



The effect of pH in the adsorption of Alizarin and Eriochrome Blue Black R onto iron oxides

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ABSTRACT

The adsorption process of two dyes as a function of pH on three different adsorbents (goethite, Co-goethite, and magnetite) has been analyzed. Typical anionic adsorption behavior was observed for both dyes onto goethite and Co-goethite. The adsorption level was practically constant in the range of pH studied when the adsorbent was magnetite. The constant capacitance model (CCM) was employed to fit the experimental results. The surface complexes proposed from the adsorption data were in agreement with the patterns obtained from FTIR spectroscopy and a molecular mechanics calculation. Goethite has very good performance as adsorbent of Alizarin and Eriochrome Blue Black R. The presence of a foreign cation in Co-goethite does not improve the adsorption abilities of goethite. At low pH, the amounts of Alizarin and Eriochrome Blue Black R adsorbed on goethite and Co-goethite are similar. However, a higher dependence with the increase of pH is observed by Eriochrome Blue Black R. On magnetite, the dye adsorption shows less affinity for both dyes. Electronic and steric considerations can explain the trends found in the adsorption of the two dyes on the three iron oxides studied in this work.

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1. Introduction

Synthetic dyes are extensively used in many fields of up-to-date technology. The more common chemical classes of dyes employed at industrial scale are the azo, anthraquinone, sulfur, triphenylmethyl, indigoid, and phthalocyanine derivatives. Because of their commercial importance, the impact [1] and toxicity [2,3] the dyes released in the environment have been extensively studied. The adsorption often uses as a method of treatment of aqueous solutions to remove dissolved contaminating organic compounds. The adsorption processes provide an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available. Mall et al. [4] and Bailey et al. [5] presented a critical review of low-cost adsorbents for wastewater treatment.

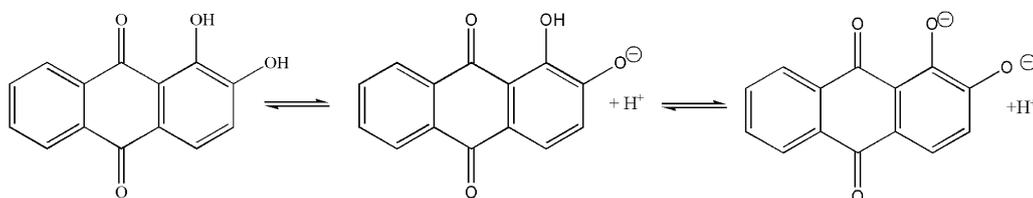
The surface properties of iron oxides are widely known. The adsorption ability of the iron oxides arises from the intervention of hydroxyl groups during dissociative chemisorption of the adsorbate [6]. In aqueous systems, the surface of these oxides coordinates with hydroxyl ions or water molecules, which share their lone electron pairs with Fe. Upon adsorption, the water molecules usually dissociate resulting in a surface covered by hydroxyl groups. The surface hydroxyl groups – with amphoteric properties – are the

functional groups of iron oxides and they are the chemically reactive entities at the surface of the solid. These hydroxyl groups may be singly, double and triply coordinated to Fe atoms having different reactivity. The overall density of these groups depends on both the crystal structure and the extent of development of the different crystal faces and is different for different oxides.

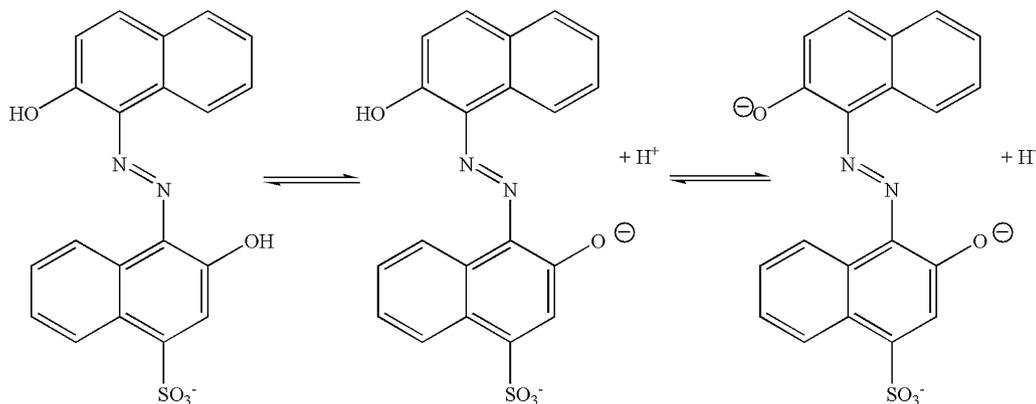
The solution pH affects the surface charge of the adsorbents as well as the degree of ionization of the materials present in the solution. The hydrogen and hydroxyl ions are adsorbed quite strongly, and therefore, the adsorption of other ions is affected by the pH of the solution. The change of pH affects the adsorptive process through dissociation of functional groups on the active sites of the adsorbent. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of the adsorption process. The surface adsorbs anions favorably at lower pH due to the presence of H⁺ ions, whereas the surface is active for the adsorption of cations at higher pH due to the excess of OH⁻ groups [7].

In a previous manuscript [8], we explored the efficiency of the iron oxides to remove synthetic dyes from aqueous solutions as a function of initial dye concentrations and the contact time on adsorption process. The goal of the present work is to study the effect of pH on the adsorption efficiency, looking at the adsorption process as a function of pH of two dyes with anthraquinone and azo groups (Alizarin and Eriochrome Blue Black R, respectively) onto three different adsorbents (goethite, Co-goethite and magnetite). FTIR spectra were obtained monitoring the changes of the

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Scheme 1. Alizarin structures depending on pH.



Scheme 2. Eriochrome Blue Black R structures depending on pH.

vibrational bands of the adsorbed dyes on the oxides at different solution's pH.

Alizarin has been extensively employed since ancient times for dyeing textile materials [9]. The adsorption of Alizarin has been studied on organic clays and mesoporous silica and hybrid gels, between other adsorbents [10,11].

Eriochrome Blue Black R is an azo dye. Most of the azo dye compounds are resistant to bacterial activity. Biological treatment alone cannot be used to remove them from effluents within acceptable times [12]. The results obtained here may transfer to other dyes with a similar chemical structure. Several researches on azo dyes (with sulfonic groups) adsorption, mainly on carbon [13,14] to wastewater treatment have been published but practical problems are common (recovery and efficiency).

The surface properties of goethite are well known. The presence of a foreign cation in the goethite structure can modify the properties of this oxide. We employed goethite and Co-substituted-goethite to search the effect of this substitution in the adsorption behavior. The magnetic properties of magnetite are attractive additional aspects to take into account in the removal of dyes from aqueous solutions (Schemes 1 and 2).

2. Materials and methods

2.1. Materials

The adsorbents used in this work were prepared in our laboratory. Goethite and Co-goethite were synthesized from Fe(III)

salt solutions in alkaline media [15]. Magnetite was obtained by mixing 50 mL $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ 2.6 mol L^{-1} with 600 mL boiling aqueous solution containing 5 mL N_2H_4 at 15%. Then 30 mL NH_3 27% and 50 mL NaNO_3 2 mol L^{-1} were added drop to drop to the system with stirring and heating constants. The suspension boiled during approximately 60 min and cooled at room temperature.

The samples were characterized by chemical analyses and X-ray diffraction. In goethite and Co-goethite only one phase is present; however, in magnetite the appearance of a secondary phase (goethite) is detected (content <3%). The specific surface area of the samples was measured by the classical Brunauer–Elmet–Teller method using a multiple point adsorption nitrogen process (BET-N_2).

Alizarin with a λ_{max} (nm) = 531, and Eriochrome Blue Black R with a λ_{max} (nm) = 527 were the commercial textile dyes used in this study. All reagents used in this study were of an analytical grade. Table 1 lists the chemical characteristics of Alizarin and Eriochrome Blue Black R in aqueous solution.

2.2. Methods

2.2.1. Potentiometric titrations

Acid–base titrations were employed to determine surface site density. As the surface sites ($\equiv\text{FeOH}$) are amphoteric, they can be either the protonated form ($\equiv\text{FeOH}_2^+$) or the deprotonated form ($\equiv\text{FeO}^-$). Acid–base titrations of the surface provide concentration of protonated and deprotonated sites, which can then lead to the sites density [19]. $\equiv\text{FeOH}$, $\equiv\text{FeOH}_2^+$ and $\equiv\text{FeO}^-$ represent functional

Table 1
Chemical characteristics of Alizarin and Eriochrome Blue Black R in aqueous solution.

Chemical formula	Molecular weight (g mol^{-1})	Acidity constants		
		$\text{p}K_{\text{a}1}$	$\text{p}K_{\text{a}2}$	$\text{p}K_{\text{a}3}$
Alizarin ($\text{C}_{14}\text{H}_8\text{O}_4$)	240	5.25 ^a	11.50 ^a	–
Eriochrome Blue Black R ($\text{C}_{20}\text{H}_{14}\text{O}_5\text{SN}_2$)	394	1.00 ^b	7.31 ^c	13.80 ^c

^a Ref. [9].

^b Refs. [16,17].

^c Ref. [18].

Table 2
Surface sites density, surface acidity constants, specific surface area and total specific capacitance for the iron oxides used.

Oxide	Acidity constants		BET surface area (m ² g ⁻¹)	Site density (sites nm ⁻²)	Total specific capacitance (F m ⁻²)
	Log K ₁	Log K ₂			
Goethite	8.2	-10.0	68.8	1.7	4
Co-goethite	6.4	-10.0	56.1	1.7	4
Magnetite	4.4	-9.00	41.7	2.7	5

neutral groups, positively charged and negatively charged on the solid surface.

Potentiometric titrations of aqueous suspensions of iron oxides (3 g L⁻¹) were carried out under N₂ atmosphere with magnetic stirring, with a Metrohm E536 potentiograph equipped with a combined electrode. Small aliquots of either base or acid (NaOH or HCl) 0.1 mol L⁻¹ were added every 10 min.

Table 2 shows the values of surface sites density, surface acidity constants, specific surface area and total specific capacitance.

2.2.2. Adsorption measurements

The solution pH values ranged from 3 to 11. A known amount of each oxide (50 mg of goethite and Co-goethite, and 100 mg of magnetite) was added to 25 mL of dye solution. The initial dye concentration used for each adsorbent were selected on the base of the adsorption isotherms [8]. The pH was adjusted by the addition of HCl or NaOH. The ionic strength was kept constant with 0.05 mol L⁻¹ NaCl. After 2 h of equilibration period, aliquots were removed from the suspension and filtered. The quantity of each dye adsorbed onto iron oxides was determined spectrophotometrically and subtracted from the initial concentration to determine the adsorbed amount.

2.2.3. Infrared (IR) spectroscopy analysis

FTIR spectra of the solid samples dispersed in KBr disks were obtained to analyze the interaction between dyes and the different iron oxides at the oxidic surfaces. Oxide samples with the adsorbed dye were filtered from the test solution, washed several times with bidistilled water, dried in air, and diluted in KBr at 1:40 ratio. FTIR spectra of Alizarin, Eriochrome Blue Black R, goethite, Co-goethite and magnetite were also obtained using the KBr method. The ratio of sample to KBr was 1:100 for pure dyes and oxides.

2.2.4. Treatment of adsorption data

MINEQL⁺, Version 4.0, was employed in this work to model the adsorption of Alizarin and Eriochrome Blue Black R on the iron oxides in aqueous solution in the pH range 3–11. The constant capacitance model (CCM), widely explained in other works, was used to account for the surface charge effects on adsorption for all systems [20,21]. Table 3 lists the reactions used for modeling the dyes complexation on oxides surfaces and the corresponding surface constants.

Table 3
Equilibrium constants describing the adsorption of Alizarin and Eriochrome Blue Black R complexes onto goethite, Co-goethite and magnetite fitted by MINEQL⁺ (0.05 mol L⁻¹ NaCl, 298 K).

Surface complexation reactions	Log K		
	Goethite	Co-goethite	Magnetite
(1) ≡X + A ²⁻ ⇌ ≡X - A ²⁻	15.45	15.60	14.52
(2) ≡X + A ²⁻ + H ⁺ ⇌ ≡X - AH ⁻	23.50	21.85	19.70
(3) ≡X + A ²⁻ + 2H ⁺ ⇌ ≡X - AH ₂	27.57	23.00	22.80
(4) ≡X + E ²⁻ ⇌ ≡X - E ²⁻	17.00	17.00	16.75
(5) ≡X + E ²⁻ + H ⁺ ⇌ ≡X - EH ⁻	25.20	24.83	23.80
(6) ≡X + E ²⁻ + 2H ⁺ ⇌ ≡X - EH ₂	32.20	30.28	27.40

A: Alizarin; E: Eriochrome Blue Black R; ≡X: represents a surface site (≡FeOH₂⁺, ≡FeOH, or ≡FeO⁻).

2.2.5. Theoretical section

2.2.5.1. *The program.* The software MM2 from the Package included in Chem3D ultra5.0 from Cambridge Soft was used to model the goethite and magnetite surface. The goal was to test steric effects of the surfaces–dyes interaction therefore ab initio electronic characteristics were not included in the parameterization. However, there are possibilities of modeling the van der Waals interactions through dipole–dipole interactions.

The group of Liapis et al. [22] has reported the results of the study of the conformation and lateral mobility of a charged adsorbed

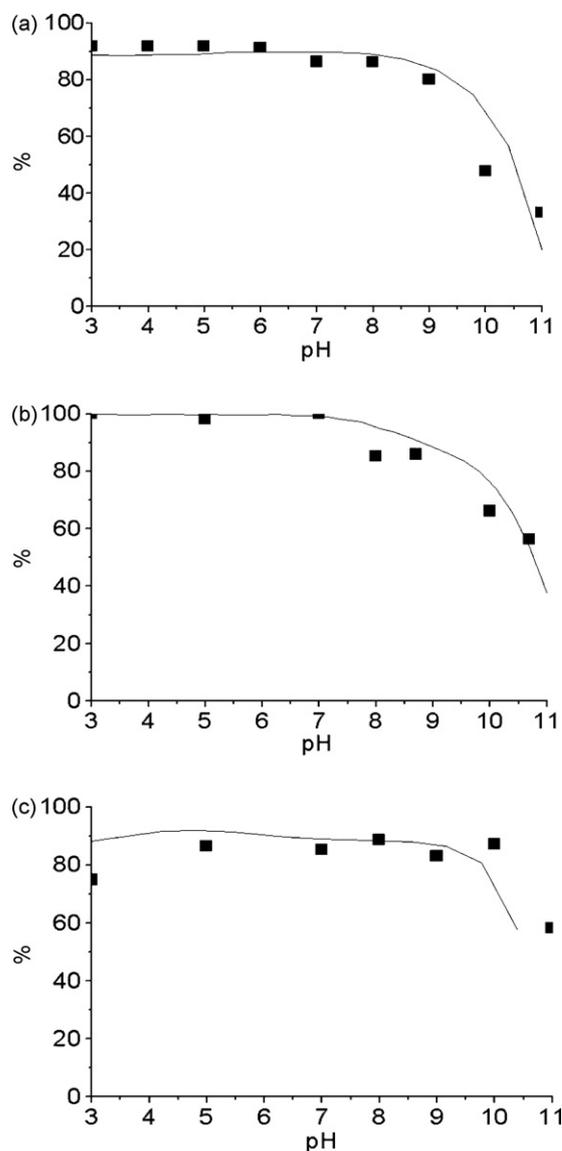


Fig. 1. Adsorption-edge of Alizarin as a function of pH and $I=0.05$ mol L⁻¹. (a) Goethite = 2 g L⁻¹, initial dye concentration = 4.17×10^{-4} mol L⁻¹; (b) Co-goethite = 2 g L⁻¹, initial dye concentration = 3.13×10^{-4} mol L⁻¹; (c) magnetite = 4 g L⁻¹, initial dye concentration = 3.13×10^{-4} mol L⁻¹. (■) Experimental data; (—) theoretical total.

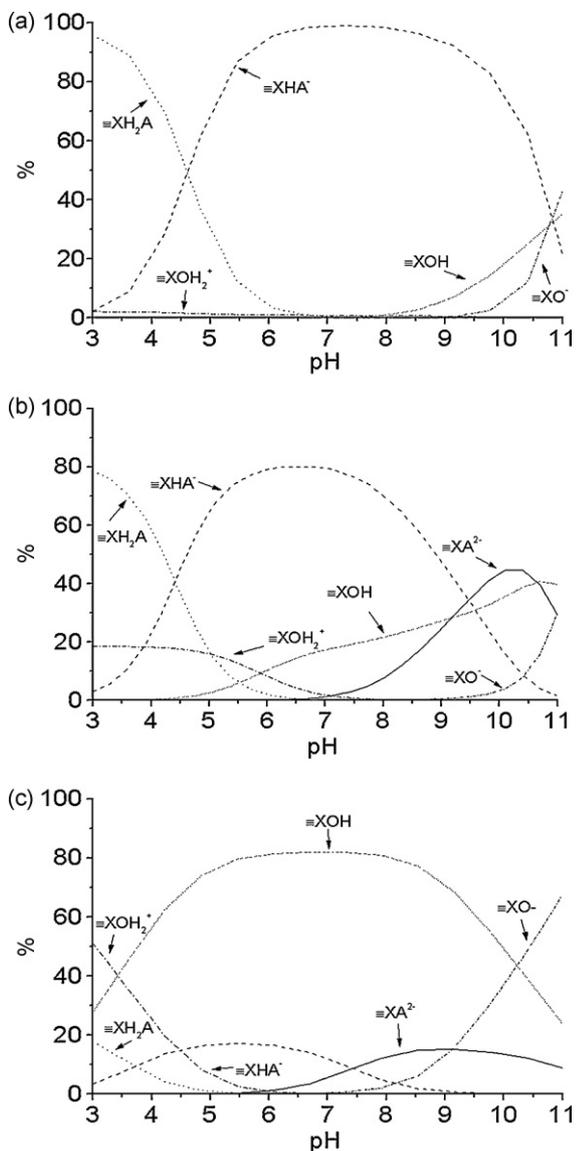


Fig. 2. Surface complexes as a function of pH. (a) Goethite: total concentration of surface sites = $3.8 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{A}^{2-}] = 4.17 \times 10^{-4} \text{ mol L}^{-1}$; (b) Co-goethite: total concentration of surface sites = $3.8 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{A}^{2-}] = 3.13 \times 10^{-4} \text{ mol L}^{-1}$; (c) magnetite: total concentration of surface sites = $7.5 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{A}^{2-}] = 3.13 \times 10^{-4} \text{ mol L}^{-1}$.

biomolecule. Other authors include the molecular mechanics or dynamics calculation as an additional tool of characterization, many times of limited value in quantitative aspects but very useful in terms of visualization of the best adsorption forms considering a charged surface [12]. Molecular dynamics studies, such as the ones cited in Ref. [22], have different goals and are related to diffusion processes, where the water should be explicitly considered [23,24]. The main point was the local dissociation of water on the surface, giving rise to a dipolar surface in the case of magnetite but not in the case of goethite. Zhang et al. [25] used CAChe system taken into account the [100] crystalline face of $\alpha\text{-Fe}_2\text{O}_3$. Only the geometry of the adsorbate was optimized in the calculation using the energy gradient method. We consider the local interaction of surface charged species with the dye.

2.2.5.2. The surface complexation models. Goethite ($\alpha\text{-FeOOH}$) is usually described using the $P6mm$ group. The structure of this oxyhydroxide consists of double rows or ribbons of edges having Fe octahedra that run parallel to [001]; these double rows are sepa-

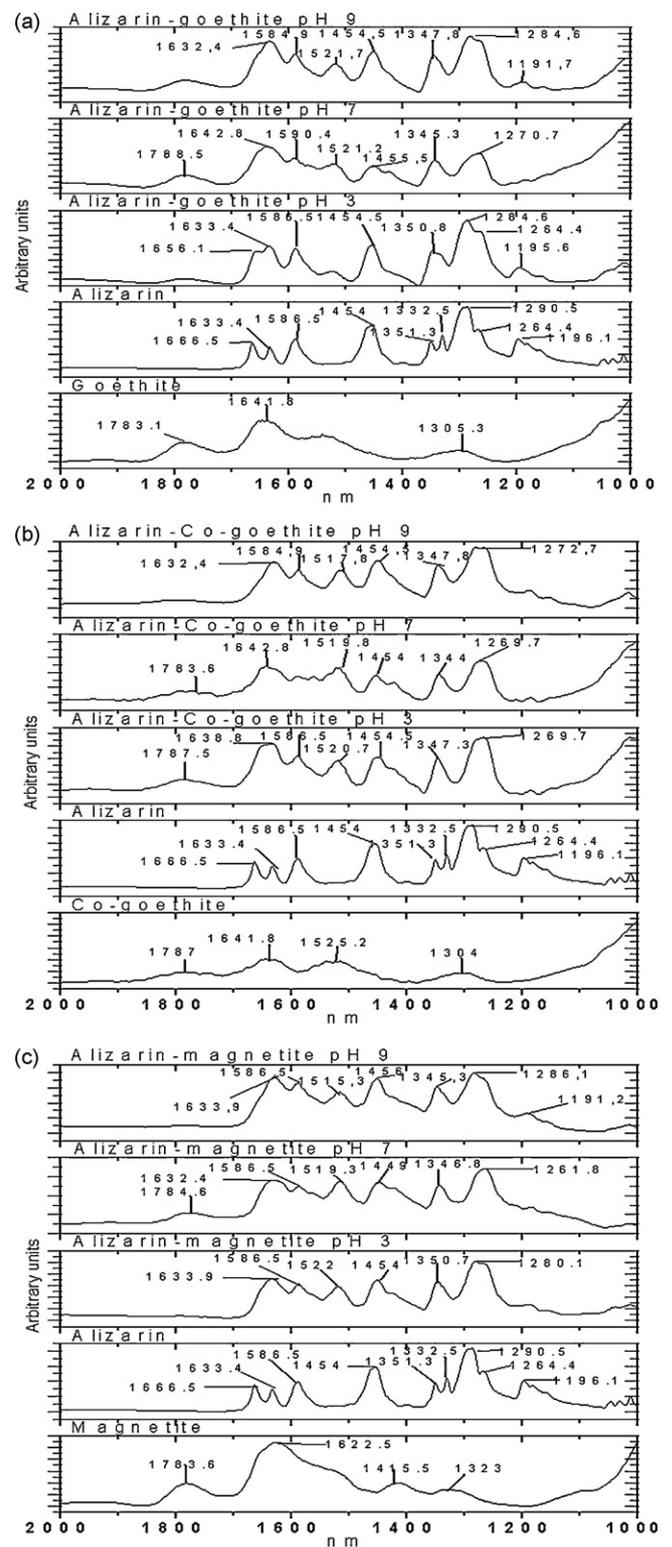


Fig. 3. (a–c) FTIR spectra of Alizarin on the three adsorbents at pH 3, 7 and 9.

rated by vacant double rows of channels that also run along [001]. The double rows are formed by polyhedra that share two hydroxide groups. In general, the distance Fe–Fe varies between 2.9 and 3.4 Å.

Magnetite (Fe_3O_4) has the spinel (MgAl_2O_4) structure, with a cubic closely packed oxygen array, and iron in both fourfold and sixfold coordination. Magnetite has the cubic $Fd3m$ space group. In general, the Fe–Fe distance varies between 3.89 and 3.21 Å.

Table 4
Steric energies differences for the adsorption of Alizarin on magnetite and goethite models (in kcal mol⁻¹).

Adsorbent	Alizarin		
	Neutral	Ionized OH ⁻¹	Ionized OH ⁻¹ , ionized OH ⁻²
Magnetite, neutral pH 6.8	0	-392.5	-341.4
Magnetite, protoned pH <6.8	0	-711	-641.9
Magnetite, alkoxide pH >6.8	0	-620	-554
Goethite, neutral pH 9.1	0	-45.6	-79.1
Goethite, protoned pH <9.1	0	-67.4	-164.6
Goethite, alkoxide pH >9.1	0	-10.5	+38.7

The surfaces were modeled with all their O as OH (neutral), with one central ionized -OH as O⁻ (negative charge and parameters of alkoxide) and with one central OH protonated as OH₂⁺ (positive charge with O as oxonium). Three different surfaces for each adsorbent model were tested. From the surface acidity constants the distribution of the three types of surfaces sites for each oxide was established and the corresponding PZC were calculated. These values were 6.7 for magnetite, 8.2 for Co-goethite, and 9.1 for goethite. They agree with those reported by other authors [26,27].

The Alizarin was modeled neutral, with one OH ionized and with the two OH ionized. The Eriochrome Blue Black R was modeled with only the SO₂ ionized and with SO₂ ionized and one OH ionized. Three different forms for Alizarin and two different forms for Eriochrome Blue Black R were analyzed.

The results were presented considering the surface and the dye of each other at infinite distance vs. the dye and the surface at bonding/interactions distance plus a minimization of steric energy for each selected form (of the dye and the surface). The steric energy values have no meaning as absolute values, but as relatives ones. They can be comparing in the same group of materials (magnetite, goethite) but not between them.

3. Results and discussion

3.1. Alizarin

3.1.1. Adsorption data

Alizarin is not very soluble in water but soluble in aqueous alkaline solutions in the pH range 7.82–12.87. At pH below 5.2 most Alizarin occurs in the form of yellow-colored undissociated molecules. At pH between 6.8 and 10.1 most Alizarin occurs as red monovalent anions. At pH above 12.1 it dissociates into divalent anions with a bluish violet color [10].

Fig. 1 shows the adsorption edges of Alizarin on goethite, Co-goethite and magnetite as a function of pH at room temperature.

When goethite is the adsorbent, the experimental data show maxima adsorption between pH 3 and 8 (see Fig. 1). At pH above 8 the amount of adsorbed Alizarin decreases following a typical anionic adsorption behavior. In Co-goethite from pH 7 the adsorp-

Table 5
Steric energies for the adsorption of Eriochrome Blue Black R on magnetite and goethite models (in kcal mol⁻¹).

Adsorbent	Eriochrome Blue Black R		
	Neutral	Ionized SO ₃ H	Ionized SO ₃ H, ionized OH
Magnetite, neutral pH 6.8	0	-695	-587
Magnetite, protoned pH <6.8	0	-735	-648
Magnetite, alkoxide pH >6.8	0	-654	-526
Goethite, neutral pH 9.1	0	-35	-38
Goethite, protoned pH <9.1	0	-69	-141
Goethite, alkoxide pH >9.1	0	-8.2	+38

tion level decreases with the increase of pH. The similarity in the adsorption patterns of goethite and Co-goethite may be attributing at the low-substitution level of Fe for Co, which in this case it is only of the 5.5%. Magnetite exhibits the lowest affinity for this dye and there is a little effect of the pH in the adsorption process. Since the adsorption experiences with magnetite carried out at low-surface covering (dye concentration/surface sites ratio lower than in goethite and Co-goethite) there is an excess of surface sites. In this way, the dye accounts with enough active sites in all the pH range to join at the surface.

Applying the CCM, a good fit with the experimental data was obtained for the adsorption of Alizarin on goethite and Co-goethite. For magnetite, the model slightly underestimates the experimental results at the higher pH.

To understand the adsorbate-adsorbent interaction, Fig. 2 shows the fractions of the different surface species as a function of pH. When the adsorbent is goethite the dominant species are: ≡XH₂A at low pH; ≡XHA⁻ in the pH range 4.5–11; and in these conditions

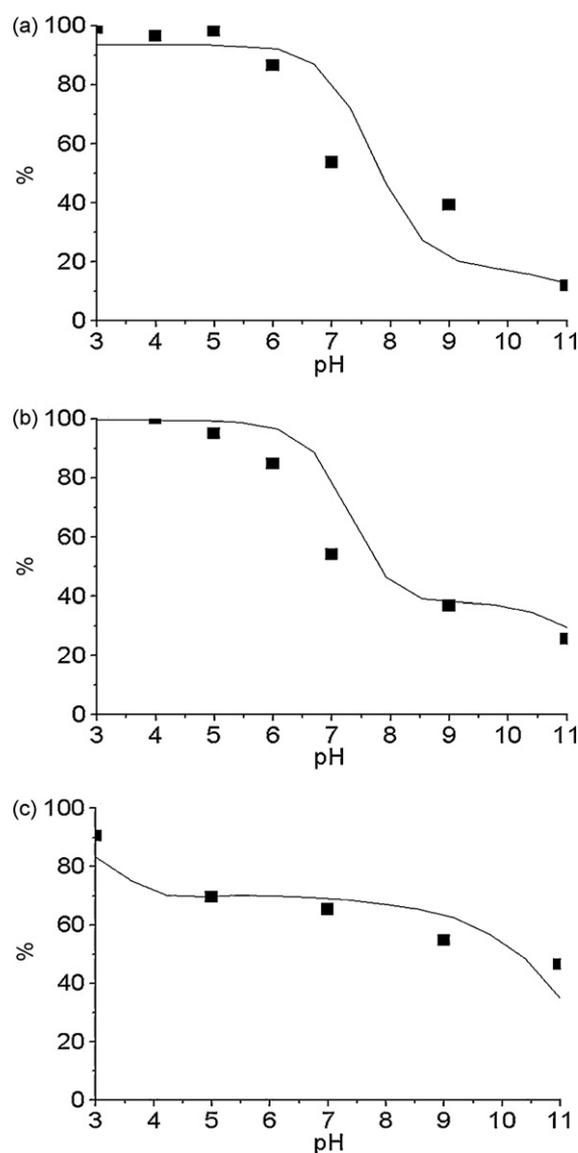


Fig. 4. Adsorption-edge of Eriochrome Blue Black R as a function of pH and $I = 0.05 \text{ mol L}^{-1}$. (a) goethite = 2 g L^{-1} , initial dye concentration = $1.9 \times 10^{-4} \text{ mol L}^{-1}$; (b) Co-goethite = 2 g L^{-1} , initial dye concentration = $2.50 \times 10^{-4} \text{ mol L}^{-1}$; (c) magnetite = 4 g L^{-1} , initial dye concentration = $2.50 \times 10^{-4} \text{ mol L}^{-1}$. (■) Experimental data; (—) theoretical total.

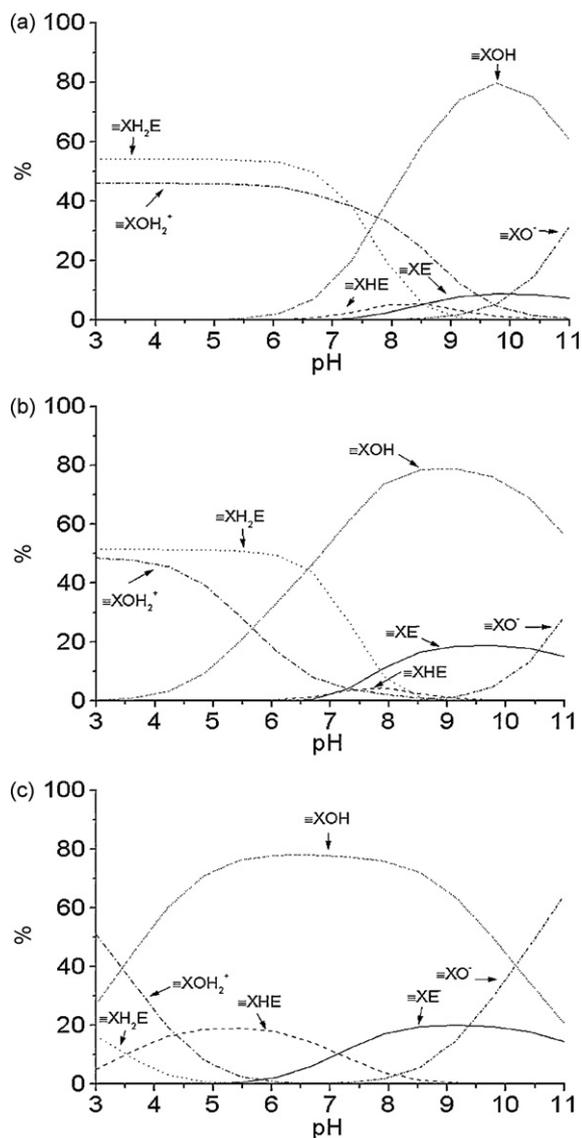


Fig. 5. Surface complexes as a function of pH. (a) Goethite: total concentration of surface sites = $3.8 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{E}^{2-}] = 1.90 \times 10^{-4} \text{ mol L}^{-1}$; (b) Co-goethite: total concentration of surface sites = $3.8 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{E}^{2-}] = 2.50 \times 10^{-4} \text{ mol L}^{-1}$; (c) magnetite: total concentration of surface sites = $7.5 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{E}^{2-}] = 2.50 \times 10^{-4} \text{ mol L}^{-1}$.

$\equiv\text{XA}^{2-}$ is not detectable in this pH range. In Co-goethite $\equiv\text{XH}_2\text{A}$ species distribution is similar to goethite, while $\equiv\text{XHA}^-$ species predominates between pH range 4.5 and 9.5 and above pH 9.5 $\equiv\text{XA}^{2-}$ is the predominant species. In magnetite is evident a lower surface covering since, in all the pH range the bare surface sites prevail. On the other hand, the low impact of the $\equiv\text{XH}_2\text{A}$ species is well manifest.

According to the pK_a values for Alizarin, up to pH 5.25 the non-dissociated species prevails. At the same pH range, the surface species $\equiv\text{FeOH}_2^+$ is the predominant. Cañamares et al. [9] proposed that Alizarin is always ionized on the silver metal surface, even at the lower pH. Besides, the deprotonation order of the OH groups of Alizarin changes on the surface with respect to the aqueous solution: the OH in position 1 is the first to be ionized instead of that in position 2 as occurs in the solution. This ionization leads to a large electronic delocalization in the aromatic moiety.

Alizarin forms aggregates at pH below 7.8. Aggregation may also occur on the adsorbate surface. Venkata and Sarthy [28] argued

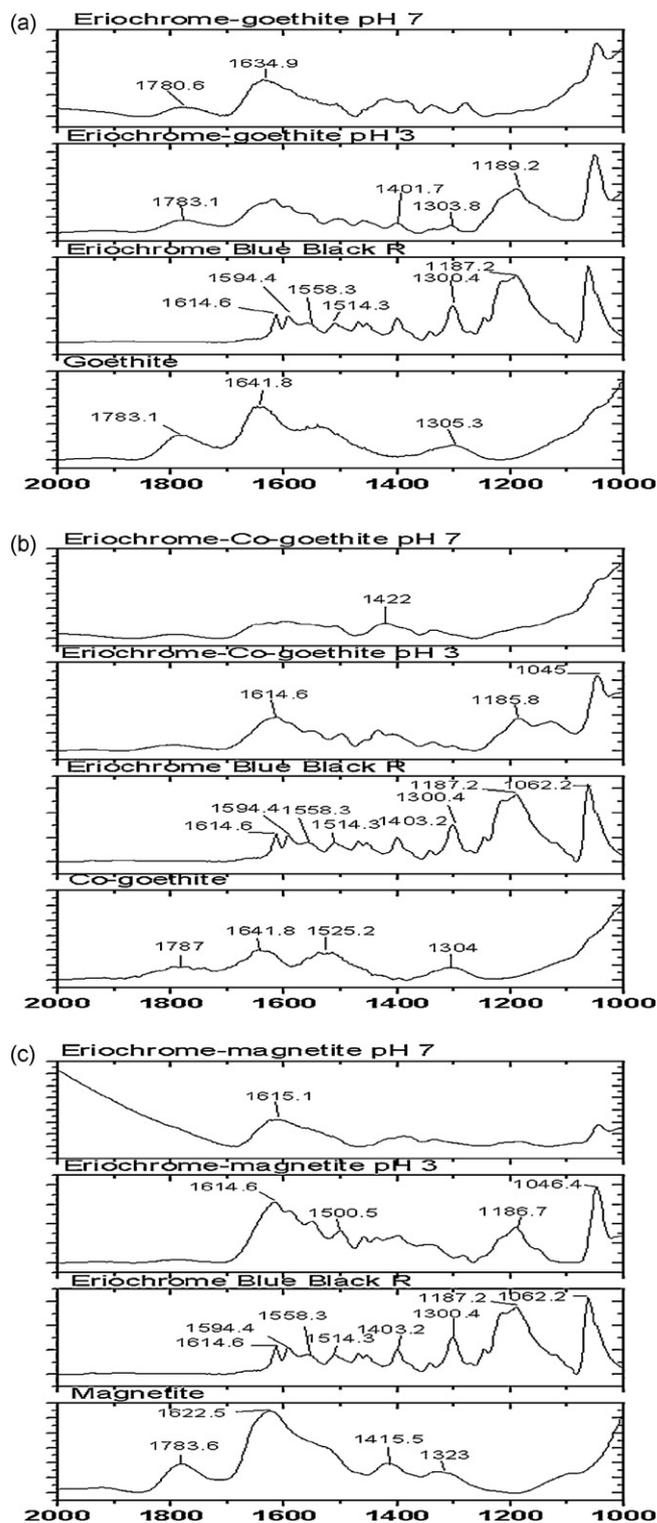
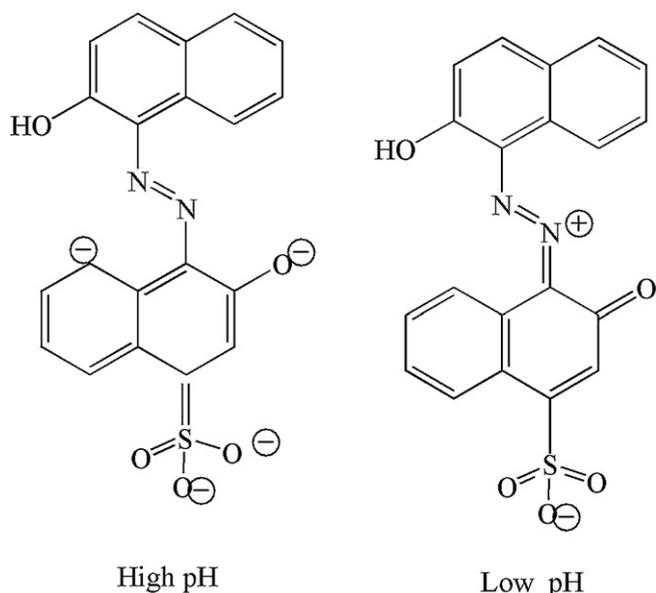


Fig. 6. (a–c) FTIR spectra of Eriochrome Blue Black R on the three adsorbents at pH 3 and 7.

that when aggregation occurs, each dye particle behaves as a single molecule of the dye. Other authors considered aggregates of three or four molecules to model the adsorption of organic dyes molecules to kaolinite [29]. Harris et al. [30] to usefully fitting the experimental data proposed in the case of cationic dyes a purely hydrophobic adsorption of aggregates to the silica face of kaolinite as the predominant mechanism at low pH. However, with the experimental conditions used in this work a good fit with the exper-



Scheme 3. The most probable species of Eriochrome Blue Black R at low- and high-pH values.

imental data could be obtained considering mononuclear surface complexes with single dye molecules. These results suggest a possible disaggregation by the dye-adsorbent interaction although the adsorption as aggregates cannot be discarded [31].

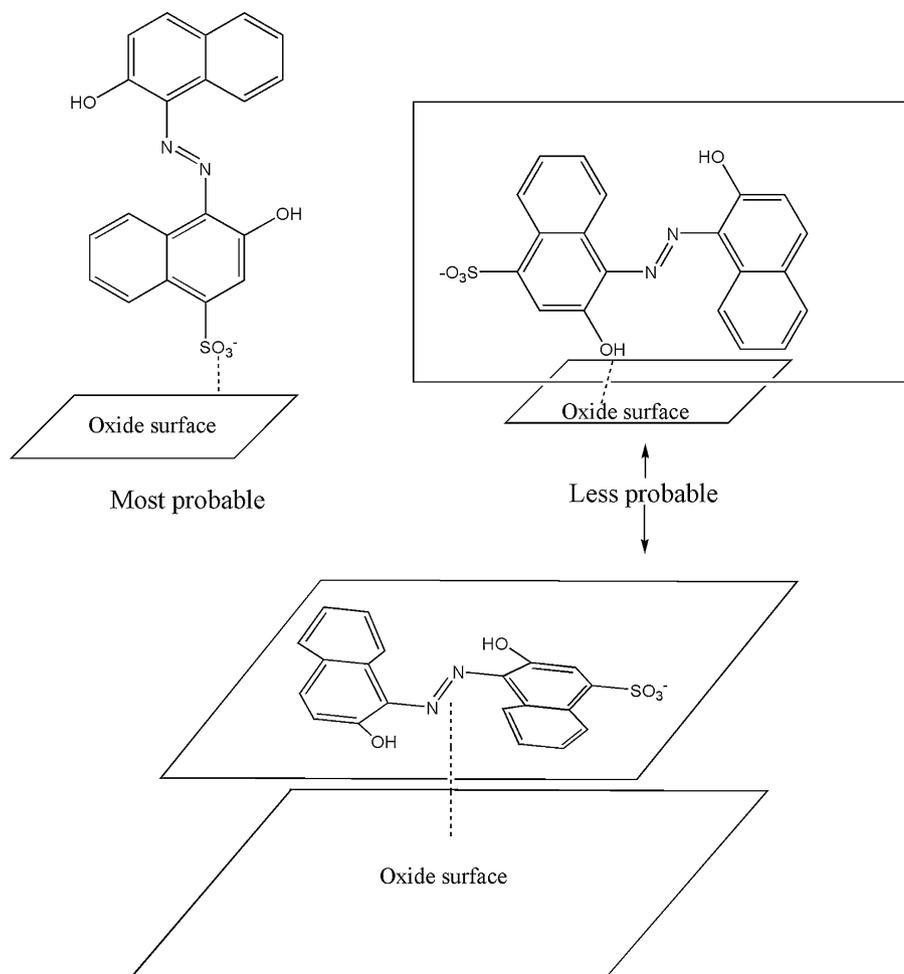
3.1.2. FTIR spectroscopy

Fig. 3 shows the FTIR spectra for Alizarin adsorbed on goethite, Co-goethite and magnetite at pH 3, 7 and 9.

The characteristic bands of Alizarin are $\nu(10\text{-C=O})$, 1666.5 cm^{-1} ; $\nu(9\text{-C=O})$, 1633.4 cm^{-1} ; $\nu(\text{Ar C=C})$, 1586.5 and 1454 cm^{-1} ; $\delta(\text{OH})$, 1351.3 and 1332.5 cm^{-1} ; $\nu(\text{C-O})$, 1290.5 and 1264.4 cm^{-1} and carbonyl C-C-C at 1196.1 cm^{-1} . The bands of $\nu(9\text{-C=O})$ at 1633.4 cm^{-1} and $\nu(10\text{-C=O})$ at 1666.5 cm^{-1} appear separated because of the intramolecular hydrogen bonding between 9-C=O and 1-OH. The band of carbonyl C-C-C at 1196.1 cm^{-1} means stretching and bending modes of three carbons in the Alizarin anthracene skeleton: the center carbon belongs to the 9- or 10-C=O carbon, and the other two carbons belong to both sides of the C=O carbon [32].

Moriguchi et al. [32] on the basis of FTIR results of Alizarin Red S (ARS) adsorbed on hydroxyapatite (HAP) proposed two possible structures: salt form and a chelate form. The salt form presents the bonding of the two vicinal phenolate ions 1-, 2-O⁻ of Alizarin on the solid surface, while in the chelate form, a chelation consisting of 1-O⁻ and 9-C=O of Alizarin on two surface sites occurs. In the later form, the 2-OH group remains undissociated and a unique band corresponding to $\delta(\text{OH})$ is observed.

Alizarin on goethite at pH 3 shows two adsorption bands concerned to $\nu(10\text{-C=O})$ and $\nu(9\text{-C=O})$ that appeared at 1656.1 cm^{-1} (that shift towards higher wavelength) and 1633.4 cm^{-1} (without suffer any change). The association of these bands is particularly noticeable. Further two types of bands related to C-O modes at 1-, 2-positions ascribed at $\nu(\text{C-O})$ -1 and $\nu(\text{C-O})$ -2, are present at 1350.8 and 1284.6 cm^{-1} . The band that appears at 1521.2 cm^{-1}



Scheme 4. The most probable species of Eriochrome Blue Black R.

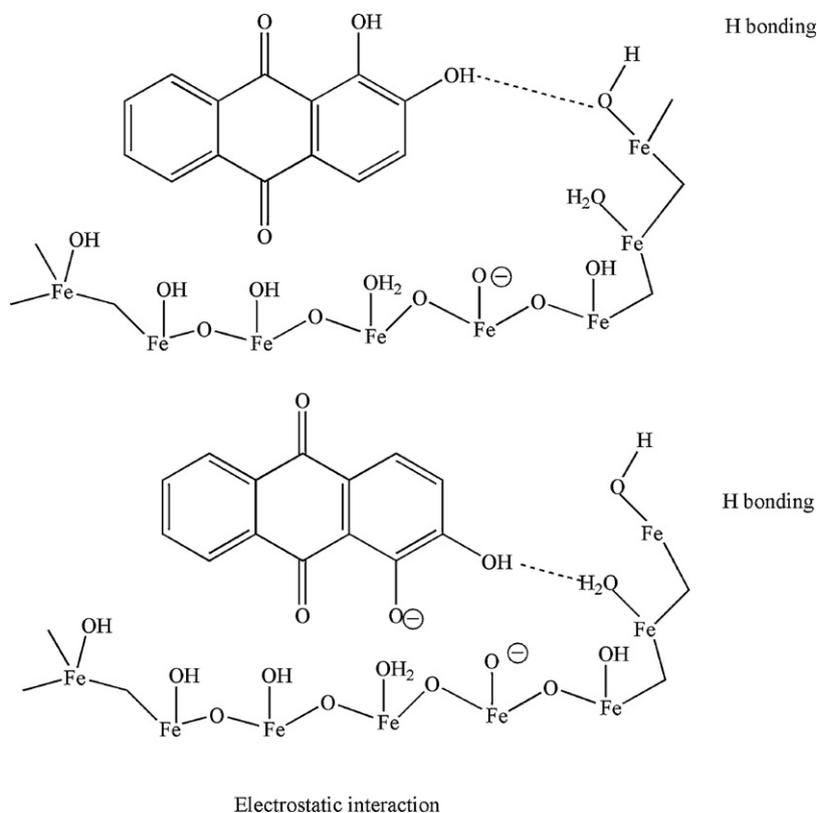


Fig. 7. Electrostatic and hydrogen bonding interactions with different Alizarin structures.

corresponds to $\nu(\text{C}=\text{O})$ coupled with $\nu(\text{C}=\text{C})$ and it is assigned by Moriguchi [32] in the system alizarin Red S and Ca^{2+} of hydroxyapatite at the chelate formation.

At pH 7 the two bands ascribed to $\nu(10\text{-C}=\text{O})$ and $\nu(9\text{-C}=\text{O})$ disappeared and the presence of a single broad band at 1642.8 cm^{-1} is observed. This higher association observed at pH 7 indicates differences in the adsorption pattern of Alizarin at both pH.

The two bands corresponding to $\nu(\text{C}-\text{O})$ -1 and $\nu(\text{C}-\text{O})$ -2 are also present at 1345.3 and 1270.7 cm^{-1} but at lower frequency. The band at 1521.2 cm^{-1} is more evident than at pH 3. The FTIR pattern does not show significant changes with that obtained at pH 7.

On Co-goethite, at pH 3 Alizarin shows a single band assigned to $\nu(\text{C}=\text{O})$ at 1638.8 cm^{-1} . The two bands corresponding to C–O modes at 1-, 2-positions ascribed to $\nu(\text{C}-\text{O})$ -1 and $\nu(\text{C}-\text{O})$ -2, are present at 1347.3 and 1269.7 cm^{-1} . At pH 7 the same pattern is observed. The two bands ascribed to $\nu(10\text{-C}=\text{O})$ and $\nu(9\text{-C}=\text{O})$ are not solved and only a single band at 1642.8 cm^{-1} is present. The corresponding bands of C–O stretching region are registered at 1344 and 1269.7 cm^{-1} . A similar pattern is observed in the FTIR spectrum at pH 9.

FTIR spectra of Alizarin-magnetite at pH 3, 7 and 9 show a similar pattern. The presence of associated broad bands corresponding to $\nu(10\text{-C}=\text{O})$, $\nu(9\text{-C}=\text{O})$ and the bands $\nu(\text{C}-\text{O})$ -1 and $\nu(\text{C}-\text{O})$ -2 can be observed as in the other oxides. The band ascribed at chelate formation also appears. In this oxide the FTIR spectra practically is the same at all studied pH.

Following the assumption by Moriguchi and other authors as cited in [32], we suggest that the appearance of a single $\nu(\text{C}=\text{O})$ band, brightly observed in our work at pH 7 and 9, is not only due to salt formation between 1-, 2- O^- groups of Alizarin and metal of the surface oxide but also due to the occurrence of equivalent electronic resonance between 1-, 2- O^- and 9-, 10-C=O groups. The band at approximately 1520 cm^{-1} present in all the spectra suggests the existence of the chelate form via 1- O^- and 9-C=O of

Alizarin, as an alternative adsorption mechanism. However, the absence of the band ascribed at $\delta(\text{OH})$ in the spectra of Alizarin adsorbed corresponding to the 2-OH group could be suggesting that the salt form is the prevailing. The presence of the band at $\approx 1520\text{ cm}^{-1}$ also could occur by coupled of the fundamental bands in the Alizarin adsorbed even in absence of chelate formation.

3.1.3. Results of the MM2 analysis on Alizarin

For Alizarin, Table 4 shows the results of MM2 calculation for magnetite and goethite, neutral, protonated and with oxygen as alkoxide. In the case of goethite, the neutral surface has lower interaction energy than the protonated one ($-45.6\text{ kcal mol}^{-1}$ vs. $-67.4\text{ kcal mol}^{-1}$). This trend is clear also for the doubled ionized Alizarin ($-79.1\text{ kcal mol}^{-1}$ vs. $-164.6\text{ kcal mol}^{-1}$) being the difference in this case higher. All the neutral compounds are considered the basis of comparison and in this sense the reported value is 0 (Tables 4 and 5).

In the case of magnetite, the values of the steric energies interaction for neutral, protonated and alkoxide forms with Alizarin are very high and favorable. However, the interaction of neutral sites is the less favored. In this way, no clear changes in adsorption with pH would be expecting with these results.

3.2. Eriochrome Blue Black R

3.2.1. Adsorption data

Fig. 4 shows the effect of pH on the affinity of Eriochrome Blue Black R to goethite, Co-goethite and magnetite at room temperature.

The Eriochrome Blue Black R adsorption-edge on goethite and Co-goethite displays typical anionic adsorption behavior. Significant amounts of Eriochrome Blue Black R adsorbed at pH values above the PZC indicate that the chemical contribution at the adsorp-

tion process is important. The total amount of Eriochrome Blue Black R adsorbed on goethite and Co-goethite is very similar.

Fig. 5 shows the surface species distribution for the three oxides with Eriochrome Blue Black R. The species $\equiv\text{XH}_2\text{E}$ prevails on goethite up to pH 7.5, this range decreases in Co-goethite (up to pH 5) and in magnetite, this species only dominates at pH lower than 3.5. This species adsorbs at pH values where the surface displays a positive charge.

3.2.2. FTIR spectra

Fig. 6 shows the FTIR spectra for Eriochrome Blue Black R adsorbed on goethite, Co-goethite and magnetite at pH 3 and 7.

This dye has asymmetrically substituted $-\text{N}=\text{N}-$ bonds with a weak stretching band around $1450\text{--}1500\text{ cm}^{-1}$. Vinodgopal et al. [33] and Bandara et al. [12] assigned the 1514.3 cm^{-1} band to $-\text{N}=\text{N}-$ bond vibrations or to aromatic ring ($\text{C}=\text{C}$) vibrations sensitive to the interaction with azo bonds. The bands at 1558.3 , 1594.4 and 1614.6 cm^{-1} were assigned to $\text{C}=\text{C}$ stretching vibrations. The SO_2 symmetric and asymmetric vibrations were seen at 1187.2 and 1300.4 cm^{-1} , respectively.

After adsorption at pH 7 the symmetric peak at 1187.2 cm^{-1} and the asymmetric peak at 1300.4 cm^{-1} for vibrations of the $-\text{O}-\text{S}-(\text{O}_2)$ group almost disappeared or were very weak for the three iron oxides studied. This suggests the participation of single and double sulfur links $\text{S}-\text{O}$ and $\text{S}=\text{O}$ in the bond formation with the oxide surface. This is indicative that the azo dye adsorption mechanism on all iron oxides is the same at this pH.

At pH 3 FTIR of Eriochrome Blue Black R on goethite shows a strong peak attributed to the SO_2 symmetric vibration at 1189.2 cm^{-1} , and a weak SO_2 asymmetric vibration peak at 1303.8 cm^{-1} . The presence of these bands suggests a different adsorption mode at low pH where the sulfonic group can bond at the surface more weakly. This adsorption probably takes place through O from SO_3^- , without the involvement of the SO_2 group.

de Souza Macedo et al. [34] proposed a relevant adsorption mechanism taking place between the aromatic rings, $-\text{N}=\text{N}-$ and $-\text{N}=\text{C}-\text{C}=\text{C}-$ of Remazol Yellow GR 110 and the surface sites of mesoporous activated carbon.

For Co-goethite, the SO_2 symmetric vibration appeared at 1185.8 cm^{-1} while the asymmetric peak for vibration of the $-\text{O}-\text{S}-(\text{O}_2)$ group almost disappeared. The same pattern is observed for magnetite where the SO_2 symmetric vibration appeared at 1186.7 cm^{-1} . Schemes 3 and 4 show the most probable species of Eriochrome Blue Black R.

3.2.3. Results of the MM2 analysis on Eriochrome Blue Black R

With neutral goethite no difference is observed between single and double ionized Eriochrome Blue Black R (Table 5), whereas with protonated goethite the difference between these species is higher (-69 kcal mol^{-1} vs. $-141\text{ kcal mol}^{-1}$). The change from double to a single-ionized Eriochrome Blue Black R produces a lower strength interaction. On the other hand, the repulsion strengths are present on the deprotonated goethite surface.

In the case of magnetite, the values of the steric energies interaction for all kind of surfaces with Eriochrome Blue Black R are very high and favorable (Table 5). No meaningful changes in adsorption with pH would expect.

4. General discussion of adsorption

Calculations not shown were carried out for the covalent bonding to the surface for Alizarin and Eriochrome Blue Black R. In both cases, the steric energies were more positive than those presented in Tables 4 and 5 and the adsorption through covalent bonding would be less favored.

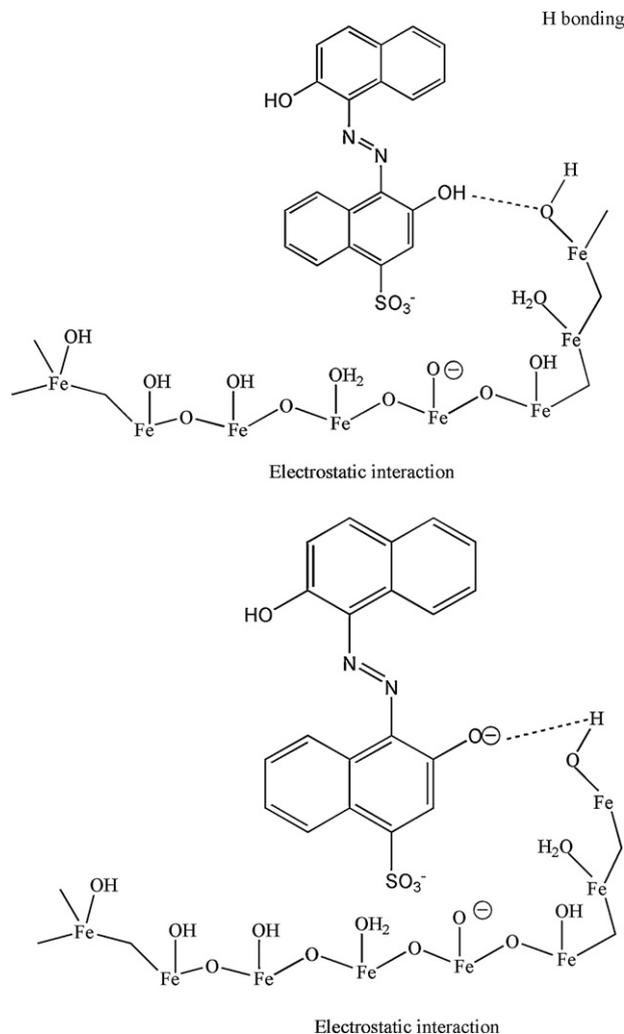


Fig. 8. Electrostatic and hydrogen bonding interactions with different Eriochrome Blue Black R structures.

Looking at the steric energies values and the experimental results there are several points of agreement, especially with the decrease of the dye uptake beyond pH 9.1 or 8.2 for goethite and Co-goethite and the almost constant adsorption uptake up to pH 10 for magnetite in the case of Alizarin. For the three oxides, Eriochrome Blue Black R shows a sharper dependence of the dye removal vs. pH. Although in magnetite, this effect is less evident. This fact implies a different adsorption process for Eriochrome Blue Black R than Alizarin, where the dye participates at the surface changing the surface charges. On the other hand, the fittings of Eriochrome Blue Black R removal vs. pH show that the surface charges are modulating the adsorption, following the expected behavior of the oxides with pH.

There is not any evidence from the FTIR studies on dried adsorbate-iron oxide samples to justify a different behavior of magnetite concerning goethite and Co-goethite. However, it is important to take into account that in the case of magnetite the dye concentration:surface sites ratio is lower than in goethite and Co-goethite. Even more, the values of the steric energies interaction for all kinds of magnetite surfaces with Alizarin and Eriochrome Blue Black R are very high and favorable, such as observed in Table 5.

Figs. 7 and 8 show the proposed general forms of adsorption for both dyes. The theoretical and molecular modeling employed agrees to our FTIR and adsorption data obtained at different pH.

The acidity and basicity of surface hydroxyl groups of goethite is of special relevance since these properties govern the primary charging of these surfaces and consequently the binding behavior of different sorbates. Crystallographic considerations indicate that the singly, doubly and triply coordinated hydroxyl groups exist in the goethite surface. These groups are also termed A, B or C types, respectively. All three types of hydroxyl groups coexist on the more exposed planes in goethite. The goethite (110) surface has an amphoteric character since both A and B types of sites coexist, and they are good proton donor and/or acceptor. However, the protonation of the triply coordinated hydroxyl sites is not feasible since the oxygen atom is already fully saturated by four chemical bonds. Owing to differences in the numbers of underlying Fe atoms that are coordinated to the surface functional groups, the acidity and hence, reactivity of the different types of hydroxyl groups should vary to some extent [6,27]. On the other hand, magnetite differs from goethite in that it contains both divalent and trivalent iron. Its formula can be written as $Y[XY]O_4$ where $X=Fe(II)$, $Y=Fe(III)$ and the brackets denote octahedral sites. The $Fe(II)/Fe(III)$ ratio is 0.5 and $Fe(II)$ ions occupy the tetrahedral sites and $Fe(III)$ ions occupy octahedral sites. The interface structure of magnetite on (111) plane shows two nonequivalent surface oxygen types in the ratio 70:30 ($O_4-Fe_{oh}-O_4-Fe_{td1\ oh\ td2}:O_4-Fe_{td1\ oh\ td2}-O_4-Fe_{oh}$) being the octahedral irons the principal ions involved in this interface [6,35]. Octahedral (111) face of magnetite contains singly and doubly coordinated hydroxyl groups. It is obvious, that surface hydroxyl configuration of the preferentially exposed faces of goethite and magnetite are quite different; this should result in marked differences in OH reactivity giving to magnetite higher amphoteric properties [36]. Therefore, this partially explains the different adsorption behavior vs. pH of magnetite with respect to goethite and Co-goethite.

5. Conclusions

Goethite has very good performance as adsorbent of Alizarin and Eriochrome Blue Black R. At low pH the amount of Alizarin and Eriochrome Blue Black R adsorbed on goethite and Co-goethite are similar. However, a higher dependence with the increase of pH is observed by Eriochrome Blue Black R. The presence of a foreign cation in Co-goethite does not improve the adsorption abilities of goethite for these dyes. Magnetite is the oxide that shows the less affinity for Alizarin and Eriochrome Blue Black R.

These results suggest that iron oxides are promissory adsorbents in the recovery of waste aqueous effluents. They can adsorb reactive dyes over a wide pH range through physical or chemical interactions. Besides, the magnetic properties of magnetite particles allow the fast magnetic separation of metal ions from industrial effluents.

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