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The use of solution microcalorimetry to evaluate chemically modified fish scales as a viable adsorbent for heavy metals

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Abstract Here, we report for the first time the direct and simultaneous determination of kinetic and energetic parameters of Cr(VI) sorption on chemically modified fish scales (GA-scale) using solution microcalorimetry. Characterization has suggested that electrostatic interactions between scales collagen positive charges and chromate negative charges constitute the majority of the interactions. The microcalorimetric kinetic data of Cr(VI) sorption on GA-scale were successful adjusted to a three-parameter exponential function. The enthalpies of Cr(VI) sorption on GA-scale are highly exothermic (from −226.43 to −183.79 kJ mol^{-1}), and Cr(VI) interaction energies decrease as initial Cr(VI) in solution increases. The kinetic and thermodynamic from solution microcalorimetry results suggest that the interactions GA-scale/Cr(VI) occur mainly by surface reactions. The maximum adsorption capacity of GA-scale for Cr(VI) was found to be comparable with some commercial adsorbent samples.

Keywords Solution calorimetry · Kinetics · Thermodynamics · Fish scales · Cr(VI) sorption

Introduction

Naturally occurring materials are the locations of several chemical reactions and commonly juxtapose minerals, aqueous solutions, atmospheric and soil gases, microbial organisms, and/or organic matter. Fundamental understanding of the chemical processes occurring at such interfaces is important to find new and economically viable materials and methods suitable for uses in several branches of science and industry [1].

In this study, we used scales of Brazilian Corvina fish (*Micropogonias furnieri*), a waste product from fishery, as a new adsorbent. Fish scales are a suitable sorption material for at least two reasons: (i) fish scales present a highly developed structure of the surface offering an adsorptive potential to a variety of dissolved material in water; (ii) the availability of the material—the scales are at the moment considered only as a waste material [2].

A novelty of the study presented herein is the direct use of solution microcalorimetry to evaluate kinetic and energetic parameters of Cr(VI) sorption on fish scales. Real time monitoring immersion microcalorimetry, being a direct reaction investigation method, may, therefore, be of specific advantage in the study of specific processes occurring at solid/liquid interfaces without the need for additional analytical investigation [3]. This technique allows the simultaneous determination of both the quantity and the energy of reaction. The experimental yield can potentially give information on kinetics and thermodynamics of the process, energetics, and analysis. The energy profile, which is the energy of the bonded phase as a function of loading, is essential for characterizing solid/liquid interfaces [4, 5]. However, less attention has been paid to the direct microcalorimetric investigations of heavy metals interactions on naturally occurring materials. As will be shown, this data are invaluable for understanding the sorption characteristics at fish scale/heavy metal interfaces.

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Materials and methods

Reagents and solvents

Water was used after double-distillation. All the chemicals/reagents used in these studies were of Analytical Reagent Grade. Aqueous solutions of Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ (VETEC, São Paulo, Brazil) in pH 4.0 HAc/NaAc buffered solution (ionic strength of 1.0×10^{-4} mol L^{-1}). A stock solution with a concentration of 5.0×10^{-3} mol L^{-1} of Cr(VI) was prepared and subsequently diluted.

Preparation and chemical modification of the adsorbent

The scales of Corvina fish (*M. furnieri*) were collected from the Fishermen's Market located in Aracaju, state of Sergipe, Brazil. Mature fish scales were washed repeatedly with water to remove adhering dust and soluble impurities form their surface. The fish scales were allowed to dry at 40 °C for 6 h. The fish scale collagen was stabilized under mild conditions using 0.025% (w/v) glutaraldehyde aqueous solutions at pH 7.4, as described earlier [6]. The chemically modified Corvina scales (hereafter described as GA-scale for simplicity) were cut into small 5 mm × 5 mm square membranes of 0.5 mm of thickness and conditioned in a dark air-free flask.

Characterization of the adsorbent

The morphological characterization of the scales was carried out with a scanning electron microscope (SEM, JEOL-JSM 6360-LV). The samples were coated with gold (thickness of about 12 nm), and then SEM micrographs were obtained. Infrared spectral data for scales before and after Cr(VI) sorption were obtained on a Perkin Elmer 1600 series FTIR spectrophotometer and diffuse reflectance accessory at a resolution of 4.0 cm^{-1}. Thermogravimetric analyses (TG and DTG) of the materials were made using masses of about 10 mg, under nitrogen atmosphere from 25 to 1,000 °C, in a SDT 2960 thermoanalyzer, from TA Instruments.

Microcalorimetry measurements

Microcalorimetric determinations were performed in a C80 microcalorimeter (SETARAM), which is capable of maintaining a baseline of ±0.12 μW with a temperature stability of $\pm 10^{-4}$ °C. Experimental determinations were performed using the membrane breaking (thin Teflon®) technique, as described elsewhere [7]. Briefly, 100 mg of GA-scale and 1.0 mL of acetic acid/sodium acetate buffer solutions at pH 4.0 were put into the lower end of the calorimetric vessel. Additionally, 2.0 mL of a Cr(VI) solution were put in the lower part of the calorimetric vessel. Calorimetric output is of thermal power (dq/dt; mW) as a function of time (t; s) and consequently the integral of this data to time t is equal to the interaction energy (J). The thermal effects of thin Teflon® membrane breaking for the empty cell and the dilution of the Cr(VI) solution in the reaction cell were found to be negligible. The calorimetric experiments were carried out using Cr(VI) solutions of 1.0, 3.0, and 5.0×10^{-3} mol L^{-1}, at 25, 35, and 45 °C. The detectable calorimeter signals (power vs. time) were analyzed using the SETSOFT software (SETARAM). Each experiment was performed in triplicate runs and values are the average of them.

The amount of Cr(VI) sorbed in each calorimetric experiment was calculated by using the following Eq. 1 [8]:

$$q_t = \frac{(C_i - C_t) \cdot V}{m} \quad (1)$$

where q_t is the fixed quantity of Cr(VI) per gram of fish scales after sorption equilibrium, in mol g^{-1}, C_i is the initial concentration of Cr(VI) in mol L^{-1}, C_t is the concentration of Cr(VI) present after sorption equilibrium, in mol L^{-1}, V is the volume of the solution in L, and m is the mass of fish scales in g.

Results and discussion

General considerations of chemical composition of fish scales and glutaraldehyde reaction of collagen

Fish scales are composed of an extracellular matrix, mainly type I collagen, and hydroxyapatites [$Ca_{10}(PO_4)_6(OH)_2$ or $Ca_5(PO_4)_3OH$] [9]. Needle-shaped crystals of apatites can be found in the osseous layer and in fibrillary plates. The collagen structure is composed of polypeptide chains with a triple-helical structure, and they are aggregated through hydrogen bonds to form collagen fibers [10]. However, collagens are soluble in both saline and acidic solutions. In order to overcome this undesirable characteristic, crosslinking reactions have been used for efficient insolubilization of collagen structure.

Glutaraldehyde possesses unique characteristics that render it one of the most effective crosslinking reagents. It can react with several functional groups of proteins, such as amine, thiol, phenol, and imidazole by several means such as aldol condensation or Michael-type addition [11, 12]. The linkage formed by the reaction of glutaraldehyde with an amino group has shown exceptional stability at extreme pH's and temperatures [13]. However, its chemistry has been quite controversial.

Glutaraldehyde structure in aqueous solution is not limited to the monomeric form. Commercial solutions are usually polymeric with significant amounts of α,β-unsaturated aldehydes that are able to form rings by loss of water molecules by aldol condensation. In fact, water is the medium in which commercial glutaraldehyde is supplied and in which the crosslinking reaction with proteins is carried out, and glutaraldehyde was found to react with this solvent in various ways. Upon dilution, the polymerized glutaraldehyde is slowly converted to monomers, thus inducing a great variation in the relative abundances of monomeric and polymeric species, according to the pH and glutaraldehyde concentration of the solution [11].

Characterization of the materials

Basic information on the structure is necessary for developing the use of fish scales as adsorbents. Some features of GA-scale can be seen in the SEM micrographs (Fig. 1). The lower region is rich in inorganic material containing high proportions of calcium and phosphorus, whereas the upper region is rich in proteins [14]. Electron microscopic investigation of scales of the GA-scale also revealed sheet-like structures composed of vertically oriented collagen fibers. Several fractures are also detectable along the radial discontinuity lines (details not shown), probably as a consequence of (poly)glutaraldehyde crosslinking or air-drying. The presence of calcification appeared to be needle-like or flaky crystals of apatites [15]. However, this morphologic characteristic is difficult to observe when the scales were cut longitudinally, possibly because of the specimen preparation. The orientations of apatite crystals seem to be random in nature.

TG-DTG plots of Corvina scales are shown in Fig. 2. The scales are mostly composed of different organic matters, water, and some amount of minerals. On heating Corvina scales, two main weight loss events are shown at the following temperature ranges: 25–230, 250–630 °C. In the DTG curve, two main peaks can be observed. The first event has been related to the superficial water releasing. The second event corresponds to the thermal degradation of the polymeric chains of collagen followed by the carbon material elimination. No differences of the thermal behavior of raw Corvina scale and GA-scale were clearly observed. Similar results are described in the literature concerning thermal analysis of fish scales [9, 13].

Bound water molecules was mainly being lost until about 230 °C, and the fragmentation of the macromolecule occurred until about 600 °C due to formation of gaseous elements. After about 600 °C, there was no significant change in weight with some amount of residue left. Thus, organic components of fish scales should be absent after

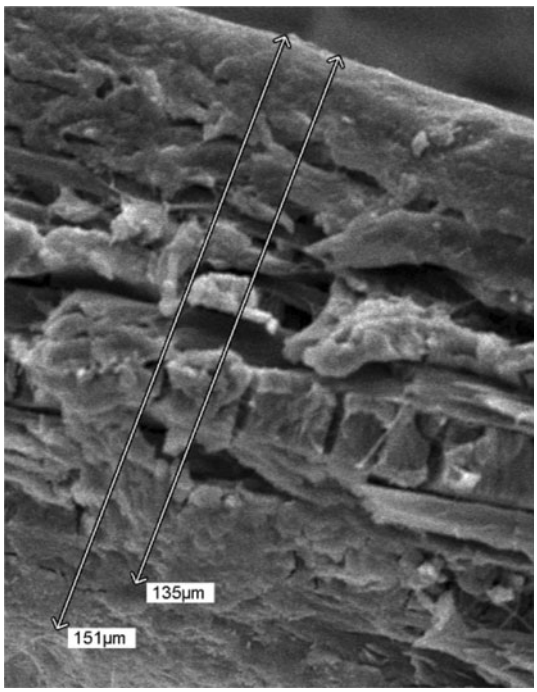

Fig. 1 SEM micrographies of GA-scale. Magnifications of ×300 (*upper figure*), ×500 (*middle figure*), and ×20,000 (*lower figure*)

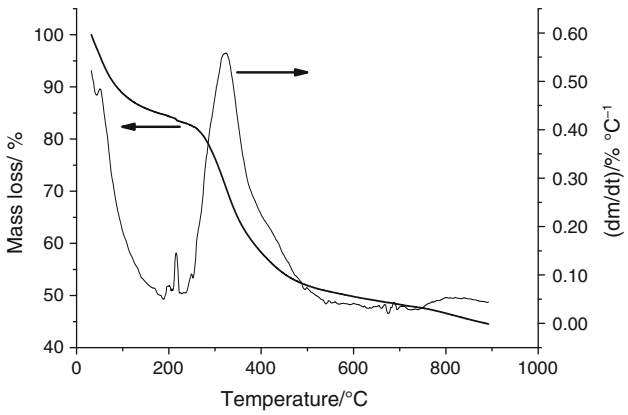

Fig. 2 TG/DTG curves of GA-scale

about 650 °C. The total residue content was found to be ~45 wt%, due to the presence of apatites in the scales [9].

Figure 3 shows the FTIR spectra of GA-scale before and after Cr(VI) interaction. The spectrum of raw scales was typical with O–H and N–H stretching band at 3,257 cm^{-1}, NH–CO band at 1,633 cm^{-1}, and the methyl bending band at 1,448 cm^{-1}. The spectra recorded absorption bands of P–O due to PO_4^{3-} groups in the 1009, 675 and 664 cm^{-1} region, which are characteristic of the inorganic phase (mainly hydroxyapatite), as well as of the H–O band of sorbed water [16, 17]. The amide I band, with characteristic frequencies in the range from 1,600 to 1,700 cm^{-1}, was mainly associated with stretching vibrations of the

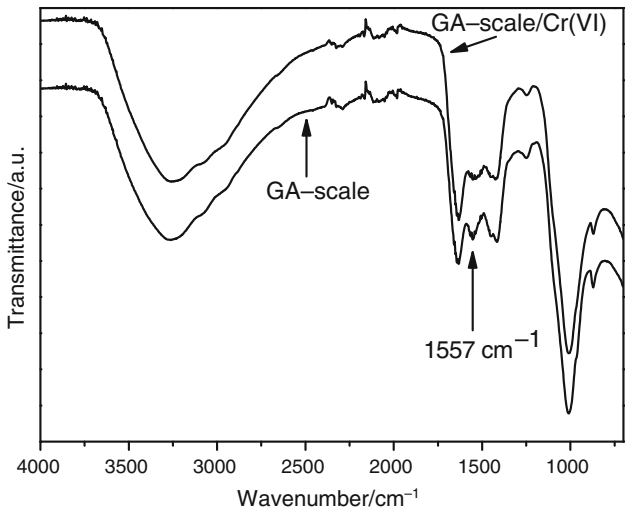

Fig. 3 FTIR spectra of GA-scale before and after interaction with Cr(VI)

carbonyl groups (C=O bond) along the polypeptide structure. When comparing with the normal absorption range of the amide II bands position (1,550–1,600 cm^{-1}), the position is found to be shifted to lower frequency, 1,557 cm^{-1}, which suggests the existence of hydrogen bonding in the collagen structure [18].

Collagen fiber is low soluble in water but is a hydrophilic material. Water molecules are tightly bound to specific sites on collagen chains, or filling in the spaces between molecules ("interstitial waters") [19]. These water molecules stabilize the triple helix structure of the collagen structure. From FTIR data, it is suggested that water molecules bind to the C=O and C–N polar groups of the collagen. For hydroxyapatite, during hydration processes, water was found to form strong electrostatic interactions with the calcium and the phosphate ions. This leads to several hydration layers exhibiting a strongly ordered character. Within these layers water mobility is reduced drastically [19].

The uptake abilities of scales from different fish species should be similar because most fish scales contain significant portions of organic protein (collagen), and the analysis of the structure of collagen shows that it contains the possible functional groups, such as hydroxyl, carboxyl, amine, and amides, that can be involved in interactions at fish scale/heavy metal interface. The FTIR spectrum of GA-scale with Cr(VI) sorbed is more or less the same in relation to the raw GA-scale. After Cr(VI) sorption, the relative intensity of the amide II spectral peak (1,557 cm^{-1}) slightly decreased in intensity. From the literature reports, it is an indication that hydrophobic groups of the amide II of collagen structure seem to be a potential interaction site for Cr(VI) sorption on GA-scale [9, 14]. On the other hand, the mineral phosphate spectral region (900–1,200 cm^{-1}) seems not to be affected. So, it is more likely that the main Cr(VI) sorption sites are located on the collagen fibers of Corvina scales. At low pH values, positively charged surface sites are formed, resulting in an overall positive surface charge. This is likely to assist in the attraction of negatively charged chromate ions to GA-scale functional groups through electrostatic forces. So, electrostatic interactions between GA-scale positive charges and chromate negative charges seem to constitute the majority of the interactions [14, 16].

Analysis of Cr(VI) sorption by solution microcalorimetry

In aqueous solutions, Cr(VI) anion is not a simple monovalent anion but rather a series of chromate anions depending upon the pH of the solution. The chromate may be represented in various forms such as H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$ in the solution phase as a function of pH. Between pH 2 and 6, $HCrO_4^-$ and $Cr_2O_7^{2-}$ are in equilibrium. As the pH increases, this form shifts to CrO_4^{2-} and $Cr_2O_7^{2-}$. At pH greater than 7.5, CrO_4^{2-} is the only chromate species in aqueous phase [20]. So when the pH is changed, the existed form of Cr(VI) will influence the Cr(VI) uptake. At low pH, the adsorbent surfaces become positively-charged due to strong protonation, electrostatic force between the positively-charged surface and the negatively-charged $HCrO_4^-$ and $Cr_2O_7^{2-}$, as well as the interaction between cations and $HCrO_4^-$ and $Cr_2O_7^{2-}$ in the internal sorption sites of the scales, will enhance the Cr(VI) sorption. However, when the pH value is less than 4, $HCrO_4^-$ and $Cr_2O_7^{2-}$ can transform $H_2Cr_2O_7$ and electrostatic interaction will reduce accordingly. With increase of pH, the degree of protonation of the surface reduces gradually and hence sorption capacity decreases in the pH range of about 5–7. Furthermore, the lower affinity of Cr(VI) sorption above pH 7 has been attributed to the strong competition between HCrO4$^-$, $Cr_2O_7^{2-}$, and OH^- since more OH^- anions are present in solution [20].

Microcalorimetric kinetic data are the foundation of mechanistic investigations, and many of the systems of interest at solid/liquid interfaces are complex and present considerable difficulties in analysis. Typical profiles of the microcalorimetric outputs are illustrated in Fig. 4. In order to obtain accurate kinetic parameters for fast processes from microcalorimetric outputs (up to about 40 min), it is necessary to apply Tian equation (Eq. 2) [21].

$$S_{\mathrm{corr}}(t) = S_{\mathrm{orig}}(t) + \tau\left(\frac{\mathrm{d}S_{\mathrm{orig}}(t)}{\mathrm{d}t}\right) \quad (2)$$

where $S_{\mathrm{corr}}(t)$ is the corrected calorimetric signal (W), $S_{\mathrm{orig}}(t)$ is the original calorimetric signal (W), τ is the time

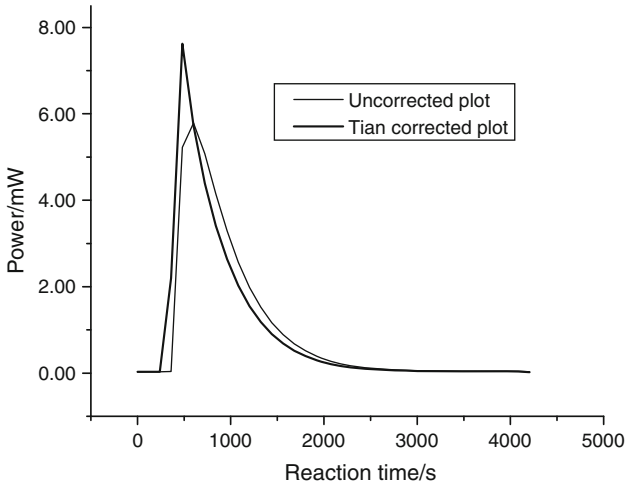

Fig. 4 Typical microcalorimetric plot of Cr(VI) sorption on GA-scale, at different initial Cr(VI) concentrations. The *thin curve* is the uncorrected calorimetric output and *thick curve* is the calorimetric outputs after Tian equation correction

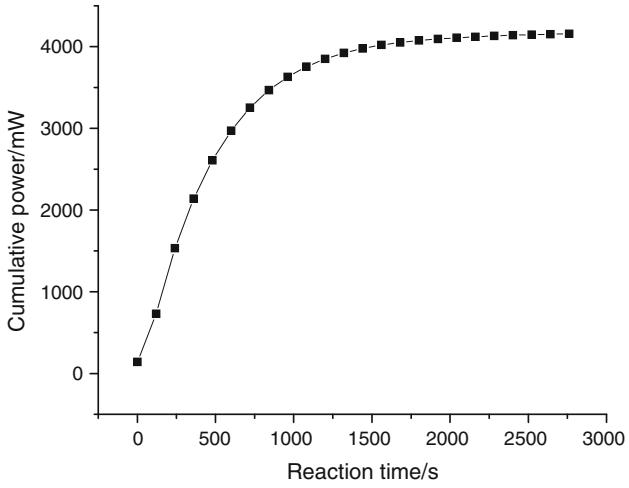

Fig. 5 Cumulative heat flow curves of Cr(VI) sorption on GA-scale

constant of the calorimeter (150 s, in this study) and $[dS_{orig}(t)/dt]$ is the time derivative of the original calorimetric signal.

In general, a sharp increase in heat flow occurred in the first 2 min of interaction followed by a decline in heat flow. The base line used for the integrations was selected as linear from first to last point, joining the two extreme points selected on the curves. Microcalorimetry gives directly the curve of the heat release as a function of coverage, which is the real signature of the energetic distribution for a given solid/probe couple. The non symmetric calorimetric plots suggest that the Cr(VI) sorption is not ideal and the surface of the support (GA-scale) is not energetically uniform [22]. This behavior is typical of most noncrystalline adsorbents [18].

In this study, the kinetic modeling for Cr(VI) sorption was performed using isotherms built from the cumulative values of heat of sorption, as exemplified in Fig. 5. The cumulative calorimetric outputs are fitted to a simple three-parameter exponential function shown in Eq. 3 [23]:

$$Q_{int} = Q_{int}^{m}(1 - \exp^{-(k \cdot t)^{n}}) \quad (3)$$

where Q_{int} and Q_{int}^{m} denote the heat flow release at a given time t and the maximum energy release of a given sorption process, respectively. The term k is the rate constant and n is another constant, whose value is related to the kinetic order and varies according to the sorption mechanism. In order to evaluate the fitting of the exponential kinetic model, chi-square (χ^2) tests were done according to Eq. 4 [24]:

$$\chi^2 = \sum \frac{(Q_{int,e} - Q_{int,m})^2}{Q_{int,m}} \quad (4)$$

where $Q_{int,e}$ and $Q_{int,m}$ are the energy release at a given time t, which were calculated using experimental data and the exponential kinetic model, respectively. The χ^2 statistic test is basically the sum of the squares of the differences between the experimental data and theoretically predicted data from models. If modeled data are similar to the experimental data, χ^2 will be a small number; if they are different, χ^2 will be a large number. Good agreements of the experimental and calculated data were found using the exponential model for all contact time evaluated ($5.00 \leq \chi^2 \leq 7.43$).

The kinetic and thermodynamic parameters of Cr(VI) sorption on GA-scale are presented in Table 1. In this study, the sorption rate constants (k) decrease when initial Cr(VI) concentration increases. It is a reasonable assumption of an initial predominant mechanism of chemical nature rather than adsorbate diffusion into the internal sorption sites. A possible external phenomenon to conform to this picture may be a surface enhancement associated with a highly energetic heterogeneous sorbent surface [25]. At low metal concentration, the metal adsorption involves the higher energy surface sites. As the metal ion concentration increases, the higher energy surface sites are saturated and sorption begins on the lower energy surface sites, resulting in a decrease of the sorption efficiency [25].

The kinetic orders calculated (n) increase when initial Cr(VI) concentration increases. For sorption the value of n was customary from one to two [26]. In this study, the fact that $n > 1$ in almost all cases suggests that the process may be limited by surface reactions [27]. Although we can reasonably assume that Cr(VI) ions could diffuse into the adsorbent pores, it seems that Cr(VI) diffusion is not the rate-limiting process.

It should also be known that the sorption heat measured from solution microcalorimetry is an integral heat since

Table 1 Energetic and thermodynamic parameters of isothermal Cr(VI) sorption on chemically modified Corvina scales

Thermodynamics					Kinetics/exponential modeling		
Temperature/°C	$C_i/10^{-3}$/mol L^{-1}	$-Q_{int}$/J g^{-1}	n_{int}/μmol g^{-1}	$-\Delta H_{int}$/kJ mol^{-1}	n	k/min^{-1}	R^2
25	1.0	0.939	4.147	226.43	1.13	0.145	0.984
	3.0	1.160	5.623	206.30	1.19	0.166	0.999
	5.0	1.406	7.650	183.79	2.23	0.067	0.996

Average standard deviation $-Q_{int}$ (%) = 3.5

Average standard deviation n_{int} (%) = 4.8

Average standard deviation $-\Delta H_{int}$ (%) = 5.1

Average standard deviation of n (%) = 8.1

Average standard deviation of k (%) = 7.7

there are different sites in fish scales for Cr(VI) interaction. The interaction enthalpy $\Delta_{int}H$ can be calculated directly by the following Eq. 5 [26, 27]:

$$-\Delta_{int}H = \frac{Q_{int}}{n_{int}} \quad (5)$$

where Q_{int} is the integral interaction energy (J g^{-1}) and n_{int} is the number of moles of Cr(VI) sorbed on GA-scale (mol g^{-1}).

An error analysis of the results (details not shown) has shown that reproducibility is good, and that absolute errors in both sorption energy and amount of Cr(VI) sorbed are typically less than 6.2%. The enthalpies of Cr(VI) sorption on GA-scale are highly exothermic, and both interaction energies (Q_{int}) and Cr(VI) amounts sorbed decrease as initial Cr(VI) in solution increases. The reaction times, from 30 to 40 min, did not change appreciably, in relation to the initial Cr(VI) concentration in solution. Continuous variations of energy of sorption with coverage have been reported by several researchers as due to the heterogeneous nature of surfaces [21, 22]. It is the most frequent situation where the surface is heterogeneous: the adsorption enthalpy decreases with coverage.

In general, the sorption enthalpy at solid/solution interfaces is an average result of chemical bonding (exothermic) and diffusional (endothermic) processes [27]. Typically, interactions that occur with intense adsorbate diffusion present small and relatively similar values of $\Delta_{int}H$. Solvent and solute transport through adsorbent materials is generally described following an adsorption–diffusion mechanism, where molecules first diffuse from the bulk phase to the adsorbent surface. Next, they adsorb to the sites on the surface and diffuse through the adsorbent structure, driven by the chemical potential gradient within the pores [26].

In this study, the high exothermic results observed are in agreement with interaction of Cr(VI) species to sorption sites at adsorbent surface. Exothermic heats of interaction also indicate the dominance of attractive forces between the surface and the adsorbing specie, and/or attractive forces between adsorbed molecules on the interaction sites. The $\Delta_{int}H$ value (experimentally measured) can also be used as a measure of the interaction force between adsorbate and adsorbent, giving an indication of the bonding strength. The magnitude of $\Delta_{int}H$ increased as the Cr(VI) sorption is increased. This increase in $\Delta_{int}H$ has been attributed to repulsive lateral interactions between adsorbed molecules; these repulsive interactions increased in magnitude as the adsorption increased [28]. At higher loading, repulsive lateral interactions between the adsorbed species, which are endothermic, might increase, decreasing the exothermic net heat of sorption at higher loadings.

Sorption of hydrated (poly)anions onto a hydrophilic polymer network inevitably disturbs the order of solvent molecules in the nearest environment and releases them to the external liquid. In other words, adsorbed molecules are attracted probably due to long-distance electrostatic interactions between oppositely charge groups. During the formation of the ionic bonds between the Cr(VI) anion and the collagen on GA-scale, the counterions should gain a higher degree of freedom and increase the interaction entropy [28].

Conclusions

In this study, chemically modified scales of Brazilian Corvina fish were characterized and used for sorption of Cr(VI) from aqueous solutions. The FTIR spectra of Corvina scales, before and after Cr(VI) sorption, indicate that electrostatic interactions between Corvina scales positive charges and chromate negative charges seem to constitute the majority of the interactions. The kinetic data were successfully modeled to a simple three-parameter exponential function. The kinetic and thermodynamic results suggest that the interactions at scales/Cr(VI) is limited by

surface reactions. The magnitude of $\Delta_{int}H$ increased as the Cr(VI) sorption is increased, suggesting repulsive lateral interactions between adsorbed species. The maximum sorption capacity observed for Cr(VI) on chemically modified Corvina scales (about 22 mg g^{-1}) is comparable with literature reports [29–33], especially in relation to some commercial activated carbon samples.

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