Fe_3O_4/SiO_2/APTMS Nanoparticles with Core-Shell Structure as Potential Materials for Cooper Removal

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In this paper the preparation and characterization of 3-aminotrimethoxysilane functionalized silica-coated magnetite nanoparticles with core-shell structure (Fe_3O_4/SiO_2-APTMS) are presented as well as the ability of these nanoparticles to remove Cu^{2+} ions from aqueous solutions. Magnetite nanoparticles (Fe_3O_4) were synthesized by the co-precipitation of $FeCl_2$ and $FeCl_3$ (1:2 molar ratio) with sodium hydroxide. To improve the chemical stability of Fe_3O_4 nanoparticles, a silica layer was coated onto the surface of magnetic nanoparticles. The SiO_2 network was obtained by the hydrolysis of a mixture of tetraethoxysilane (TEOS) and 3-aminopropyltrimethoxysilane (APTMS) at room temperature and pH = 7. The resulting nanoparticles with core-shell structure were characterized by infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), X-ray diffraction (XRD) while the ability to remove the Cu(II) ions from aqueous solution was proved by UV-Vis spectroscopy.

Keywords: magnetite nanoparticles, the silica-coated core-shell, adsorbents cooper(II) ion removal

In the last years a considerable attention has been paid to the preparation and characterization of the Fe_3O_4 nanoparticles or Fe_3O_4 based particles with core-shell structure [1]. The synthesis of these nanoparticles is justified owing to their potential to act as remarkable adsorbents for heavy metals (Cu, Pd, Co, Ni, Hg), due to their high surface area as well as the possibility to be easily and quickly removed from solution when external magnetic fields are imposed [2-5].

Although the Fe_3O_4 nanoparticles are non-toxic and could be easily synthesized by co-precipitation methods they have limited chemical and thermal stability [6]. This is why, the formation of a passive coating (inert materials such as organic or inorganic compounds, metals [7,8], including silica [9], carbon [10] and biopolymers [11–14]) on the surfaces of Fe_3O_4 nanoparticles could prevent their dissolution or aggregation in solution [15].

The purpose of this study is to obtain amino functionalized silica-coated magnetite nanoparticles with core-shell structure ($Fe_3O_4/SiO_2/NH_2$) in order to be used for heavy metals removal from aqueous solutions. The synthesis of amino functionalized silica-coated magnetite nanoparticles starts from Fe_3O_4 nanoparticles and hydrolyzed tetraethoxysilane (TEOS) and 3-aminotrimethoxysilane (3-APTMS) mixture. The SiO_2 network formation is promoted by increasing the pH increase from acidic *p*H up to slightly basic *p*H. The resulted nanoparticles with core-shell structure (Fe_3O_4/SiO_2/APTMS) were characterized by infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and transmission electron microscopy (TEM). Also, the adsorption capacity of silica-coated core-shell magnetite nanoparticles toward Cu(II) ions from an aqueous solution was studied.

Experimental part

Materials

Anhidrous iron (III) chloride ($FeCl_3$), iron (II) chloride heptahydrate ($FeCl_2 \cdot 7H_2O$), sodium hydroxide (NaOH, used for preparation of 5M NaOH solution), TEOS (tetraetoxysilan) were analytical grade and were used without further purification. Distilled water was used throughout the experiments.

Equipment

Vibrational spectra were recorded using a Shimadzu 8400 spectrometer in the wavenumbers range of 400 – 4000 cm^{-1}.

X-ray diffraction analysis was performed using a Shimadzu XRD 6000 diffractometer at room temperature. In all the cases, Cu K_α radiation from a Cu X-ray tube (run at 15mA and 30 kV) was used. The samples were scanned in the Bragg angle, 2θ range of 10 – 80^0, with a sampling interval of 0.02.

TEM measurements were performed on a Tecnai G2 F30 S-TWIN high resolution transmission electron microscope (HR-TEM) equipped with selected area electron diffraction detector (SAED). The microscope was operated in transmission mode at 300 kV while TEM point resolution was 2Å and line resolution was 1Å.

UV-Vis measurements were made using a Thermo Evolution 300 spectrometer operated in transmission or diffuse reflectance over the range of 190-1100nm.

Synthesis of Fe_3O_4/SiO_2-APTMS

Samples of 10 mL tetraethoxysilane (TEOS) were hydrolyzed under magnetic stirring with 15.5 mL deionized water, at room temperature and *p*H = 3. To this gel, 1g Fe_3O_4 (Fe_3O_4 prepared by the co-precipitation of $FeCl_2$ and $FeCl_3$ (1:2 molar ratio) with sodium hydroxide [16] (fig. 1)) and 5mL 3-aminotrimethoxysilane (APTMS) were added under vigorous stirring until a homogeneous sol is obtained.

Copper (II) removal experiments

The ability of Fe_3O_4/SiO_2-APTMS to be used for Cu(II) ions removal from aqueous solutions was tested by UV-Vis spectroscopy. With this purpose in view, an amount of 0.3g Fe_3O_4/SiO_2-APTMS was immersed in 5 mL 0.5mM $CuSO_4$ solution at *p*H=5.5 (realized with phosphate buffer) and let 1, 3, 6, 25h to interact. Then, the Fe_3O_4/SiO_2-APTMS

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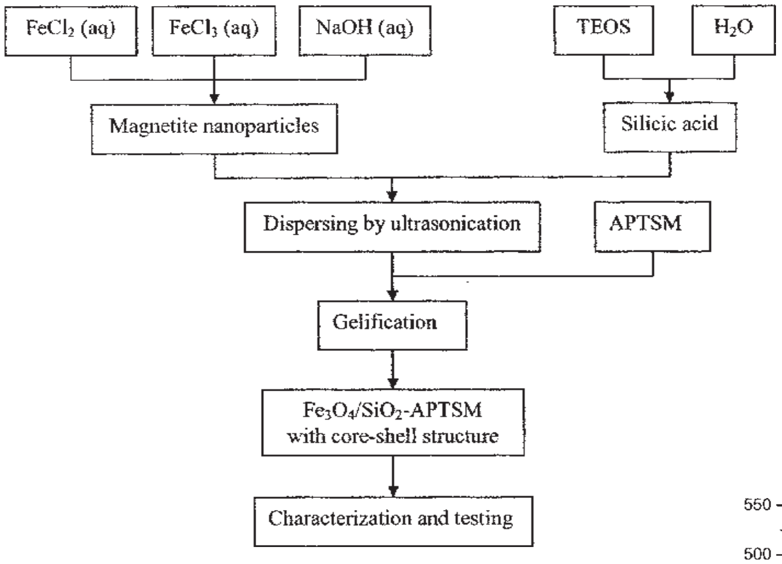

Fig. 1. Fe_3O_4/SiO_2-APTMS synthesis flow chart

beads are magnetically removed and the concentration of solution before and after Cu(II) retention is analyzed by UV-Vis spectroscopy. The calibration curve is presented in figure 2. For this purpose 5 solutions having 0.01, 0.05, 0.1, 0.5 and 1mM Cu(II) ion concentration and *p*H=5.5, each of 5 mL volume, were prepared and mixed with 1mL NH_3 25%. The absorbance of each standard was measured at 650 nm wavelenght.

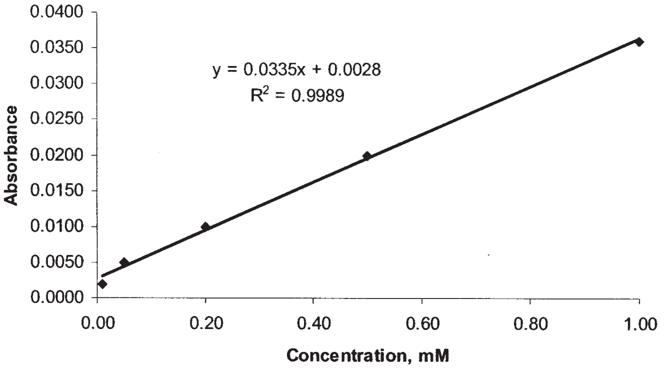

Fig. 2. Calibration curve of copper, at 650nm

Results and discussion

XRD measurements

The structure of Fe_3O_4, Fe_3O_4/SiO_2 and Fe_3O_4/SiO_2-APTMS were analyzed by XRD spectroscopy. The XRD pattern (fig. 3) of Fe_3O_4 exhibits only the characteristic peaks of cubic magnetite (ASTM 0075-1609) and consequently proves its purity. The XRD pattern of the Fe_3O_4/SiO_2 and Fe_3O_4/SiO_2-APTMS exhibit the most important peaks of the magnetite together with the typical broad peak of amorphous SiO_2. It has to note that the addition of the APTMS in the synthesis step of amino functionalized Fe_3O_4/SiO_2 (Fe_3O_4/SiO_2-APTMS) induces a slight shift of the characteristic amorphous SiO_2 peak from 2Theta = 22.78 to 22.2^0 which means a small increase of the interplanar distance, that is probably due to the presence of the functional group.

IR measurement

Infrared spectrum of the synthesized Fe_3O_4/SiO_2-APTMS (fig. 4) exhibits the characteristic peaks of Fe_3O_4 and SiO_2 as well as the propylamino moiety of the APTMS functionalizing agent. Magnetite absorbs at 445 and 568 cm^{-1}, these absorption bands are attributed to the torsional vibration and stretching mode of the Fe-O bond from Fe_3O_4 [17]. Silica absorbs at 779, 1047 and 1129cm^{-1} corresponding to the stretching of Si–O–Si bond from the silica particles [18]. In fact, the overlapped bands between 830 and 1300cm^{-1} are due to the obtained Si–O–Si networks with different polycondensation and or protonation degree. The variation of polycondensation degree is mainly due to the presence of the two silica network precursors, TEOS and APTMS, whereas the variation of protonation degree of the hydrosilicates is due to the incomplete condensation of Si-OH groups. The primary amino groups absorb at 779, 1333, 1378, 1586 and 1770 cm^{-1} while the propylene groups are visible especially at 2935cm^{-1}. Due to the very complex system, many peaks are overlapped not only in the 830 – 1300 cm^{-1} region.

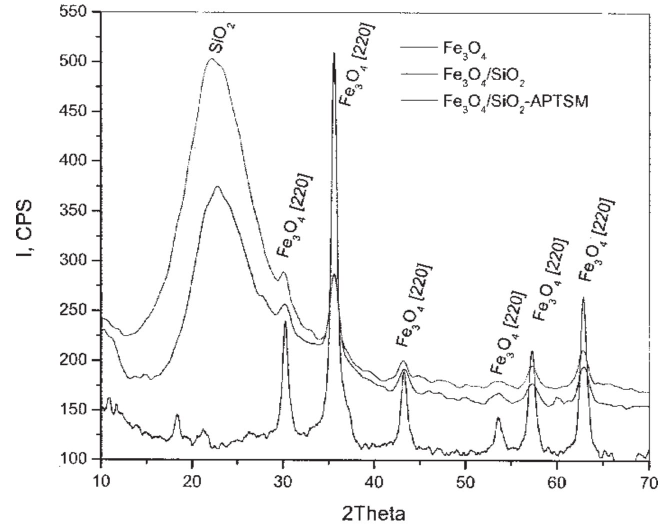

Fig. 3. XRD patterns of Fe_3O_4, Fe_3O_4/SiO_2 and Fe_3O_4/SiO_2-APTMS

TEM measurement

The transmission electron microscopy images (fig. 5 a, b) allow the determination of the size of the Fe_3O_4/SiO_2-APTMS particles as well as the core shell nature of this material. The mean diameter of the spherical Fe_3O_4/SiO_2-APTMS nanoparticles is less than 20-25nm. The core-shell structure of the Fe_3O_4/SiO_2-APTMS nanoparticles consists in the magnetite core (darker regions) being well embedded into silica network (lighter regions). Analyzing the selected area electron diffraction – SAED pattern (fig. 5c, d), even if the magnetite is present, the interferences of magnetite are less important (comparing with the SAED pattern of pure magnetite) due to the presence of the SiO_2 shell.

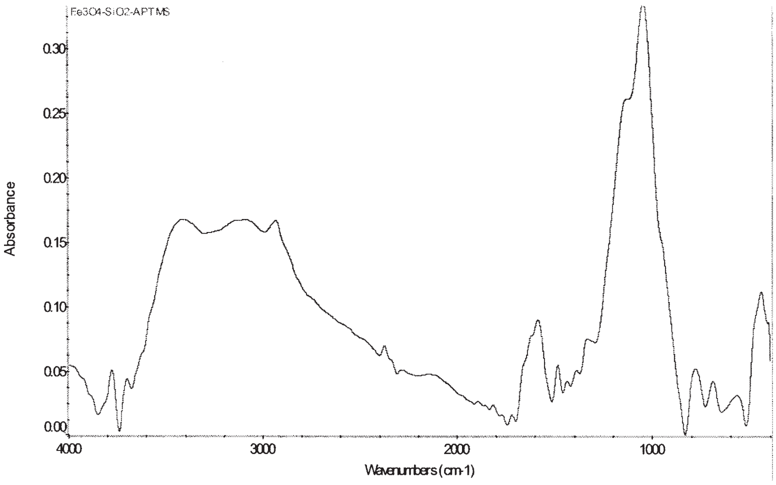

Fig. 4. FTIR spectrum of the synthesized Fe_3O_4/ SiO_2-APTMS

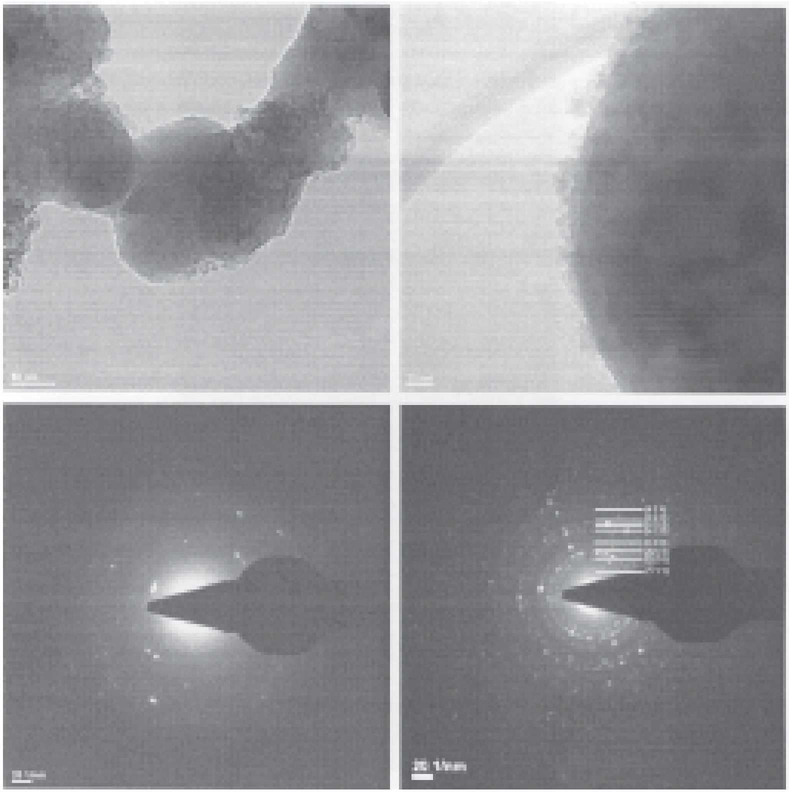

Fig. 5. a,b) TEM images, c) SAED pattern of Fe_3O_4/SiO_2-APTMS and d) SAED pattern of Fe_3O_4

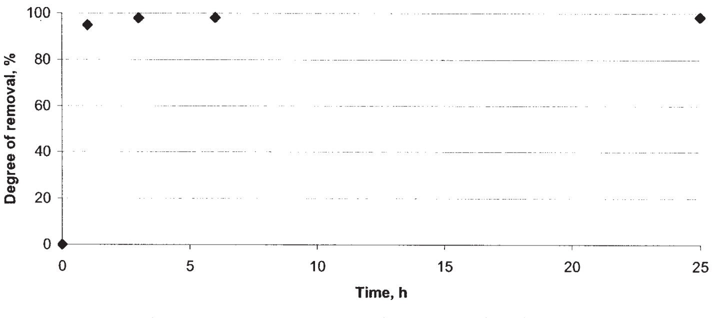

Fig. 6. Copper removal using Fe_3O_4/SiO_2-APTMS

Table 1

SPECTROPHOMETRIC DATA OF Cu(II) ION REMOVAL BY USING Fe_3O_4/SiO_2-APTMS

Time, h	A	C, mM	Degree of removal, %
0	0.0196	0.5003	0.00
1	0.0037	0.0260	94.81
3	0.0032	0.0111	97.78
6	0.0032	0.0104	97.91
25	0.0031	0.0100	98.00

Tests of Cu(II) ion removal capacity

Analyzing the concentration of the Cu^{2+} ions in the aqueous solution it can be noticed that the Fe_3O_4/SiO_2-APTMS magnetic system has the capacity to retain divalent ionic species of cooper. It can be stated that almost 95% of the total content of Cu^{2+} ions is removed in 1h treatment (fig. 6). The obtained results are listed in the Table 1. The results are mean values of triplicate experiments.

The removal capacity of the Fe_3O_4/SiO_2-APTMS core-shell system can be determined as a ratio between the quantity of the retained Cu(II) ions (mg) and the quantity of Fe_3O_4/SiO_2-APTMS core-shell system (g). The total removal capacity of Cu^{2+} of the Fe_3O_4/SiO_2-APTMS core-shell system is about 62 mg Cu^{2+}/g Fe_3O_4/SiO_2-APTMS; this value was determined by immersing for 1 h 0.1g Fe_3O_4/ SiO_2-APTMS in 5 mL of 0.5M $CuSO_4$ solution.

Conclusion

The synthesis of a new Fe_3O_4/SiO_2-APTMS core-shell system was presented. This Fe_3O_4/SiO_2-APTMS core-shell system was characterized from compositional and morphological point of view as well as from the point of view of removal capacity of Cu(II) ions from aqueous solutions.

Besides the very good affinity the kinetic of removal is also very important. Based on the presented data it can assume that the Fe_3O_4/SiO_2-APTMS magnetic system can be used for the Cu(II) ion removal from aqueous media. The removal of the Cu(II) ions has a fast kinetic, needing 1h for ~95% removal of Cu^{2+} (for a solution of 0.5M Cu^{2+}). The maximum copper removal capacity of this Fe_3O_4/SiO_2-APTMS system is 62 mg Cu^{2+}/g Fe_3O_4/SiO_2-APTMS.

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