

The bifunctionality of silica gel modified with Congo red

Short Communication

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Abstract: Silica gel was chemically modified with Congo red and characterized by Fourier transform infrared spectroscopy, elemental and thermogravimetric analysis. The pH-sensitive immobilized Congo red retains the same properties as its solution counterpart and could be applied as solid indicator. The functionalized silica gel was also employed to extract different cations from water solutions. The concentration of cations extracted was determined by inductively coupled plasma optical emission spectrometry. The solid support is able to selectively extract silver and copper from water solutions and retains its properties after treatment with different organic and inorganic solvents.

Keywords: Silica gel • Congo red • pH indicator • Solid-phase extraction

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1. Introduction

Each year the textile industry introduces large quantities of dyes into water streams. Water-soluble azo dyes are characterized by nonbiodegradability and toxicity. Conventional wastewater treatment is ineffective for the removal of azo dyes. The most widely used method for azo-dye removal is adsorption onto various adsorbents—activated carbon, active Al_2O_3 , TiO_2 or mesoporous silica [1-7]. However, the adsorption process strongly depends on the modifications made to the adsorbent [8-12].

Adsorption of dye compounds onto solid surface can be applied as solid pH indicators. Zaggout *et al.* immobilized alizarin red S [13], phenol red [14], methyl red [15], and thymol blue [16] into sol-gel matrices and observed that each dye exhibits similar behavior as its solution counterpart. Miled *et al.* coated optical fibers with bromothymol blue-activated silica and studied their pH sensing properties [17]. They found that the immobilized dye compound could also be used for solid-phase extraction of metal ions from water solutions. Fan *et al.* functionalized silica gel with alizarin violet for selective extraction of lead [18].

Congo red dye is a popular pH indicator that changes colour from blue to red at pH 3.0-5.2. Previous studies

by Seçkin *et al.* demonstrate postgrafting of Congo red onto mesoporous silica resulting in hybrid materials with properties of azo dyes and inorganic frameworks [19].

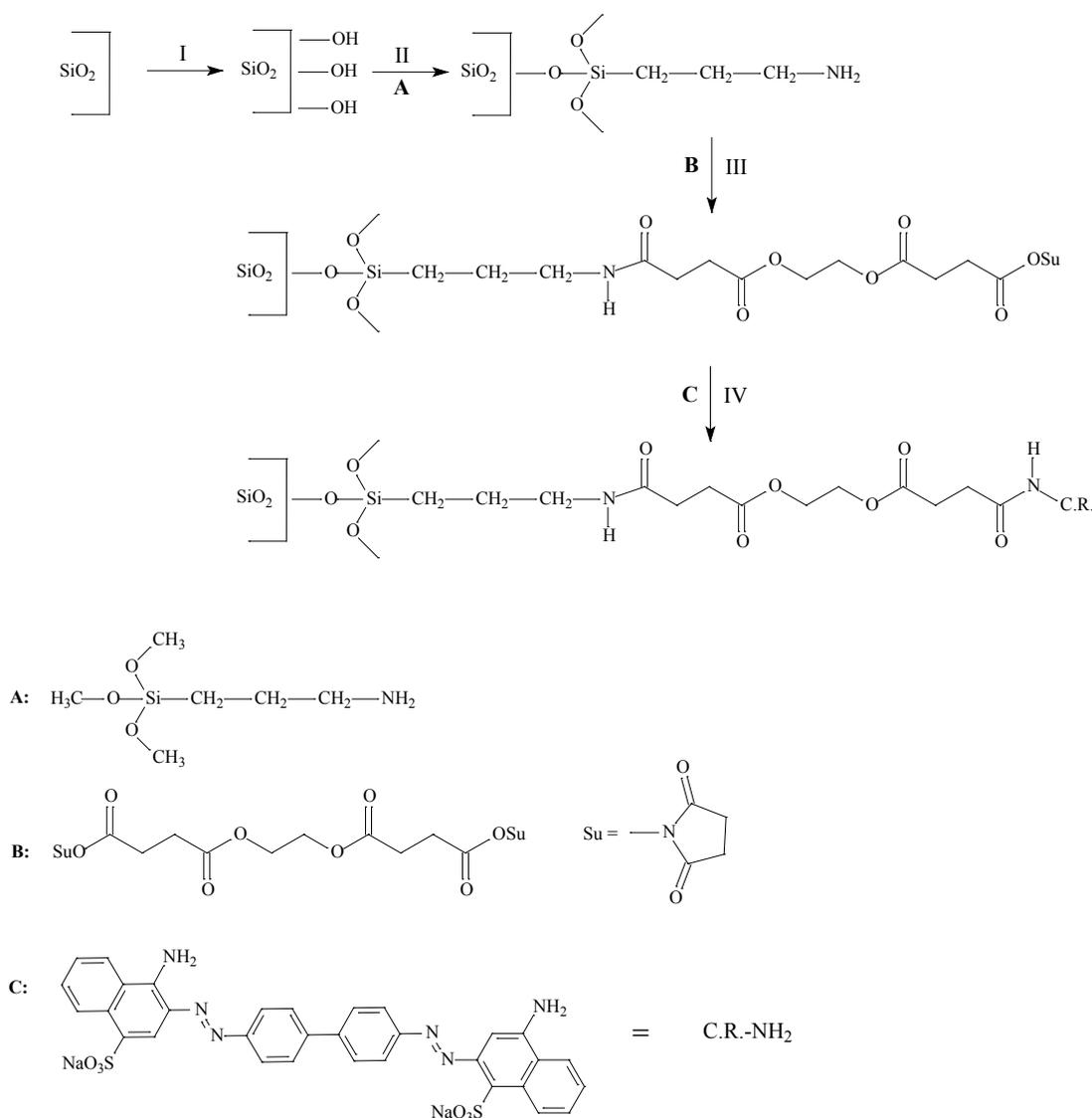
This paper presents the synthesis and analysis of Congo red chemically functionalized onto silica gel. The immobilized azo dye retains its pH-sensing behaviour. Moreover, it selectively extracts silver and copper ions from water solutions. So far, the modified silica gel for ion extraction has a variety of chelating groups for silver [20-22] and for copper [23-25] sorption. In the present work, the functionalized silica gel works as a solid indicator and a sorbent for silver and copper extraction.

2. Experimental Procedure

The support studied was prepared following the procedure outlined in Scheme 1. SiO_2 hydration (I) and silanization procedures (II) were previously described [26].

III. Ethylene glycol-bis(succinic acid N-hydroxysuccinimide ester) (Sigma) (1.0 g, 2.2 mmol) was dissolved in chloroform (50 mL). Then 2 g of aminopropyl silica gel (the product of the silanization procedure) was added and the mixture was stirred and heated at reflux for 72 h. The precipitated intermediate product was used in the next synthetic step.

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Scheme 1. Synthesis of the support studied.

IV. Sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid (Congo red) (Sigma) (2.2 mmol) was dissolved in acetonitrile (50 mL). Then 2 g of the intermediate product was added and it was stirred and heated at reflux for 4 days. The product was precipitated and washed until the filtrate showed no characteristic color.

Anal. found **C**, 9.13; **N**, 1.64; **H**, 1.98.

For infrared measurements, a silicon wafer, which is penetrable by the infrared beam, was used to get better quality of a spectrum. The spectra were recorded on IFS 66v/s Fourier transform infrared (FTIR) spectrophotometer from Bruker, equipped with a MCT detector (125 scans, resolution 2 cm^{-1}). The elemental analysis of the support studied was carried out on a Vario ELIII (Elementar, USA) analyzer, while thermogravimetric

studies were carried out in a Setaram TGA at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under helium atmosphere.

Congo red (Sigma) solutions (70 mg L^{-1}) were prepared in bi-distilled water and 0.1 M HCl to observe colour change in different pH condition. Immobilized Congo red on silica gel was treated with doubly distilled water and 0.1 M HCl aqueous solution. The absorbance of Congo red water solutions was recorded using an ultraviolet/visible (UV/VIS) spectrophotometer from Agilent with a 1 cm quartz cuvette. The spectrophotometer was interfaced with a computer operated by UV/VIS ChemStation software. The UV/VIS spectra for immobilized dye were recorded on Varian UV/VIS/NIR. UV/VIS absorbance spectra were measured at room temperature in the range 200–800 nm.

The perchlorates Cu(II), Ag(I), Ni(II), Ca(II), Mg(II) and Pb(II), were purchased from Aldrich and were used without any purification. Doubly distilled water was used for solution preparation. Standard solutions (10 mg L⁻¹) for batch experiments of metal ions were prepared by dissolving metal perchlorates in the following buffers: NaAc-HAc (pH 3.0-6.0) and KH₂PO₄-Na₂HPO₄ (pH 6.0-8.0). The pH measurements were made using an Elementron pH meter calibrated against standard buffer solutions, pH 4.0 and 6.0.

The support (adsorbent) was added (0.02-0.10 g) to 10 mL of metal ion solutions. The mixture was stirred for 5-30 min at room temperature. Then the solution was centrifuged and the supernatant was used to determine the concentration of metal ions. An inductively coupled plasma-optical emission (ICP-OES) spectrometer from Varian was used to determine the concentrations of metal ions before and after preconcentration.

The adsorption capacity Q (mg g⁻¹) and the adsorption percentage E (%) were calculated from the batch experiments using the following equation:

$$Q = \frac{(C_i - C_f)V}{W} \quad (1)$$

where C_i and C_f represent the initial and final concentrations of metal ions (μg mL⁻¹) respectively; V represents the total volume of metal solution (L); and W represents the mass of the modified silica gel (g).

$$E(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

Moreover, Langmuir isotherm was used to predict adsorption capabilities of metals in the support studied. The isotherm was evaluated by batch method. Eq. 3 presents the linearized equation for describing adsorption data for solid-liquid systems:

$$\frac{C_e}{N_f} = \frac{1}{bN_f^s} + \frac{C_e}{N_f^s} \quad (3)$$

where C_e is the equilibrium concentration of the metal ion (mol L⁻¹), N_f is the amount of the solute adsorbed on the surface of the adsorbent (mol g⁻¹), N_f^s is the maximum sorption capacity of the sorbent, and b is the Langmuir adsorption constant (L mol⁻¹).

In order to investigate the sorption and desorption of metal ions, a mini-column was packed with 40 mg of the support studied. The copper (silver) solution (optimum pH, 20 mL) was passed through the column. The adsorbed Cu (Ag) ions were desorbed by passing

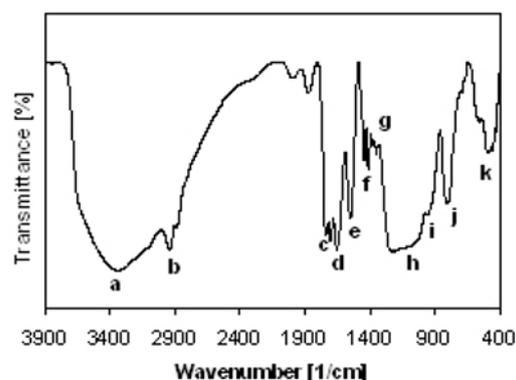


Figure 1. FTIR spectrum of the support studied where peaks were assigned: **a:** O-H stretching; **b:** C-H stretching; **c:** C=O bonds of an ester; **d:** angular vibrations of the water molecule; **e:** C=O bonds of an amide; **f:** N-N frequencies; **g:** azo-mode; **h:** siloxane vibrations; **i:** silanol deformation; **j:** Si-O-Si stretching; **k:** Si-O-Si bending

20 mL of 0.3 mol L⁻¹ HNO₃. The concentration of Cu (Ag) ions in the eluate was determined by ICP-OES.

3. Results and Discussion

The support studied was characterized by the FT-IR spectroscopy (Fig. 1). A broad band between 3200 and 3500 cm⁻¹ was assigned to the O-H stretching frequency of silanol groups and the remaining adsorbed water. The typical N-H stretching band (3400-3500 cm⁻¹) was difficult to identify. The broad and intense band at 1100 cm⁻¹ was assigned to the siloxane vibration (Si-O-Si), while bands at 782 and 448 cm⁻¹ were attributed to Si-O-Si stretching and bending, respectively. A band appearing at 2930 cm⁻¹ was assigned to the C-H stretching vibrations region. The support studied is characterized by the presence of two groups of carbonyl stretching frequencies. The position of a band at 1550 cm⁻¹ (C=O) in the spectrum indicated the presence of the primary amide. The signals at 1702 and 1738 cm⁻¹ are assigned to ν(C=O) vibrations of the ester group. Bands of phenyl ring (~1600 cm⁻¹) and sulfonate (~1100 cm⁻¹) were difficult to identify due to the strong signals from angular vibrations of water and siloxane vibrations, respectively. According to the elemental analysis data, the support studied contains 1.64% of nitrogen. This data enables the amount of ligands attached onto the surface to be determined, which is 0.17 mmol g⁻¹. The relatively low value could be explained by poor yield of the final step of the synthetic procedure.

Thermogravimetric curve data (see Supplemental Information) shows loss of mass as an effect of

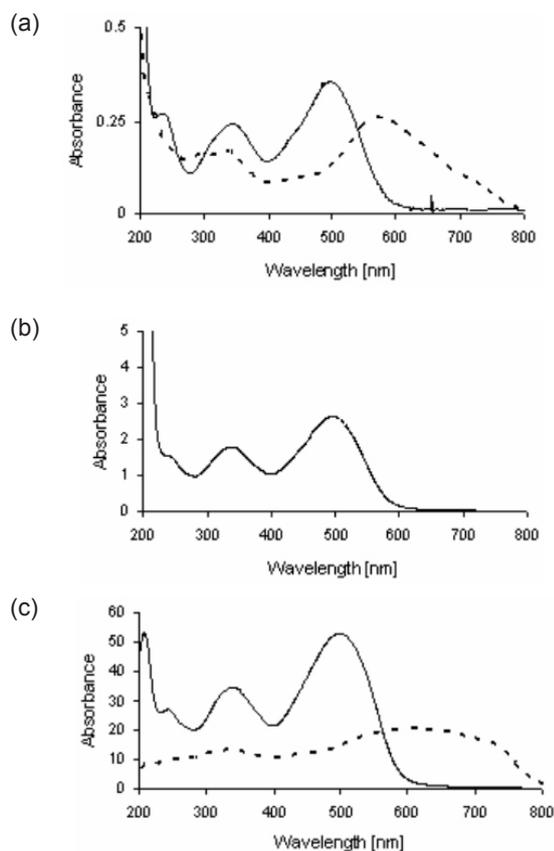


Figure 2. UV/VIS spectra: (a) free Congo red in water (—) and aqueous 0.1 M HCl solution (---); (b) the silica gel functionalized with Congo red; (c) the silica gel functionalized with Congo red treated with water (—) and aqueous 0.1 M HCl solution (---)

continuous heating in a helium atmosphere. First, an insignificant mass loss of about 1% is caused by physically adsorbed solvent applied in the synthesis. Further mass loss is observed until 900 K (mass loss of about 10%) due to the elimination of part of the ligand and some silanol groups.

The UV/VIS spectra (Fig. 2) of free Congo red and the functionalized silica gel were obtained for acidic and base forms of the molecules. The silica gel modified with Congo red exhibits band at 496 nm (red color). When the silica surface is treated with distilled water it shifts slightly to 499 nm and the absorbance dramatically increases. The significant shift is observed after treatment with strong acid (0.1 M HCl) solution to 578 nm. The sample surface changes colour from red to deep blue (acidic form of Congo red) resulting from protonation of azo groups. The observed process is reversible; the colour of the surface reverts back to red in the presence of a strong base (0.1 M NaOH) solution. The behaviour of functionalized silica gel is similar to free dye solution. An aqueous solution of Congo red exhibits a band at

498 nm, which corresponds with the basic form of the compound discussed. The acidic form of free Congo red is characterized by the presence of the absorption band at 576 nm. The disappearance of the absorption band at 498 nm is accompanied by a change in colour, from red to blue.

The complexing ability of the modified silica gel was examined by a batch experiment. Initially, different amounts of the functionalized silica gel with Congo red (0.02–0.1 g) were added to 10 mL of perchlorate solution. Satisfactory results were observed when 0.1 g of the support studied was used. Moreover, the effect of stirring time was tested in the range of 5 to 30 minutes. The complete extraction process of Ag(I) and Cu(II) were observed after several minutes. However, the following experiments were carried out for 30 minutes so as to not overlook the extraction process of coexisting ions. Finally, the stability of the support studied was also investigated by treatment with different organic solvents (methanol, methylene chloride) and aqueous solutions (HCl, NaOH). Chemically treated supports were washed with doubly distilled water and used for complexing studies of different ions. No significant difference in the extraction percentage was observed in the samples before and after chemical treatment, which confirmed their stability in different media.

Cation adsorption by the functionalized solid supports is highly pH-dependent. In low pH environments, metal ion adsorption is insignificant because of the protonation of functional groups. On the other hand, strong alkali environments (pH > 7) cause hydrolysis of divalent ions. The important region, in which the sorption of metal ions is considerable, ranges from pH 5.0 to pH 7.0. The optimum pH value for copper adsorption was 6.0, while for silver the results were similar for pH 6.0 and 7.0. Finally, pH 6.0 was chosen as the optimum value for further experiments.

The absorption of different ions onto functionalized silica gel was carried out by the addition of 0.1 g of the support studied into 10 mL of metal ions solution (10 mg L⁻¹). After 30 min of stirring, residual ions in the supernatant were determined by ICP-OES. Fig. 3 presents the extraction percentage of different cations (pH 6.0) calculated from the concentration data in the supernatant. The results indicate that the support studied is able to extract Cu(II) and Ag(I) ions (about 70%) from aqueous solutions in the presence of other metal ions (Ni, Pb, Ca, Mg). Previously, we have obtained several magnetic [27] and non-magnetic [28,29] modified solid supports, which were able to extract copper(II) cations from aqueous solution and the extraction percentage varied from 70 to 90%. Therefore, the silica gel functionalized with Congo

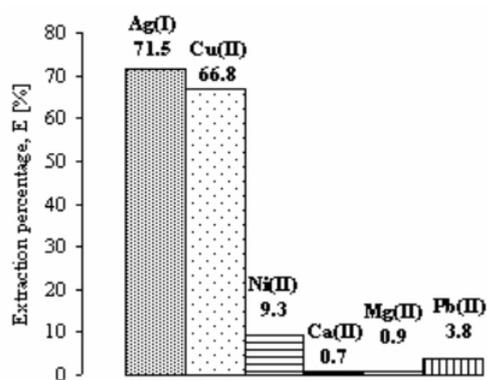


Figure 3. The extraction percentage of different cations by the support studied in pH 6.0

red presents slightly less complexing ability towards Cu(II) against a background of the previously obtained adsorbents. However, the support studied could be synthesized making use of Congo red that comes from textile industries: the organic pollutant-azo dye can be immobilized onto silica gel and then applied to the removal of other pollutants. Moreover, the adsorbent studied can be easily regenerated in acidic conditions and reused repeatedly without a significant decrease in effectiveness, which was confirmed by column studies. In acidic conditions ($0.3 \text{ mol L}^{-1} \text{ HNO}_3$), azo and amine groups are protonated, which enables desorption of copper and silver ions. However, under acidic conditions, a fraction of the sites occupied by metal ions may replace by H^+ . Therefore, doubly distilled water was

applied to neutralize the sorbent. After the recondition, the sorbent studied was used in an analogous cycle several times. The concentration of desorbed ions was determined by ICP-OES and the recovery of Cu(II) and Ag(I) ions exceeded 90% every time.

Finally, the adsorption parameters of copper and silver on the sorbent surface were investigated by the Langmuir isotherm model. We assumed monolayer coverage of the sorbent studied. Langmuir constants were determined by using the adsorption data through batch experiments at the optimum pH condition and room temperature. The experimental data fit the Langmuir model as demonstrates by the correlation coefficients, which were all higher than 0.990: 0.9925 (0.9942) for copper (silver), respectively. Langmuir adsorption constants (b) amounted to 0.45×10^4 (0.72×10^4) [L mol^{-1}], while the maximum sorption capacity of the sorbent was (N_f^s) 1.13×10^{-4} (0.94×10^{-4}) [mol g^{-1}].

4. Conclusions

In summary, the findings presented demonstrate successful chemical modification of silica gel by Congo red. The functionalized silica surface responds to pH and could be applied as a solid pH sensor. Moreover, it effectively extracts copper and silver ions in the presence of other metal ions and could be used for separation of those cations from water samples.

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