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Inorganic magnetic support for sodium cation scavenging

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ABSTRACT

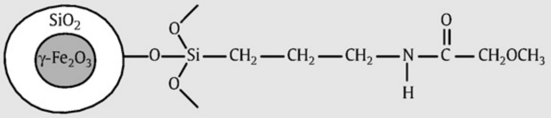
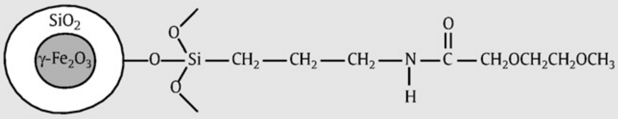
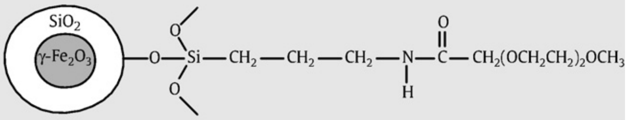
Three different magnetic iron oxide-silica matrices with polyoxaalkyl units have been obtained in a multi-step synthesis. The structures of the matrices were confirmed by Fourier transform infrared spectroscopy, while their surface morphology was analyzed by scanning electron microscopy. The scavenging ability was studied by ultraviolet–visible measurements. The results demonstrate very good scavenging efficiency of compounds studied against sodium cations (Na^+). The complexing abilities of the magnetic iron oxide-silica surfaces were compared with those of the previously studied analogously modified non-magnetic silica surfaces.

1. Introduction

Magnetic iron oxide of appropriate particle sizes and shapes is characterized by the superparamagnetic properties. The phenomenon of superparamagnetism also strongly depends on the magnetic interactions between particles and on various surface effects [1]. Magnetic iron oxide is suitable for medical application as it is stable and harmless to the living tissues [2,3]. It also can be used in the environmental studies as an agent for removal of metal ions from aqueous and non-aqueous solutions [4]. However, to be used for this purpose the support must have its surface modified to show a desired functioning. On the other hand, silica gel is widely used as a solid support for immobilization of various organic compounds [5–8]. Both inorganic matrices, iron oxide and silica gel, are characterized by good selectivity, no swelling and good mechanical stability. Nevertheless, silica gel is the most popular substrate for surface studies and the number of organofunctional groups that can be immobilized on its surface is impressive and still increases. The functional groups are attached directly or via a spacer that is in general a silylating agent. The precursor participates in further incorporation of functional groups in the inorganic framework. The combined supports (iron oxide and silica gel) find application inter alia in magnetic resonance imaging (MRI). Ferumoxsil is a commercially available superparamagnetic iron oxide-silica surface having poly[N-(2-aminoethyl)-3-aminopropyl] pendant group, which is applied as contrast agent in MRI [9].

Previously, we have studied the scavenging ability of the non-magnetic silica surface modified by polyoxaalkyl units [10]. It is well known that compounds having polyoxaalkyl units are widely used for complexing of alkali and alkaline earth metal ions [11–16]. The complexing ability depends on the ligand type (cyclic or open-chain) and the number of ethereal groups. Modified silica gel can be applied for selective extraction of mentioned metal ions [17–19]. We have already obtained effective systems for sodium cation scavenging. In this paper, the improved solid surface with polyoxaalkyl units, having magnetic properties due to the presence of iron oxide matrix has been studied. We report the synthesis of three magnetic solid supports 1–3 (Table 1) and the complexing ability of sodium cations from popular water soluble dyes in the form of sodium salts. Moreover, we have

Table 1
The structures of compounds studied **1**–**3**.

No	Compounds studied
1	
2	
3	

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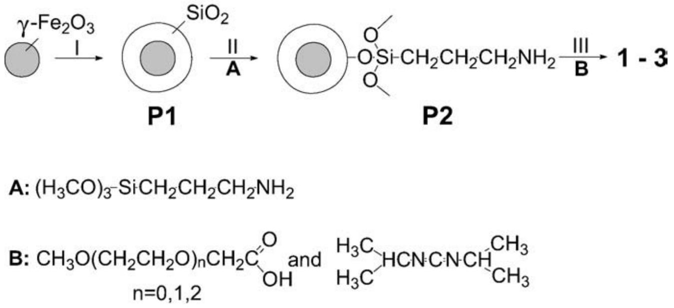

Scheme 1. Synthesis of compounds studied **1**–**3**.

tested the supports in the purification process of water solution using the designed dual-purpose flow system.

2. Experimental details

2.1. Synthesis of compounds studied

Compounds **1**–**3** were prepared following the procedure outlined in Scheme 1. The multi-step synthesis consisted of three general stages. The initial procedure (I) was applied in order to coat the magnetic support with silica. The application of sol–gel technique precluded destruction of iron–oxide matrix structure and ensured the formation of a uniform silica layer. Afterwards, the silica surface was modified in silanization procedure (II) with silane coupling agent having amine groups. Finally, the reactive primary amine groups participated in the reaction with acidic substrates to form compounds **1**–**3**.

I. Magnetic iron oxide-silica matrix preparation (sol–gel technique): Sodium silicate water solution (27% SiO_2 in 14% NaOH, Sigma; 100 ml) and γ-Fe_2O_3 (13.5 g; 0.08 mol) was introduced into a beaker equipped with a mechanical stirrer. The mixture was then diluted by distilled water (to 500 ml) and mechanically stirred in ultrasonic bath for 30 min at room temperature. After that the temperature was increased up to 80 °C and hydrochloric acid was added to adjust pH to 6–7. The magnetic iron oxide-silica precursor (P1) obtained was filtered using a glass microfibre filter and washed repeatedly with distilled water and methanol.

II. Silanization procedure: Precursor P1 (obtained from 13.5 g of γ-Fe_2O_3) was suspended in methanol (150 ml) and then distilled water (1 ml) and glycerol (150 ml) were added. The suspended solids were mechanically stirred in the ultrasonic bath for 30 min in room temperature. The suspension was then introduced into a three-neck round bottom flask equipped with a mechanical stirrer and a reflux condenser. 3-Aminopropyl-trimethoxysilane (Aldrich) (10.3 g; 0.06 mol) was added dropwise to the reaction mixture that was heated (90 °C) for 3 h. The intermediate product (P2) was filtered and washed repeatedly with distilled water and methanol. Finally P2 was dried under vacuum at room temperature.

III. 1 g of P2 and diethyl ether (50 ml) were introduced into a round bottom flask. Then N,N'-diisoprolylocarbodiimide (Fluka) (0.015 mol) and 1 g of acidic substrates: methoxyacetic, 2-(2-methoxyethoxy)acetic or 2-[2-(2-methoxyethoxy)ethoxy]acetic acids (Aldrich) were added. The reaction mixture was heated and mechanically stirred for 4 days to give, after the filtration and washing with hot ethanol, final products 1–3 respectively.

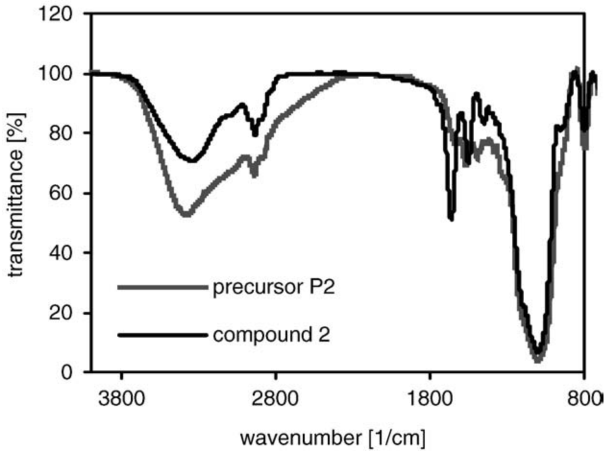

Fig. 1. FTIR spectrum of compound **2**.

Elemental analysis found: 1 N, 2.94; C, 14.01; 2 N, 2.68; C, 16.37; 3 N, 2.39; and C, 17.98.

2.2. Sample characterization

Elemental analysis of the compounds studied was carried out on a Vario ELIII (Elementar, USA) analyzer. Fourier transform infrared (FTIR) spectra of iron oxide-silica surface modified with silylating agent and compounds **1**–**3** were recorded within 400–4000 cm^{-1} on IFS 66v/s FTIR spectrophotometer from Bruker, equipped with a MCT detector (128 scans, resolution 2 cm^{-1}), in order to determine the structure of specific functional groups of precursor P2 and the compounds studied. FTIR spectra were measured for the substances pressed into KBr pellets. The surface morphology was studied in a Carl Zeiss EVO-40 scanning electron microscope, SEM (resolution 3 nm, operating voltage 80 kV).

2.3. Ultraviolet–visible experiments

The dye compounds were commercial products of Sigma (Congo red and Orange II) and Sigma-Aldrich (Fast Green) and were used without any purification. The concentration of water solutions was selected so that to obtain significant absorbance value (A) at the maximum intensity of the band (λ_{max}), (Table 2).

Complexes of compounds studied **1**–**3** with sodium cations (Na^+) were prepared by the addition of different amounts of the compounds studied (0.5–5.5 mg) to 5 ml of dye solutions and stirring the mixture for 24 h. Each sample was centrifuged and filtered before ultraviolet–visible (UV–Vis) measurements.

The absorbance of all filtrates was recorded using UV–Vis spectrophotometer from Agilent with quartz cuvette 1 cm. The spectrophotometer was interfaced with a computer operated by

Table 2
Characteristics of dye compounds.

Dye name	Molecular formula	Dye content [%]	Concentration [mol/dm^3]	Mol number in 5 ml of solution	Maximum wavelength (λ_{max}) [nm]	Absorbance (A) at λ_{max}
Congo Red	$C_{32}H_{22}N_6Na_2O_6S_2$	40	4.05×10^{-5}	0.81×10^{-7}	498	∼1.00000
Orange II	$C_{16}H_{11}N_2NaO_4S$	85	4.60×10^{-5}	1.96×10^{-7}	486	∼1.00000
Fast Green	$C_{37}H_{34}N_2Na_2O_{10}S_3$	90	0.75×10^{-5}	0.36×10^{-7}	625	∼1.00000