The use of freshwater fish scale of the species *Leporinus elongatus* as adsorbent for anionic dyes

An isothermal calorimetric study

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Abstract Fish scale of the species *Leporinus elongatus* was tested as an adsorbent for anionic Remazol dyes. Characterization has suggested that hydroxyl, phosphate, amides I, II, and III, and carbonate groups are the potential sites of adsorption. From solution calorimetry, values of thermal effects, Q_{int}, and amount of dye that interacts, n_{int}, were determined. The adsorption order observed was Yellow-dye/scale > Red-dye/scale > Blue-dye/scale. The Q_{int} and n_{int} data were successfully adjusted to the Langmuir isotherm model. The dyes removals by fish scale are exothermic processes (from -83 to -199 kJ mol^{-1}) with negative entropies and are thermodynamically spontaneous. The thermodynamic results suggest that the interactions at scale/anionic dye interfaces occur mainly by surface reactions. It was finding that fish scale is a new and suitable sorbent material for recovery and biosorption/adsorption of anionic dyes from aqueous solutions.

Keywords Solution calorimetry · Anionic dyes · Adsorption · Fish scale · Thermodynamics

Introduction

Dyes used in the textile industry represent a large and important group of chemicals among the different aqueous pollutants that get mixed in wastewater. The use of reactive dyes has grown rapidly due to the increasing use of cellulosic fibers and the technical and economic limitations of other dyes used for these fibers [1]. Most of the textile dyes are anionic due to the presence of sulfonic acid groups in their molecules to induce water solubility. Since these species are soluble in water and not easily biodegradable, they may still remain in the effluent even after extensive treatment, thus their discharge is currently one of the world's major environmental problems as some of the dyes and their metabolites are either toxic or mutagenic and carcinogenic and pose a potential health hazard to all forms of life [2, 3]. Methods for removal of dyes containing wastewaters have been the subject of different researches, in order to improve on environmental remediation technologies. Due to ability to remove different types of dye, easy handling and produce high quality treated water, the adsorption technique has already received considerable attention and several adsorbents have been developed for this purpose [4–10]. Adsorption technology is especially a promising option and can prove to be attractive in case the adsorbents do not cost much and are ready for use and do not require any expensive additional.

In recent years, many researches have focused on the use of various low-cost adsorbents with a larger compromise of selecting materials from the eco-design perspective, particularly those arising from recyclable materials. Recycling of materials reduces the environmental burden associated with acquisition of virgin resources from the ecosphere, and also reduces the burden of waste treatment. Many economic activities generate a large volume of residues, such as those from fishing, and in this context fish scales are very common residues which are released into the environment causing pollutions and emitting offensive odors. Some studies dealing with fish scales from marine

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species as adsorbent material have already been performed [11–14]. Recently, a study of characterization and Cu(II) adsorption on freshwater fish scales of the species *Leporinus elongates* has been published [15]. The *Leporinus elongatus* species has great commercial importance. Currently known as Piau, is abundant in free markets and fairgrounds in several places [16]. This species is composed by two different phases, an inorganic phase and other organic one. The inorganic phase is formed by hydroxyapatite containing small amounts of sodium, magnesium, and carbonate ions, and the organic phase, formed mainly by collagen, presents composition in mass approximately of 32% [15].

A novelty of the work presented herein is the direct use of solution microcalorimetry to evaluate energetic parameters of anionic dyes sorption on fish scale. The nature of interactions dyes/scales was investigated by isothermal solution calorimetry using the membrane breaking technique [17–21]. Simultaneous determination of interaction effects, Q_{int}, and amount of dye that interacts, n_{int}, are described. Real time monitoring solution 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. This technique allows and the simultaneous determination of both the quantity and the energy of reaction. The experimental yield can potentially give information on 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 [20–22]. However, less attention has been paid to the direct microcalorimetric investigations of dyes interactions on naturally occurring materials. The ultimate goal of this survey is to describe the effectiveness of freshwater fish scales of the species *Leporinus elongatus* to bind with anionic dyes. As will be shown, this data is invaluable for understanding the sorption characteristics at fish scale/dye interfaces.

Experimental

Reagents and samples

In order to obtain the fish scales, Piau fishes (*Leporinus elongatus*) with an average length of about 20 cm (1.5–2.0 kg) were obtained from a free market in Itabaiana-SE in the summer of 2008. The anionic dyes Remazol Yellow (RY), Remazol Blue (RB) and Remazol Red (RR) were provided by The Dystar Dyes Company and used without purification. The chemical structures of the dyes were shown earlier [19]. All other reagents were of analytical or equivalent grade purchased from Sigma Aldrich and used as received. Double-distilled water was employed throughout.

The fresh scales were washed thoroughly with running water and immersed in NaOH solution (pH 9.0) for 4 h at ambient temperature. After this, the fish scales were washed (60 min under ultrasound and 10 min of stirring double-distilled water) and dried at 333 K for at least 6 h. Then, by mixing the scales with water at 4,000 rpm during 60 s, the powder was obtained (hereafter called scales for simplicity). The powder was dried at 333 K for 24 h and sieved with a 100-μm mesh sieve, placed in polyethylene bags and stored at room temperature.

Characterization of the scales

The pure scales and scales with the adsorbed dyes (scale-RY, scale-RB, and scale-RR) were characterized by FTIR diffuse reflectance and thermogravimetry. Infrared spectra data were obtained on a Perkin-Elmer 1600 series FTIR spectrophotometer and diffuse reflectance accessory at a resolution of 4 cm^{-1}.

Determination of the point of zero charge of the scales

Experiments for point of zero charge (PZC) determination were carried out under room temperature using 0.1 g of the scales in 50 mL of aqueous solution of NaCl (0.01 mol dm^{-3}) in different initial pH values (adjusted by addition of HCl or NaOH 0.01 mol dm^{-3}) [16]. The resulting dispersions were allowed to equilibrate for 24 h with continuous stirring. The equilibrium pH values were measured using a digital pH meter (Digimed MD-20). The experiments were realized in triplicate.

Calorimetric determinations

All calorimetric determinations were performed in a SETARAM C80 mixing calorimeter [18–21], capable of maintaining a baseline of ±0.12 μW with a temperature stability of ±10^{-3} K. The experiments were carried out at 298.15 K with aqueous dyes solutions at pH 4. Samples of approximately 100 mg of scales were put into the lower part of the mixing cell closed by a circular membrane of Teflon. Into the upper part of mixing cell, a volume (3.0 cm^3) of dye solution was added. The initial dyes concentrations were from 0.01 to 5.0 × 10^{-2} mol dm^{-3}. After complete stabilization of the base line, a movable rod enables the dye solution to be pushed into the container with the scales through the membrane of Teflon and the interaction dye/scales proceeds without stirring. The curves of the detectable calorimeter signals (power, mW vs. reaction time) make sure that the dye equilibrium

conditions are reached. The base line used for the integration is selected as linear from first to last point, joining two extreme points on the curves. Thus, each individual experiment yields a thermal effect, Q_r, which is corrected by subtracting the corresponding wetting effect, Q_w, of the scales in the pure solvent. The thermal effect of membrane breaking for the empty cell was found to be negligible compared to Q_r and Q_w values. After each Q_r recording, the dye equilibrium concentration, C_{eq}, was determined in the supernatant using a spectrophotometer (Femto, 700 Plus). For this purpose, previous analytical curves were obtained in the wavelengths of 410, 520, and 600 nm for the dyes RY, RR, RB, respectively. From C_{eq} value, the dye amount that interacts, n_{int}, can be determined. Each experiment was repeated in duplicate.

Results and discussion

FTIR analysis suggests the importance of functional groups of fish scale such as hydroxyl, phosphate, carbonate, and amides during dyes interactions. The main information of the FTIR spectrum of Piau fish scale can be find in Table 1. FTIR spectrum of pure scale shows strong absorption bands at 600 and 1,036 cm^{-1}, corresponding to phosphate groups in the apatite lattice, and peaks at 876 and 1,438 cm^{-1} assigned to carbonate anions substituted for phosphate ions in the apatite lattice [16]. Similar data have been reported for fish scale of *Pagrus major* [22]. Three absorption bands attributed to amides I, II, and III [16, 23] were observed at 1,648, 1,566, and 1,250 cm^{-1}, respectively. These results indicate that the fish scale is a composite material consisting of type I collagen and calcium-deficient apatite-containing carbonate ions.

Distinction between FTIR of pure scale and the scales with adsorbed dyes are observed. Significant decrease in intensity

of the peaks at 3,400 cm^{-1}, 60.0 cm^{-1}, 1,036 cm^{-1}, and 876 cm^{-1} are shown. The peak centered around 1,438 cm^{-1} in FTIR of pure scale became narrower and was dislocated to 1,444 cm^{-1}, suggesting that the hydroxyl, phosphate and carbonate groups are the potential sites of adsorption. In addition, changes in the vibrational bands due to amides I, II, and III might indicate partial evolvement of these groups in the interactions with the dyes [23].

In Fig. 1, a crossing point was observed by plotting ΔpH (variation of the pH values before and after addition of the scales) versus initial pH values. The pH$_{PZC}$ value for the scales was found to be 6.98. The significance of this kind of plot is that a given material surface will have positive charge at solution pH values less than the PZC and thus be a surface on which anions may adsorb [24]. On the other hand, the surface will have negative charge at solution pH values greater than the PZC and thus be a surface on which cationic species may be adsorbed. It is possible that electrostatic attractions of the sulfonate groups of the dyes with the positive charges of the surface, other interactions with hydroxyl, phosphate, carbonate, and amide groups may be occurring simultaneously.

Calorimetric experiments were carried out using aqueous dyes solutions at pH 4.0, and a positively charged fish scale surface become available therefore leading to greater affinity for anionic dyes. The calorimetric responses are in Fig. 2a–c. Each peak represents the heat produced in relation to initial dye concentration in solution. The areas of the thermal effects Q_r and Q_w were integrated joining two extreme points selected on the curves of the detectable calorimeter signals (Power vs. Time) using the software Setsoft version 1.54 f (Setaram-France). It is observed that the intensity of the peaks significantly increases with the increasing concentration dyes.

Calorimetric procedure was used in order to elucidate the thermodynamic features for interactions of the anionic

Table 1 Band assignment of the FTIR spectrum of the Piau scale

| Absorption frequency/cm^{-1}	Attribution
600	Phosphate groups of hydroxyapatite
876	Carbonate anions in the hydroxyapatite lattice
1,036	Phosphate groups of hydroxyapatite
1,250	Amide III of collagen polymeric structure
1,438	Carbonate anions in the apatite lattice
1,566	Amide II of collagen polymeric structure
1,648	Amide I of collagen polymeric structure
3,400	N–H and O–H groups of collagen and hydroxyapatite
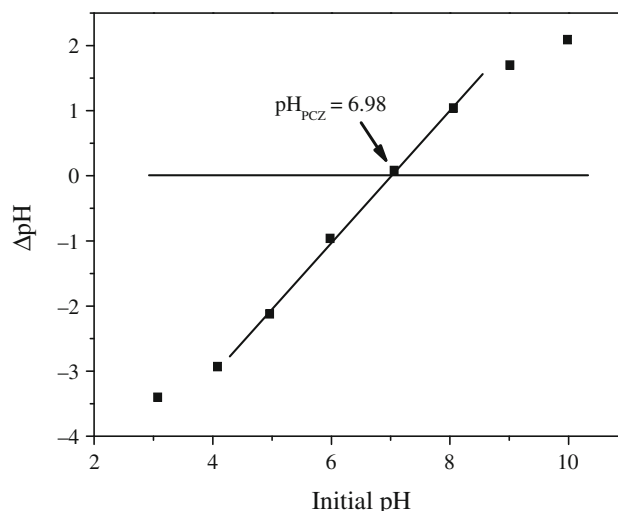
Fig. 1 Variation of pH values before and after addition of the scale versus initial pH values

dyes with scales. Interactions energies originating from the interaction of the dyes with the scales, $Q_{int} = Q_r - Q_w$, were calculated with both Q_r and Q_w normalised for 1 g of material. Adsorption results were analyzed in terms of the Langmuir isotherm model [25]. The following linearized form equations were used for this purpose:

$$\frac{C_{eq}}{n_{int}} = \frac{1}{b_L N_{mon}} + \frac{C_{eq}}{N_{mon}} \qquad (1)$$

$$\frac{C_{eq}}{Q_{int}} = \frac{1}{K Q_{mon}} + \frac{C_{eq}}{Q_{mon}} \qquad (2)$$

In Eqs. 1 and 2, N_{mon} is the maximum adsorption capacity to form a monolayer, Q_{mon} is the energy of interaction for a saturated monolayer per gram of material, b_L and K are parameters of affinity that include the equilibrium constant. Plots of C_{eq}/n_{int} against C_{eq} and C_{eq}/Q_{int} against C_{eq} give straight lines, the slopes and intercepts of which correspond to N_{mon} or Q_{mon} and b_L or K, respectively. The applicability of the Langmuir model to the adsorption data is made by the calculations of the theoretical n_{int} and Q_{int} values, from the values of C_{eq}, N_{mon}, Q_{mon}, b_L and K (Eqs. 3, 4). The good agreements of the experimental and calculated values, as can be seen in Figs. 3 and 4, show that the Langmuir model can be used to explain the adsorption data satisfactorily.

$$n_{int(teor)} = \frac{N_{mon} b_L C_{eq}}{1 + b_L C_{eq}} \qquad (3)$$

Fig. 3 Experimental and calculated values of thermal effects, Q_{int}, for (a) RY/scale, (b) RR/scale, and (c) RB/scale interaction processes. Dotted lines represent the calculated values
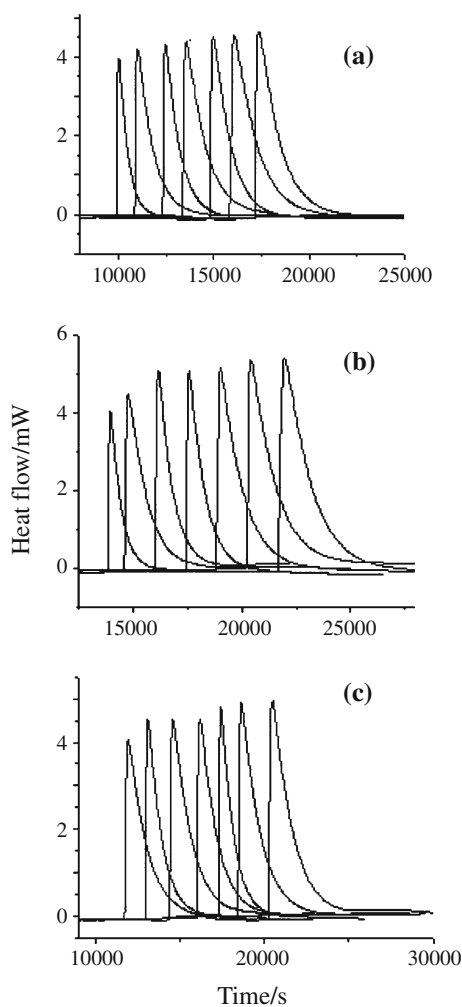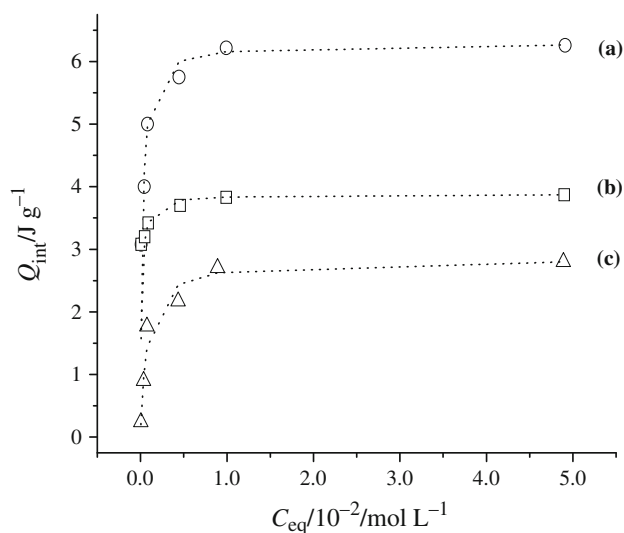

Fig. 2 Calorimetric plots for the interaction processes of: a RB/scale, b RY/scale and c RR/scale at 298.15 K. The first peak from left to right side concerns to wetting effect, Q_w, and the others are due to Q_r effects from the lower to the higher concentrations
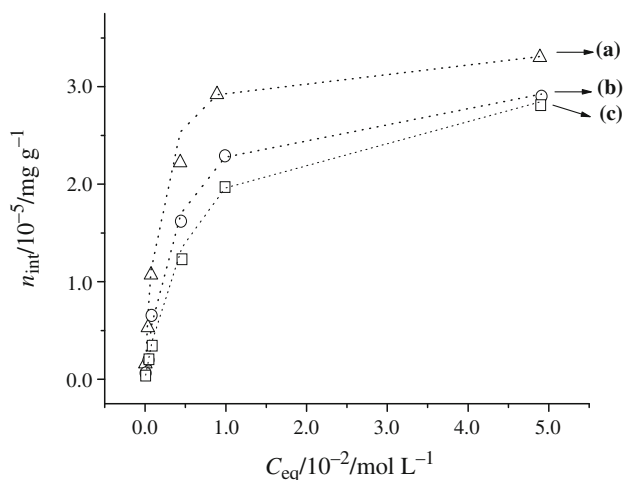

Fig. 4 Experimental and calculated values of amount of dye that interacts, n_{int}, for (a) RB/scale, (b) RY/scale, and (c) RR/scale. Dotted lines represent the calculated values

Table 2 Results of interaction for a saturated monolayer per gram of material, Q_{mon}, maximum adsorption capacity to form a monolayer, N_{mon}, and thermodynamic parameters of the interaction processes dyes/scale at 298.15 K

Interaction processes	$-Q_{mon}$/J g^{-1}	N_{mon}/μmol g^{-1}	$-\Delta_{mon}H_m$/kJ mol^{-1}	$-\Delta_{mon}G$/kJ mol^{-1}	$-\Delta_{mon}S$/J K^{-1} mol^{-1}
RB/SCALE	2.84	0.341	83.28	17.92	219.22
RY/SCALE	6.29	0.315	199.68	20.97	599.40
RR/SCALE	3.88	0.321	120.87	22.48	330.00

$$Q_{int(teor)} = \frac{Q_{mon}KC_{eq}}{1 + KC_{eq}} \tag{4}$$

From knowledge of N_{mon} and Q_{mon} values, the molar enthalpy of interactions dyes/scales for formation of a monolayer, $\Delta_{mon}H_m$, was directly obtained by means of the expression:

$$\Delta_{mon}H_m = \frac{Q_{mon}}{N_{mon}} \tag{5}$$

Other thermodynamic parameters of the interaction process including free energy ($\Delta_{mon}G$) and entropy ($\Delta_{mon}S$) were determined from K:

$$\Delta_{mon}G = -RT \ln K \tag{6}$$

$$\Delta_{mon}S = \frac{\Delta_{mon}H_m - \Delta_{mon}G}{T} \tag{7}$$

where R is the gas constant (8.314 J/mol K), and T is the thermodynamic temperature (298.15 K).

The results are shown in Table 2. The negative values of molar enthalpy of interactions dyes/scales for formation of a monolayer, $\Delta_{mon}H_m$, indicated that the processes are exothermic in nature which lie in a range −83 to −199 kJ mol^{-1} and decrease in the order RY/scale > RR/scale > RB/scale. The magnitude of $\Delta_{mon}H_m$ increased as the dye adsorption is increased. This increase in $\Delta_{mon}H_m$ has been attributed to repulsive lateral interactions between adsorbed molecules; these repulsive interactions increased in magnitude as the adsorption increased [26]. At higher loading, repulsive lateral interactions between the adsorbed species might increase, decreasing the exothermic net heat of sorption at higher loadings.

The enthalpies of dyes adsorption on scales are highly exothermic, and interaction energies (Q_{int}) decrease as initial dye concentration in solution 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 [27]. At low dye concentration, the dye adsorption involves the higher energy surface sites. As the dye concentration in solution 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 [27]. In general, the sorption enthalpy at solid/solution interfaces is an average result of chemical bonding (exothermic) and diffusional (endothermic) processes [28]. Typically, interactions that occur with intense adsorbate diffusion present small and relatively similar values of $\Delta_{mon}H_m$. 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 [29].

The exothermicity observed implies that ionic interactions make a major contribution and possible hydrophobic or hydration effects are not more important on dyes binding scale surface [30]. A compensation effect was observed between $\Delta_{mon}H_m$ and $\Delta_{mon}S$: while the adsorption of the anionic dyes was exothermic, the entropic contribution was unfavorable. The negative $\Delta_{mon}S$ values correspond to a decrease in the degree of freedom of the adsorbed species. So, the adsorption of dyes on scale is supposed to be physical in nature involving non-covalent forces of attraction [31]. The negative $\Delta_{mon}G$ values are indicative of the spontaneous nature of the interaction processes.

From the calorimetric data, it is established that scales may be used for stable bonding of anionic dyes. The experiments were carried out at pH lower the pH$_{PZC}$ of the material, thus surface positive charges enhance electrostatic attractions fish scale/anionic dyes. So, negative interaction energy values are obtained, since it is not necessary absorption energy to overcome electrostatic repulsion effect [32, 33].

This study may become attractive to characterize energetic aspects of adsorption process at solid/solution interfaces.

Conclusions

In this work, scales of Brazilian Piau fish were characterized and used for adsorption of anionic dyes from aqueous solutions in an isothermal calorimetric cell. The FTIR spectra of Piau scales, before and after dyes adsorption, suggest that the hydroxyl, phosphate, amides I, II, and III,

and carbonate groups are the potential sites of adsorption. The adsorption order observed was Yellow dye/scale > Red dye/scale > Blue dye/scale. The adsorption data were successful modeled to the Langmuir adsorption model. The exothermicity of the adsorption systems suggests ionic interactions as a major contribution. The thermodynamic results suggest that the interactions at scale/anionic dye interfaces occur mainly by surface reactions.

The results suggested that Piau fish scale is a new and suitable sorbent material for recovery and biosorption/adsorption of anionic dyes from aqueous solutions.

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