5-[4-(2-Hydroxy-ethanesulfonyl)-phenylazo]-quinolin-8-ol - polysiloxane hybrid materials for extraction and removal of Fe^{3+} ions from aqueous solutions

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The paper presents new types of organic-inorganic hybrid materials obtained from an azo dye bearing chelating groups and triethoxysilane residues and tetraethoxysilane derivatives frequently used in sol-gel processes. Hybrid materials obtained were studied in processes involving extraction and removal of Fe^{3+} ions from aqueous solutions at different pH values. The organic chromogen with alkoxysilane residues and hybrid materials before and after complexation with Fe^{3+} ions were characterized by XRF spectrometry, FT-IR spectrometry, UV-VIS reflexion spectra, color measurements in CIELAB system and thermal analysis.

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Keywords: Hybrid materials, Silica, Dye, Extraction, Chelating groups

1. Introduction

Chemical sensors are recognized as viable alternatives to conventional tools, especially for analytical problems that require acquisition of real time data such as process control, environmental monitoring and biomedical. Research in the field was dominated by finding substance-specific detectors and has been directed to develop molecular sensor usually covalently linked to transparent media, in particular for the detection of metal ions in aqueous solutions [1,2].

Support materials used in the chemical sensors must fulfill a number of requirements [3] related to the ability of immobilization of indicator species, namely: to be solvent for the reaction of the recognition of species, have positive effects on selectivity and sensitivity by selective enrichment in species considered to be impermeable to ion contaminants, to prevent interference phenomena of light and to have mechanical stability. Also during the operation were required and other properties of chemical sensors, especially related to life during the operation, the absence of crystallization phenomena, migration, reorientation of components, stability to temperature, light and chemicals and in some instances light transparency [4,5].

One of our objective was to accomplish some of these requirements by covalent grafting a sensitive organic molecule onto an inorganic matrix formed by sol gel processes therefore being solved phenomena like aggregation, hysteresis, extraction at high ionic strength, swelling and non-uniformity of the material.

There are a lot of factors that have an influence on the hydrolysis and condensation and as a consequence on structure of the obtained networks. Thus, the behavior of an azo chromogen grafted onto silica organic modified networks was studied in relationship with the extraction, chelating and color properties.

2. Experimental

2.1 Materials

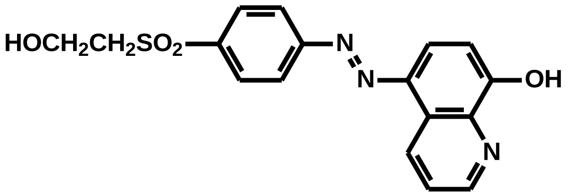
Tetraethylorthosilicate (TEOS), 3-isocyanatopropyltriethoxysilane (NCOTES), methyltriethoxysilane (MeTES), 1,4-diazabicyclo[2.2.2]octane (DABCO), titanium (IV) isopropoxide (TIP) and acetylacetone (AA) were purchased from Aldrich and used as received. Tetrahydrofuran (THF) and N-methylpyrrolidone (NMP) were purchased from Carlo Erba and were purified by distillation followed by anhydrization on molecular sieves 3Å (Merck). Acetic acid, sodium acetate, hydrochloric acid, ferric sulfate, ammonium thiocyanate and sulfuric acid were used as they were received as commercial products (Chimopar).

Silicon anhydride (SiO_2 content: 83.71%) from Merck and iron (III) sulphate (iron content: 22%) from Loba were used as standards for quantitative XRF measurements.

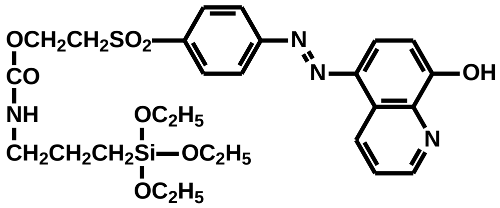
Azo chromogen 5-[4-(2-Hydroxy-ethanesulfonyl)-phenylazo]-quinolin-8-ol (HESAQ) was synthesized, purified and characterized by us, details of the procedures were presented elsewhere [6].

2.2 Procedures

For obtaining of the ion sensitive hybrids it was followed a reaction pathway that consist of the azo chromogen (HESAQ) modifying with 3-isocyanatopropyltriethoxysilane (NCOTES), followed by generating the inorganic matrix by hydrolysis-condensation of TEOS and MeTES in the presence of HESAQTES.



(HESAQ)



(HESAQTES)

Fig. 1. Chemical structure of the chromogens

Synthesis of the chromogen with alkoxysilane residue (HESAQTES)

It was prepared a solution consisting of 0.39 g HESAQ (0.0011 mole) in 40 ml THF, to which is added as a catalyst 0.06 g DABCO in 1.5 ml NMP and then 0.27 g NCOTES (0.0011 mole). The mixture was refluxed for 24 hours under nitrogen, watching the disappearance of the isocyanate group from FT-IR spectra of probes from the reaction mass analyzed at consecutive periods of time. When the reaction is complete it was obtained 40 ml solution of dye at a concentration of 1.66 g / 100 ml, which is used as such to obtain hybrids.

Obtaining the hybrid composites

A solution made from 2.45 ml TEOS, 3.25 ml HESAQTES solution previously obtained, 1.7 ml ethanol and a few drops of hydrochloric acid was stirred one hour at room temperature, and after that it was added a mixture formed from 0.07 ml AA, 0.2 ml TIP and catalytic quantities of hydrochloric acid. The mixture was maintained under vigorous stirring at the room temperature and transferred into a rotary evaporator for the removal of the volatile solvents. The residue was dried at 70^0C and finely grounded into a laboratory vibrating ball mill. It was obtained 0.5 g hybrid material (HY1) that is used for the metal uptake experiments. Organic modified hybrid material (HY2) was obtained in a similar manner from 1.15 ml TEOS and 1.3 ml MeTES.

Metal uptake experiments

Were conducted iron (III) ions uptake experiments to test the obtained hybrids for ion sensitive applications, using an aqueous solution of ferric sulfate 0.02 M and acetic acid / sodium acetate buffer solutions at pH=4-6. A 100 mg sample of hybrid material was added to solutions made from 1 ml Fe^{3+} solution 0.02 M and 49 ml from the corresponding buffer solution and mixtures were magnetically stirred in closed polyethylene bottles. Determination of the metal ion concentration was carried out withdrawing 0.5 ml Fe^{3+} from residual solution and mixing it with 2 ml ammonium thiocyanate solution 200 g/l and 0.1 ml sulfuric acid 2N. Absorbance was determined at λ=474 nm using a calibration curve. Metal uptake was examined at different intervals of time and pH values.

2.3 Measurements

UV-VIS absorption spectra of the aqueous solution of ferric sulfate during metal uptake experiments were acquired in the range 350-800 nm using a spectrometer UV-VIS-NIR Jasco V-570.

FTIR spectra of intermediates and final products were recorded on a Jasco FTIR 6300 spectrometer equipped with an ATR Specac Golden Gate (KRS5 lens), in the range 400-4000 cm^{-1} (30 scans at 4 cm^{-1} resolution).

Total color differences were measured by CIELAB method with a spectrophotometer UV-VIS-NIR Jasco V-570 equipped with an integrating sphere Jasco ILN-51 (150 mm), standard observer 10^0 (reference –spectralon).

XRF analyses were performed on a PW4025-MiniPal-Panalytical EDXRF Spectrometer. Measurements were carried out in helium atmosphere, for 300 sec., without any filter, at 20 kV and automatically adjustment of the current intensity.

Thermal analysis was conducted on a TA Q 5000 IR instrument, in nitrogen atmosphere, at a heating speed of 10^0C/min. and the temperature range 25-900^0C (samples of 5-10 mg in platinum crucibles).

3. Results and disscusion

The hybrid composites obtained as a result of sol-gel reactions which generate the inorganic matrices by hydrolysis-condensation of TEOS and MeTES in the presence of HESAQTES were analyzed by means of XRF spectrometry. The same measurements were made for iron complexes obtained after extraction experiments.

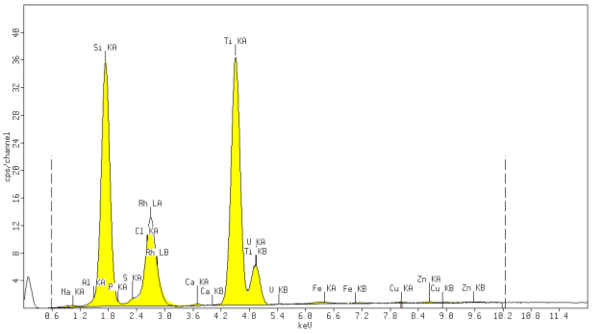


Fig. 2 X-ray fluorescence spectrum for HY1.

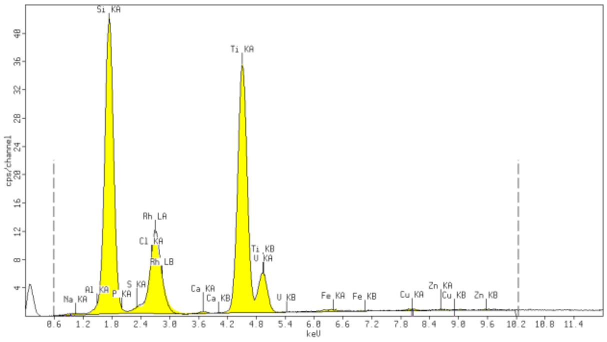


Fig. 3 X-ray fluorescence spectrum for HY2.

The analysis performed for hybrid materials HY1 and HY2 showed (Fig. 2, Fig. 3) the presence of silicon in organic-inorganic hybrid samples. Quantitative analysis shows a silicon content of about 13.5% in HY2 respectively of 12.97-12.64% for samples isolated after iron complexation at different pH values.

As it can be seen after iron uptake experiments at different pH values, the quantity of iron extracted from aqueous solutions have grown from acidic to neutral pH values (Fig. 4). The iron percentage determined by XRF in the hybrid material (HY2) is doubled if the extraction-complexation was conducted at pH=6 by comparison to results obtained at pH=4.

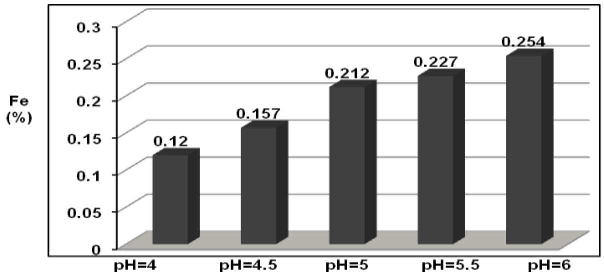


Fig. 4 Iron content of HY2 after extraction-complexation experiments at different pH values

From the infrared spectra of organic-inorganic hybrids (HY1, HY2) there were distinguished the same structural particularities such as: the absorption in the 3400-3200 cm^{-1} domain characteristic for the vibrations of ν(OH), ν(NH) and ν(CH) aromatic stretching vibrations; in 1400-1600 cm^{-1} domain are found deformation characteristic vibrations δ(OH) and δ(NH); at 1270 cm^{-1} it was detected a characteristic signal δ (H_3C-Si) only for HY2; at 2973 and 2911 cm^{-1} the asymmetric and symmetric vibrations for CH_3 characteristic only for HY2; bands situated at 916-943 cm^{-1} correspond to Si-O-Si stretching vibrations; an intense peak at 776 cm^{-1} was recorded for HY2 and was attributed to γ (H_3C-Si) deformation.

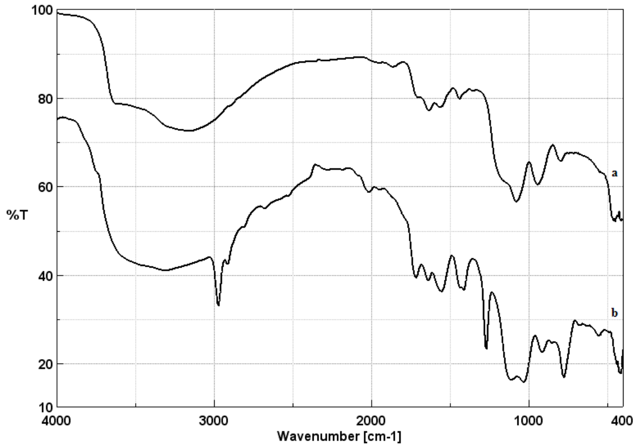


Fig. 5 FT-IR spectra of organic-inorganic hybrids a) HY1 and b) HY2

An interesting specific peak for silica matrices is situated at 1079 cm^{-1} with a pronounced shoulder for HY1 while for HY2 it is observed a doublet having the same intensity situated at 1115 cm^{-1} and 1033 cm^{-1}, corresponding to Si-O-Si stretching vibration. Accordingly to some authors [7] the presence of two peaks in that zone proves that material is more porous than that with a single peak situated at lower wave numbers, thus on this basis we can estimate that HY2 has a more porous structure than HY1.

Finally it is to be mentioned that for hybrid materials (HY1, HY2) after complexing with iron (III) ions in FTIR spectra it was detected a characteristic band situated at 581 cm^{-1} characteristic for νFe-O stretching vibration.

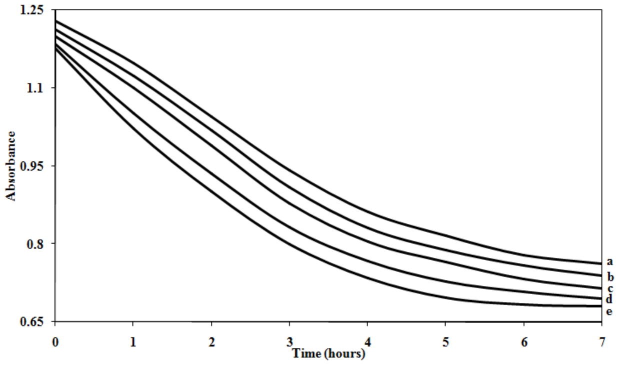


Fig. 6 Metal ion uptake capacity for HY1

The results of the Fe^{3+} ions uptake experiments showed that the process was influenced mainly by the shaking time and pH values. The metal ion uptake capacity was determined from variations in absorbance for the residual solutions during extraction-complexation, measurements at different moments indicating a reducing in absorbance at λ=474 nm. This behavior was very pronounced for the first six hours from the beginning of the extraction and after that it was found that curves became flatness.

The effect of the pH value on the uptake of iron (III) ions strongly influenced the reaction rate and the ion uptake capacity from the aqueous solution. Thus at pH=4 the reaction rate was smaller than that recorded at pH=6 and also at eight hours from the beginning the quantity of the uptake metal ion was smaller. At reduced pH the ability of the dyestuff ligand to bind metal ions is reduced due to the existence of intramolecular hydrogen bonds between hydroxyl phenolic group and nitrogen atom from the quinoline residue. While raising the pH the OH phenolic group is able to be transformed in phenolate, hydrogen bonds are broken and the complexation takes place more facile.

As a conclusion it was found that optimum pH was situated at 5.5-6, and maximum quantity of iron (III) ions uptake was recorded at eight hours from the beginning of the experiment when it was used HY1.

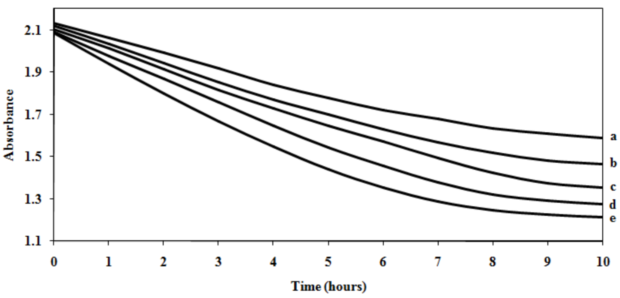


Fig. 7 Uptake of iron (III) ions by HY2

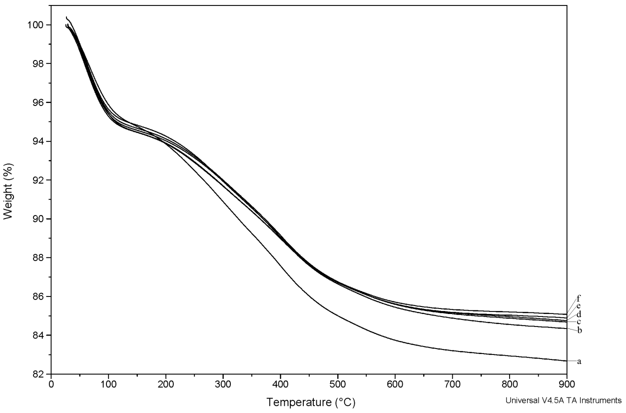


Fig. 8 TGA analysis for HY2 a) before complexing; b) pH=4; c) pH=4.5; d) pH=5; e) pH=5.5; f) pH=6

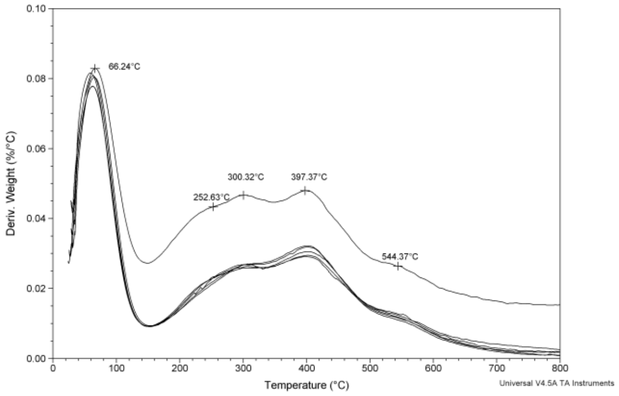


Fig. 9 DTA analysis for HY2 before and after complex formation at different pH values (4.5-6)

The HY2 material was examined before and after complex formation through thermal gravimetric analysis (TGA) and differential thermal gravimetric analysis (DTA). The experiments were conducted under nitrogen at a heating rate of 10^{0}C/min. and in the range 20-800^{0}C. Analysis of the thermogravimetry results shows the same shape of the curves corresponding to HY2 before and after complexation with Fe^{3+} ions. Three major peaks and two shoulders were observed in all the thermograms recorded. The first peak occurs at 66^{0}C and is attributed to loss of physically adsorbed water and alcohol from the pores. The second peak situated around 300^{0}C with a small shoulder at 252^{0}C which disappear during complexation at high pH values, was attributed probably to degradation of organic-functional groups bound to the silica network, dehydroxylation process and loss of the water from silica bulk. The third peak situated at 397^{0}C with a shoulder at 544^{0}C is probably due to decomposition of organic dye and further condensation of hydroxyl groups from the silica networks. After 600^{0}C the weight loss is practically un-significant, smaller than 1% and at 900^{0}C residues were calculated for all the samples studied.

It can be concluded that the residues have grown from 82.67% corresponding to HY2 before complexation to 85.07% for HY2-Fe^{3+} complex obtained at pH=6. Differences are attributable to iron oxides formed during calcinations and constitute another proof for the fact that maximum quantity of iron (III) ions uptake was recorded at pH=6 for this kind of material.

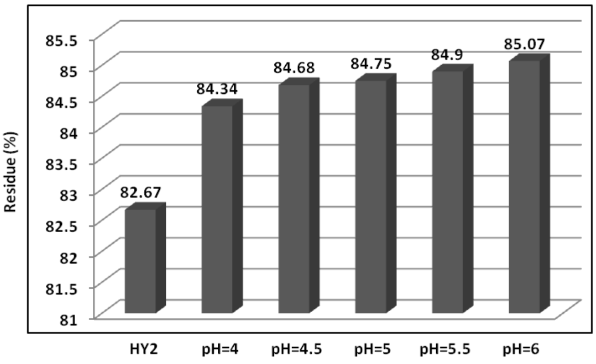


Fig. 10. Residues at TGA for HY2 hybrid materials after complexing with Fe^{+3} at different pH values

Analyzing UV-VIS reflexion spectra for the obtained hybrids it showed that for HY2 it was a great difference in reflectance after the iron (III) uptake experiment on 380-650 nm domains and for HY1 also a similar difference was recorded on 630 -700 nm domain. These data are correlated with the results obtained from color measurement experiments in CIELAB system and shade deviations.

As it can be seen from experimental data when MeTES was used for generating silica networks, after grafting the chromogen was produced a hypsochromic effect by comparison with HY1. This was due to the polarities variation in the pores of the network at the points of dye anchoring. It was assumed also that steric hindering due to methyl groups from the silica conduct to diminishing network influences onto the chromogen and probably to hindering hydrogen bonds, so the dominant wavelength for HY2 was λ_D=448 nm and for HY1 was λ_D=519.5 nm.

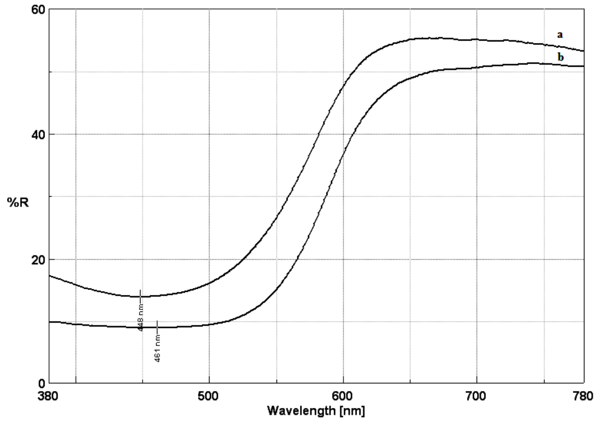


Fig. 11 Reflexion spectra for HY2 (a) before and (b) after complexation with Fe^{+3}.

The wavelength shifts to higher values for HY1 could be explained probably because of the hydrogen bonds established between Si-OH groups from the network and the nitrogen atom from the quinoline residue of the anchored azo dye, or OH phenolic group from the organic dye and Si-O-Si from the inorganic network. For HY2 the presence of methyl groups grafted on the network modify the environments of the dye surroundings and cause changes in its optical properties. These environments less polar than those resulted in unmodified silica networks conduct to a hypsochromic shift of the dominant wavelength of 71.5 nm.

Table 1. Color measurements for hybrid materials before and after the complexation.

Hybrid material			**HY2**		**HY1**	
			initial	**after complexation with Fe^{3+}**	**initial**	**after complexation with Fe^{3+}**
A	**Tristimulus Values**	**X**	47.80	36.87	30.65	22.76
		Y	35.18	24.97	19.97	15.42
		Z	5.07	3.17	4.08	3.04
	Trichromatic coordinates	**x**	0.5429	0.5671	0.5603	0.5521
		y	0.3996	0.3841	0.3651	0.3741
	CIELAB	**L**	59.32	49.97	44.69	39.27
		a	40.05	44.26	44.22	34.72
		b	36.46	31.22	25.87	22.90
B	**Tristimulus Values**	**X**	38.30	28.73	23.78	17.86
		Y	31.59	21.60	17.33	13.59
		Z	12.03	7.57	9.88	7.29
	Trichromatic coordinates	**x**	04675	0.4962	0.4663	0.4610
		y	0.3856	0.3731	0.3399	0.3508
	CIELAB	**L**	56.20	46.48	41.63	36.86
		a	23.28	28.99	29.07	21.96
		b	26.65	22.88	15.07	14.08

Hybrid material			HY2		HY1	
			initial	after complexation with Fe^{3+}	initial	after complexation with Fe^{3+}
C	**Tristimulus Values**	**X**	35.29	26.14	21.78	16.41
		Y	30.21	20.38	16.46	12.97
		Z	16.52	10.41	13.66	10.04
	Trichromatic coordinates	**x**	0.4303	0.4591	0.4196	0.4163
		y	0.3683	0.3580	0.3172	0.3289
	CIELAB	**L**	54.97	45.15	40.57	36.01
		a	18.42	24.33	24.82	18.34
		b	20.66	17.93	8.44	8.67
D 65	**Tristimulus Values**	**X**	34.61	25.63	21.28	16.07
		Y	30.06	20.23	16.35	12.90
		Z	15.29	9.63	12.61	9.28
	Trichromatic coordinates	**x**	0.4328	0.4619	0.4235	0.4200
		y	0.3760	0.3646	0.3255	0.3373
	CIELAB	**L**	54.83	44.98	40.44	35.92
		a	16.73	23.00	23.15	16.97
		b	21.85	18.79	9.82	9.83

After complex forming with iron (III) ions, luminosities of the shades diminished as it was expected and it is known from the chemistry of metal complex dyes. Differences of luminosity are negative as it was observed for both type of matrices and illuminant (A, B, C, and D65) used. The dominant wavelength for HY2 after complexation was λ_D=461 nm, and for HY1 after complex formation was λ_D=489 nm. Difference between them was of only 28 nm relative to 71.5 nm recorded for the same materials before de complex formation.

Differences between dominant wavelengths for materials studied before and after complex formation are for HY2 of (+13) nm, respectively (-30.5) nm for HY1. It has to be noted that for HY1 a large hypsochromic effect was recorded after complex formation. This fact could be explained through the possible hindered interactions between dye and Si-OH or Si-O-Si groups from the inorganic silica network after complex formation that blocked both nitrogen atom and hydroxyl phenolic group from the dye quinolin-8-ol residue.

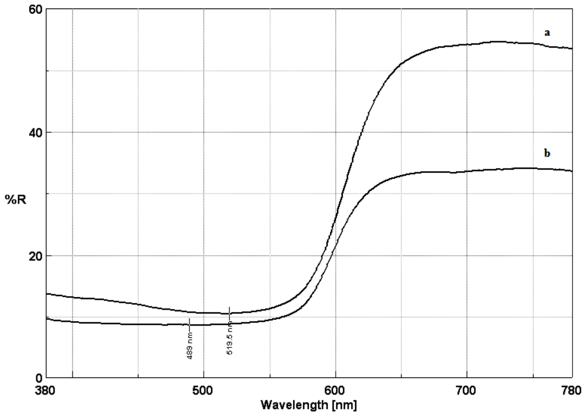


Fig. 12 Reflexion spectra for HY1 (a) before and (b) after complexation with Fe^{+3}

For the modified hybrid HY1 after complexation a shade shifting to the red region (Δa>0, Δb<0) takes place and for HY2 the shifting is to the blue region (Δa<0, Δb<0). Total color differences measured by CIELAB method are situated at 7.5 - 12 as function of illuminant used. These values are notable color differences from the standards point of view and recommend both type of materials studied as candidates for iron (III) optical sensors.

Table 2. Color differences for hybrid materials before and after the complexation.

Color differences	Illuminant type							
	A		B		C		D65	
	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1
ΔL	-9.34	-5.42	-9.72	-4.77	-9.82	-4.56	-9.85	-4.52
Δa	4.21	-9.50	5.71	-7.12	5.91	-6.48	6.27	-6.18
Δb	-5.24	-2.97	-3.77	-0.99	-2.73	0.23	-3.05	0.00
ΔE_{ab}	11.51	11.33	11.89	8.62	11.78	7.93	12.07	7.65

4. Conclusions

A chelating azo dye molecule was chemically grafted to silica inorganic networks by an anchoring agent to obtain materials that can be used as sensors and also can exhibit high potential for extraction of iron (III) ions from aqueous solutions.

Materials were characterized by means of XRF spectrometry, FT-IR spectrometry, UV-VIS reflexion spectra, color measurements in CIELAB system and thermal analysis and the results obtained show that extraction of iron (III) ions from aqueous solutions takes place more convenient at pH= 6.

Color differences of the studied materials before and after complexation with iron (III) ions are notable and recommend them as iron (III) optical sensors.

The potential usage of a large variety of silanization agents that allow great variations of the inorganic matrices, facile grafting of the dyestuff molecules on the silica surface than to other polymeric supports, inorganic matrices very well known and characterized, having a constant composition and high specific area, that allow facile analysis and interpretation of the results, good solvent resistance and thermal stability of the obtained materials are some of the advantages of 5-[4-(2-Hydroxy-ethanesulfonyl)-phenylazo]-quinolin-8-ol-polysiloxane hybrids studied by us.

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