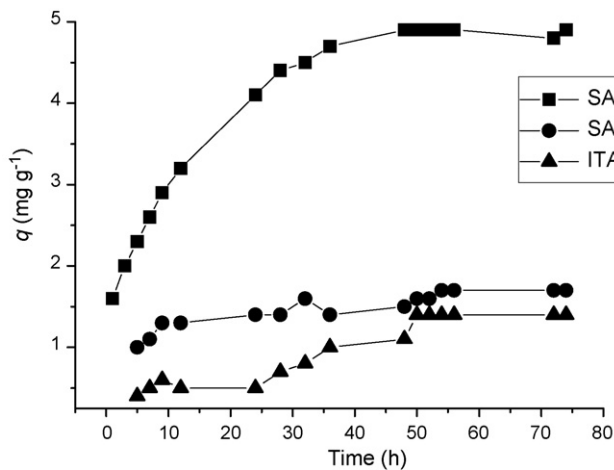


Fig. 3. Adsorption of Cr(III) for periods of up to 72 h in contact with *in natura* peat from the municipalities of Santo Amaro das Brotas-SE (SAO), Ribeirão Preto-SP (SAP) and Itabaiana-SE (ITA) ( $T = 25 \pm 0.2^\circ\text{C}$ ; equilibrium pH 4.0;  $c_i = 10 \text{ mg L}^{-1}$ ;  $m = 100 \text{ mg}$  of sorbent).

From Fig. 3 and Table 1 it can be seen that the adsorption capacity of *in natura* peat from Santo Amaro das Brotas (SAO) was much greater than that from Ribeirão Preto (SAP) or Itabaiana (ITA), with values of  $4.90 \pm 0.01$ ,  $1.70 \pm 0.01$  and  $1.40 \pm 0.01 \text{ mg g}^{-1}$  obtained, respectively, for an equilibration time of 50 h. Application of Tukey's multiple comparison test ( $P < 0.05$ ) showed that

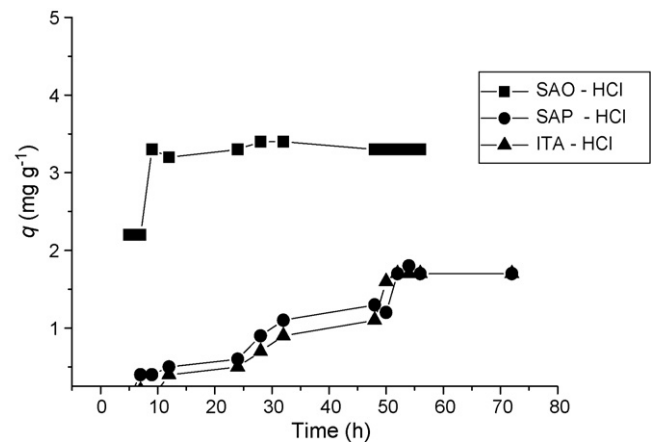


Fig. 4. Adsorption of Cr(III) for periods of up to 72 h in contact with peat from the municipalities of Santo Amaro das Brotas-SE (SAO), Ribeirão Preto-SP (SAP) and Itabaiana-SE (ITA), treated chemically with  $1.0 \text{ mol L}^{-1}$  HCl ( $T = 25 \pm 0.2^\circ\text{C}$ ; equilibrium pH 4.0;  $c_i = 10 \text{ mg L}^{-1}$ ;  $m = 100 \text{ mg}$  of sorbent).



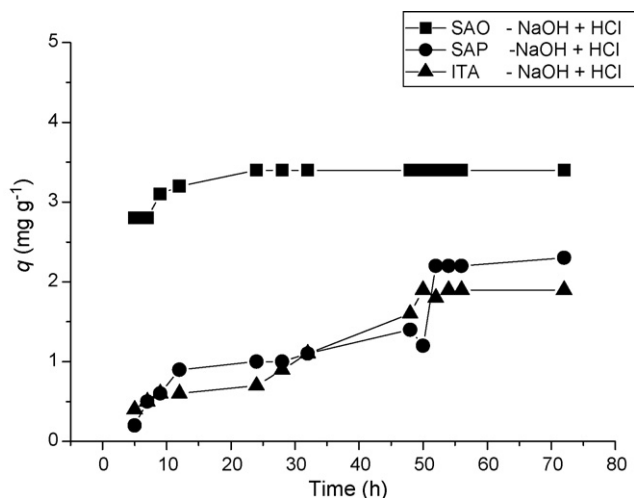


Fig. 5. Adsorption of Cr(III) for periods of up to 72 h in contact with peat from the municipalities of Santo Amaro das Brotas-SE (SAO), Ribeirão Preto-SP (SAP) and Itabaiana-SE (ITA), treated chemically with  $1.0 \text{ mol L}^{-1}$  NaOH + HCl ( $T = 25 \pm 0.2^\circ \text{C}$ ; equilibrium pH 4.0;  $c_i = 10 \text{ mg L}^{-1}$ ;  $m = 100 \text{ mg}$  of sorbent).

there was no significant difference between the results obtained for the *in natura* ITA and SAP peats ( $F = 0.818$ ;  $P = 0.417$ ). However, significant difference was found between the *in natura* ITA and SAO peats ( $F = 16.794$ ;  $P = 0.0149$ ), and the SAP and SAO peats ( $F = 13.533$ ;  $P = 0.0212$ ).

In the case of the SAO sample, pre-treatments reduced Cr(III) adsorption from  $4.90 \pm 0.01$  to  $(3.30\text{--}3.40) \pm 0.01 \text{ mg g}^{-1}$ . The reduction in adsorption was accompanied by an increase in the ash content (from 9.4 to 12.4% for the HCl + NaOH treatment) and a decrease in the carbon content (from  $53.1 \pm 0.52$  to  $45.8 \pm 0.83\%$ ), indicating that for this sample the adsorption efficiency was associated with the amount of organic material present (Figs. 4 and 5). The statistical test showed that there was a significant difference between the results obtained for SAO peat *in natura* and after treatment with HCl + NaOH ( $F = 14464.29$ ;  $P = 0.000$ ). However, HCl treatment was significantly less efficient than HCl + NaOH treatment ( $F = 73.14$ ;  $P = 0.00103$ ).

In a recent study employing these same peats [19], multiple quantitative and qualitative methods were used to identify which fraction, organic or inorganic, was responsible for metal adsorption, since adsorption of Cr(III) from aqueous solution onto peat is related to the presence of functional groups on the surface. Elemental analyses and  $E_4/E_6$  ratios indicated that the SAO peat is highly humified and rich in organics. Chemical shifts assignments of  $^{13}\text{C}$  NMR spectra indicated greater abundance of alkyl-C groups in SAO peat than in SAP and ITA peats. Results of FTIR analyses of ITA and SAP samples showed similarities, with a more prominent peak at  $1086 \text{ cm}^{-1}$  indicating a greater prevalence of Si-O groups, different to the SAO sample, which showed two more prominent peaks at  $2920$  and  $2850 \text{ cm}^{-1}$ . These peaks were probably due to C-H stretching associated with the alkyl-C. Thermal analyses of the SAO sample showed higher exothermic effect between  $300\text{--}400$  and  $500^\circ \text{C}$ . This indicated that SAO peat has higher organic matter content, corroborating results obtained using all of the techniques. Furthermore, SEM and environmental scanning electron microscopy (ESEM) characterized the surface of the peat samples, and for the SAO sample identified porous granules of organic material and typical aggregate structures of natural organic matter, respectively. Our previous work concluded that overall adsorption could be explained by the relative efficiencies of adsorption of the organic and mineral fractions of the peat [18]. The SAO peat has higher organic matter content, and hence pos-

sesses physicochemical properties that favor the binding of metal ions [10,24].

Pre-treatments increased the ash contents of the other samples, from 80.9 to 99.1% (SAP), and from 87.8 to 94.7% (ITA). These increases in the mineral fraction suggested that this was responsible for the observed increases in Cr(III) adsorption, from  $1.70 \pm 0.01$  to  $2.20 \pm 0.01 \text{ mg g}^{-1}$  (SAP) and from  $1.40 \pm 0.01$  to  $1.90 \pm 0.01 \text{ mg g}^{-1}$  (ITA). There were significant differences between the results obtained for these peats, either *in natura* or after treatment with HCl + NaOH (SAP:  $F = 1095.2$ ,  $P = 0.000$ ; ITA:  $F = 1125.0$ ,  $P = 0.000$ ), and after treatment with HCl for ITA peat ( $F = 104.165$ ;  $P = 0.0051$ ). This was not observed for SAP peat after treatment with HCl ( $F = 0.000$ ;  $P = 1.000$ ). However, the SAO peat gave higher  $q$  values, irrespective of chemical treatment (Figs. 3–5 and Table 1).

Earlier work [22] has indicated that retention of Cr by bone charcoal is due to association of Cr with the mineral phase, rather than with the carbon or organic phases. From this, it was concluded that the increase in the proportion of oxides in a treated sample accounted for an increase in the capacity of bone charcoal for removal of Cr from aqueous solutions. This was not observed in the case of the peat samples used in the present work.

Concerning contact time, it was found that adsorption equilibration was achieved after 50 h. This time is explained by a slowing of adsorption in the later stages, since initially a large number of vacant surface sites are available for adsorption, while progressively fewer remaining sites become increasingly difficult to occupy due to the existence of repulsive forces between the solute molecules of the solid and bulk phases [24,25].

Adsorption experiments investigating the influence of pH, and determination of adsorption isotherms, were undertaken using only the SAO peat (for an equilibration time of 50 h), due to its ready availability in large quantities in Sergipe State, and its higher adsorption capacity.

### 3.3. Influence of pH

Uptake by peat and microbial biomass is usually ascribed to processes including ion exchange, surface adsorption, chemisorption, complexation and adsorption-complexation. It is commonly believed that ion exchange is the most important mechanism, because humification of peat produces humic substances possessing carboxylic and phenolic acid groups within their structures, which release protons on reaction with metals [26].

The influence of pH on adsorption of Cr(III) ions was investigated using initial metal solution pHs of 3.0, 4.0, 5.0, 6.0 and 7.0. The initial pH of solutions were adjusted using either  $0.1 \text{ mol L}^{-1}$  HCl or  $0.1 \text{ mol L}^{-1}$  NaOH, after which the peat was added. The unbuffered solutions, containing Cr(III) at a concentration of  $10.0 \text{ mg L}^{-1}$ , were shaken (at  $25 \pm 0.2^\circ \text{C}$ ) for the period required for adsorption equilibration (50 h). The relationship between the amount of Cr(III) adsorbed after this period, equilibrium pH and initial solution pH is provided in Table 2.

Table 2 shows the difference in pH values before and after the adsorption process. The initial pH indicates the condition at time zero, while the equilibrium pH shows the final relationship between pH and Cr(III) adsorption. pH values tend to diminish during adsorption, suggesting that ion exchange is the dominant mechanism. From Table 2 it can be seen that equilibrium pH values of the aqueous solutions are in the range 3.1–4.0. Such pH values may be attributed to the buffering capacity of peat.

Chromium reacts with the carboxylic acid groups, releasing protons and hence reducing the pH. According to Thurman [27], the carboxylic acid functional group is one of the most important in

**Table 2**

Adsorption of Cr(III) (mean  $\pm$  S.D.) by Santo Amaro das Brotas (SAO) peat at different pH values ( $T = 25 \pm 0.2$  °C,  $m = 100$  mg of sorbent)

pH <sub>i</sub> <sup>a</sup>	pH <sub>e</sub> <sup>b</sup>	$c_e$ (mg L <sup>-1</sup> ) <sup>c</sup>	$q$ (mg g <sup>-1</sup> )	Retention (%)
3.0	3.1	$5.59 \pm 0.02$	$1.33 \pm 0.03$	$31.6 \pm 0.2$
4.0	3.8	$1.46 \pm 0.02$	$3.29 \pm 0.01$	$82.1 \pm 0.2$
5.0	4.0	$0.28 \pm 0.01$	$4.90 \pm 0.02$	$96.4 \pm 0.1$
6.0	3.4	$3.56 \pm 0.07$	$2.31 \pm 0.01$	$56.3 \pm 0.6$
7.0	3.3	$3.59 \pm 0.03$	$2.23 \pm 0.03$	$54.0 \pm 0.5$

<sup>a</sup> Initial pH.

<sup>b</sup> pH at equilibrium.

<sup>c</sup> Concentration after 50 h equilibration time using 100 mg of peat in contact with 50 mL of 10.0 mg L<sup>-1</sup> (initial concentration) Cr(III) solution.

natural organic materials. Compounds containing this functional group, which can act to buffer pH due to their weak acidity, include aromatic acids, aliphatic acids and various aromatic and aliphatic dicarboxylic acids. The presence of two acidic functional groups on an aromatic ring can result in pK<sub>a</sub>'s of between 2.9 (or lower) and 4.4. When the first (strongest) proton in these dicarboxylic structures is ionized, the negative charges repulse one another. This causes the energy required to ionize the second proton to increase. The energy of repulsion causes the pK<sub>a</sub> to increase, so that a higher pH is needed to remove another (second) proton.

According to Tipping [28], the most significant buffering by humic substances occurs in the pH range 4.0–6.0. In the present work, adsorption of chromium onto peat increased with the equilibrium pH, reaching a maximum of  $4.90 \pm 0.02$  mg g<sup>-1</sup> at pH 4.0, representing retention greater than 95% at equilibrium (Table 2).

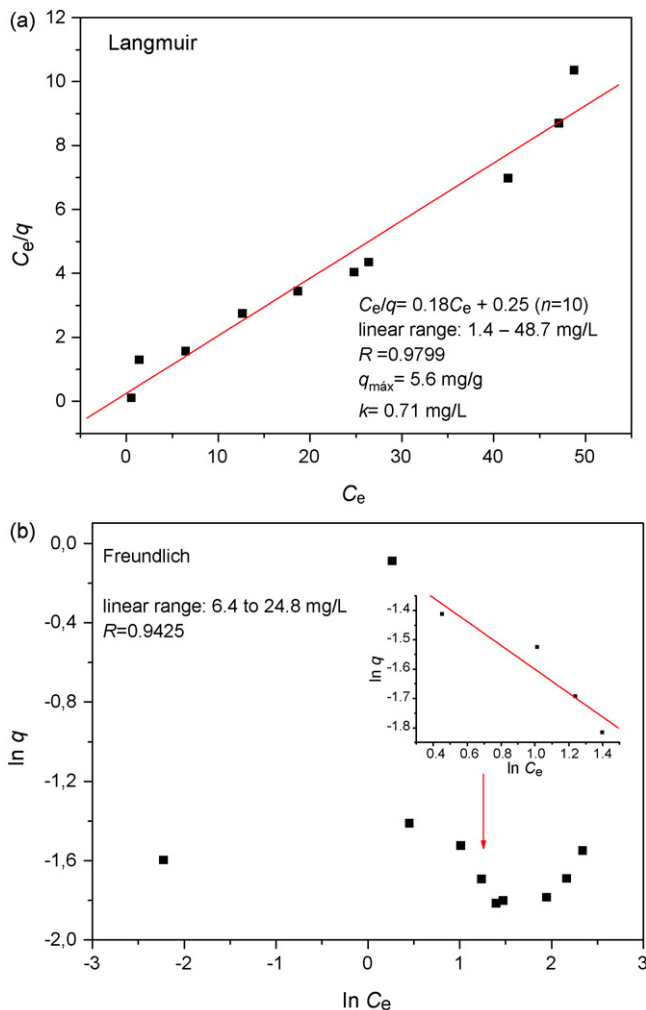
In addition to the buffering effect, it is also necessary to consider the speciation of the metal ion at different pHs. Ma and Tobin [8] showed that, while chromium mainly exists in the form of the trivalent ion at pHs between 2.0 and 3.0, neutral species tend to be formed as pH increases. Increased competition, between [H<sup>+</sup>] and metal ions for active sites on the peat, reduces biosorption of the metal at low pH. The presence of acidic surface groups on peat increases adsorption of Cr(III) ions due to electrostatic forces of attraction between the negative peat surface and Cr(III) ions in solution. Reduction in these interactions results in diminished Cr(III) adsorption at pH > 6.0, with Cr(III) tending to precipitate as Cr(OH)<sub>3</sub> [16].

#### 3.4. Adsorption isotherms

Experimental data for the adsorption of Cr(III) from aqueous solution onto the SAO peat were fitted to the most commonly used Langmuir equation. The constant values obtained for the linearised Langmuir isotherms are presented in Fig. 6a. The Freundlich model was also tested, however only showed linear correlation ( $R = 0.94$ ) in the concentration range 6.4–24.8 mg L<sup>-1</sup> (Fig. 6b), compared to a linear range of 1.4–48.7 mg L<sup>-1</sup> in the case of the Langmuir model. The values of  $q_{\max}$  and  $b$  were determined from the slope and intercept of the plots of  $c_e/q_e$  against  $c_e$ . The Langmuir equilibrium adsorption capacity,  $q_{\max}$ , for the SAO peat was 5.60 mg g<sup>-1</sup> under the conditions used. The adsorption equilibrium constant estimated by the value of the intercept was 0.71 mg L<sup>-1</sup>. For *in natura* SAO peat, a correlation coefficient ( $R$ ) of 0.98 was obtained for the linear Langmuir equation, where  $n$  is the number of points describing the data interval:

$$\frac{c_e}{q} = 0.18c_e + 0.25 \quad (n = 10) \quad (4)$$

It can therefore be concluded that the equilibrium data for the peat studied in the present work concur with the Langmuir model. This



**Fig. 6.** Adsorption isotherms for *in natura* SAO peat ( $T = 25 \pm 0.2$  °C; pH = 4.0;  $m = 100$  mg of sorbent) using (a) Langmuir and (b) Freundlich models.

is supported by agreement between the  $q$  value obtained using the Langmuir equation ( $5.60$  mg g<sup>-1</sup>), and that obtained experimentally ( $4.90$  mg g<sup>-1</sup>).

#### 4. Conclusions

Maximum uptakes of chromium, at equilibrium pH 4.0, for *in natura* peats from Santo Amaro das Brotas (SAO), Ribeirão Preto (SAP) and Itabaiana (ITA) were  $4.90 \pm 0.01$ ,  $1.70 \pm 0.01$  and  $1.40 \pm 0.01$  mg g<sup>-1</sup> (dry weight), respectively. Chemical treatments were inefficient for the SAO peat, since they reduced the adsorption capacity, from  $4.90 \pm 0.01$  to  $3.30 \pm 0.01$  mg g<sup>-1</sup>. However, these treatments increased the adsorption of chromium by the SAP peat, from  $1.70 \pm 0.01$  to  $2.20 \pm 0.01$  mg g<sup>-1</sup>, and by the ITA peat, from  $1.40 \pm 0.01$  to  $1.90 \pm 0.01$  mg g<sup>-1</sup>. The concentration of Cr in the residual solution ( $0.28 \pm 0.01$  mg L<sup>-1</sup> at equilibrium pH 4.0), after contact with the SAO peat, was below the discharge standards for several types of industrial effluent.

Elemental analysis, XRD and SEM showed that the SAO peat possessed true peat characteristics, with its elevated organic matter content being responsible for its high adsorption efficiency. Hence, this peat appears to be a viable material for decontamination of effluents containing Cr(III) ions.

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