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SYNTHESIS AND CHARACTERIZATION OF A NEW MAGNETIC MATERIAL JOIN TO GRAPHENE OXIDE AS SORBENT

Abstract:

The synthesis and characterization of new adsorbents is addressed in this work. This material is based on the coupling of magnetic nanoparticles and graphene oxide (MNPs@GO). Graphene oxide (GO) presents a high surface area to volume ratio, and high rate of diffusion in water. However it is tedious and difficult to separate GO from the aqueous solution. The coupling with magnetic nanoparticles provides an easy magnetic separation. Thus, MNPs@GO has demonstrated to be an excellent adsorbent material towards to organic compounds but not to ionic metals. For this reason, a chelating group is attached to the material surface: [1,5-bis(2-pyridyl)-3-methylene] thiocarbonohydrazide (DPTH) in order to increase the selectivity for metal ions. To establish which is the best route of synthesis, two different strategies were designed (method 1 and method 2). The two new materials obtained, called DPTH(1) and DPTH(2), were characterized and their properties as extractants were studied. Several analytical techniques were used to characterize them; TEM, XPS, CNHS elemental analysis and FT IR. To conclude, the DPTH(2) showed better properties as extractant, even at trace levels.

Keywords:

Solid-phase extraction, magnetic nanoparticles, graphene oxide, chelating functional groups, TEM, XPS, IR

JEL Classification: Q53, L65, Q56

1. INTRODUCTION

This paper studies and compares two different routes to fabricate innovative magnetic nanomaterials. These innovative magnetic materials were designed to allow the analysis of both toxic elements (heavy metals) and elements of industrial interest (noble metals) in environmental samples.

Heavy metals are related to high toxicity, for example, mercury and arsenic [1]. The main heavy metal emission points are rocks weathering and fossil fuels combustion [2]. This group is found in nature at trace levels. The available information about noble metals emissions and toxicity are discussed in several review papers [3,4]. Besides, some noble metals elements such as Ag, Au, Pt, and Pd are uncommon in the crust [5]. The main noble metal emission points are the jewellery industry and catalysis. In ecosystem, these metals can become toxic substances because of the reaction with certain substances such as chlorides. Furthermore, the materials could be used for their recovery due to the economic and industrial interest. For these reasons, the development of effective methods for extraction, preconcentration and determination of heavy metals [6] and noble metals is necessary.

A new adsorbent based on the coupling of magnetic nanoparticles (MNPs) and graphene oxide (GO) is proposed. GO is a novel two-dimensional carbon-based nanomaterial, which presents numerous oxygen-containing groups and a large surface area. These properties make it ideal for retention of analytes compared to carbon nanotubes or graphene [7-9]. As a result, a hydrophilic character is provided, resulting in high sorption capacity and selectivity for the retention and preconcentration of heavy metal ions [10,11]. On the other hand, iron oxide MNPs (Fe_3O_4) have been exploited as a solid phase material due to its biocompatibility, degradability, physiological and chemical stability, low toxicity and high magnetic response [12,13]. This last property allows a variation of classical SPE denominated magnetic solid-phase extraction (MSPE). This consists of the suspension of magnetic material into the solution which contains the analytes, providing time for the adsorption over the magnetic material and, finally, recovering it with the application of an external magnetic field. The use of classical separation processes such as filtration and centrifugation are avoided [14-16]. Furthermore, the coupling favours the dispersion over GO layer and avoiding the agglomeration [17], which could decrease the specific surface area. However, both MNPs and GO, are not selective materials. So, a chemical factor needs to be added to increase the selectivity of the coupling to metals, the anchoring of a functional group, [1,5-bis(2-pyridyl)3-methylene] thiocarbonohydrazide (DPTH) which can act as chelating agent. Besides, this functional group can be attached to MNPs (method 1) or GO (method 2). Both possibilities were studied, designing two different synthesis routes to be conducted and compared (fig. 1A, 1B).

(A)
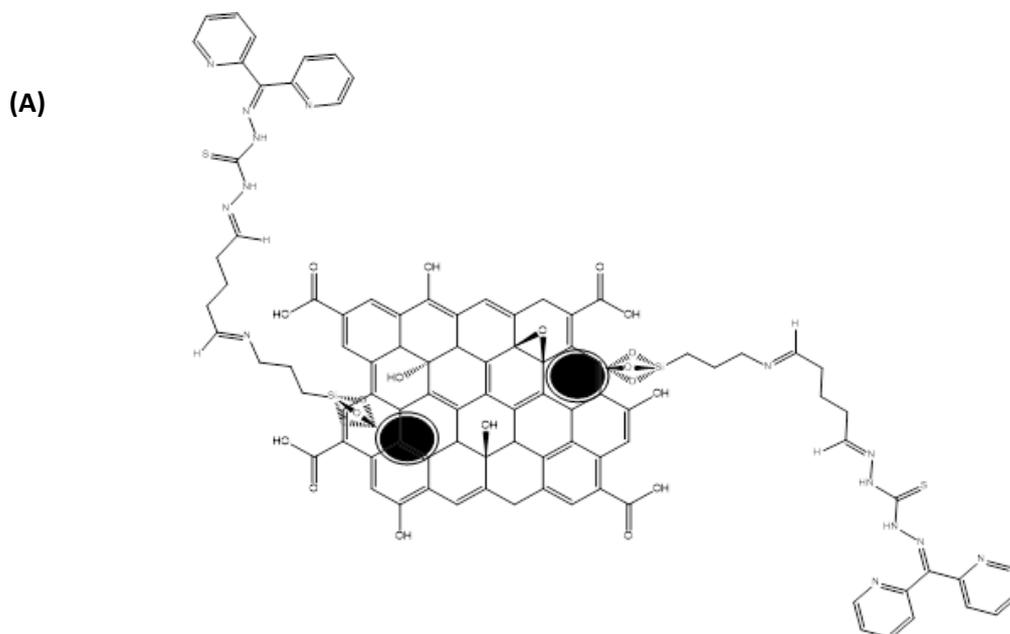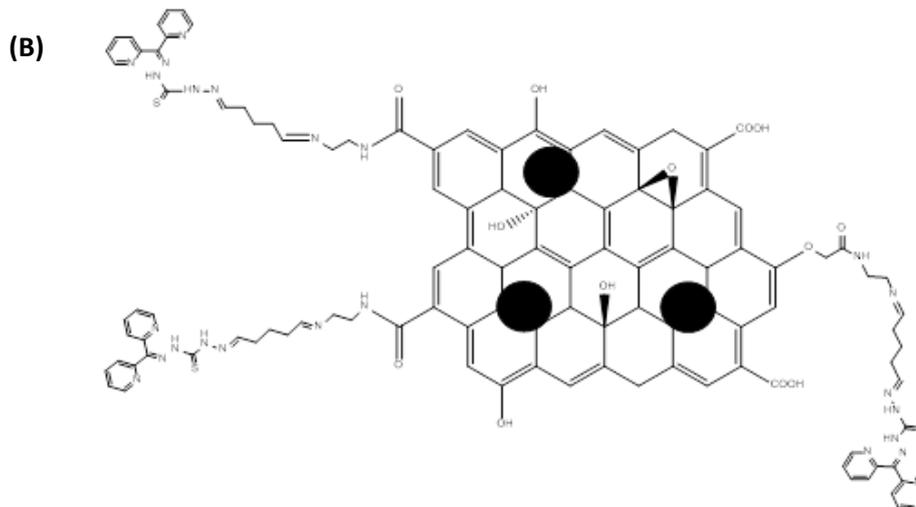
FIGURE 1 Magnetic nanomaterial structure fabricated by (A) method
1 and (B) method 2.

2. EXPERIMENTAL

2.1 Instrumentation

IR Spectra were recordered on a Perkin Elmer Spectrum 100 FTIR spectrometer (Perkin Elmer, Concord, Canada), samples were measured by using potassium bromide pellets, in which the concentrations for the samples were 0.5 % (wt/wt) approximately. XPS analysis was performed with a Physical Electronics ESCA 5701 instrument; binding energies (BE) were observed considering the position of the C 1s peak at 284.8 eV. The residual pressure in the analysis chamber was maintained below 3×10^{-9} Torr during data acquisition. The microstructures of the new functionalized MNPs were observed and studied by transmission electron microscopy (TEM, JEOL, JEM-1400). The composition of the materials (C, N, S, Fe) was studied by CHNS elemental analysis (TruSpec Micro CHNS) and the content in Fe was measured with an Analytikjena contrAA 700. The adsorption capacity of the resin was determined by a Perkin-Elmer NexION 2000 inductively coupled plasma mass spectrometer (ICP-MS).

2.2 Reagents and solutions

All the reagents used were of analytical reagent grade. Standard solutions of 1000 mg/L of Cr, Co, Ni, Cu, As, Cd, Hg, Pb, Bi, Pd, Ag, Pt and Au were purchased from Merck (Darmstadt, Germany). Working solutions were prepared by appropriate dilution of the stock solution with double distilled water (18 MΩ cm) prior to use. The graphite powder and sodium chloroacetate were procured from Merck (Darmstadt, Germany). For the synthesis of MNPs, ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ammonium hydroxide 30% (wt/wt), methanol and sodium chloride from Merck (Darmstadt, Germany) were used. Ethylenediamine (EDA) and N,N'-dicyclohexylcarbodiimide (DCC) were purchased from Aldrich Chemie (Steinheim, Germany).

2.3 Synthesis of graphene oxide

Exfoliation process described by Diagboya et al [18] was used to prepare GO from natural graphite, being purified by several centrifugation cycles.

2.4 Capacity of adsorption

For the study of the capacity of adsorption, samples were prepared mixing 5 mg of the magnetic material and 50 mL of Cd, Co, Cu, Ni, Hg, Pb, Pt, Pd, Ag and Au 50 μg/L. Both synthesized resins were studied at pH 5 and pH 8. The pH was adjusted using pH 5 buffer (acetic acid/sodium acetate) and pH 8 buffer (boric acid/borax). The suspensions were stirred for 10 min. The highest capacity of adsorption that could be obtained was 0.5 mg/g resin.

2.5 Synthesis of MNPs-GO

Method 1.

The synthesis and functionalization of MNPs were discussed in elsewhere [19]. The magnetic materials synthesized following the method 1 (Fig. 1) and method 2 (Fig. 2) were functionalized with the chelating functional group, and called DPTH (1) and DPTH (2), respectively. The structure of DPTH is shown below (Fig. 4).

FIGURE 4 DPTH structure joined to MNPs

Then, 500 mg of GO and 500 mg of functionalized MNPs were mixed in water and stirred for 10 minutes. The mix is incubated at 65ºC for 8h. The Fe_3O_4 decorated GO suspension was cooled to room temperature and separated from the solution with the aid of external permanent magnet, washed with deionized water and ethanol. Finally, the precipitate was dried at 80ºC for 24h [20].

Method 2. 300 mg of GO was suspended in 300 mL of deionized water. The mix was sonicated 15 minutes and 1.5 g of NaOH was injected. Then, 1.5 g of $Cl-CH_2COONa$ was added in order to convert hydroxyl and epoxy groups in carboxylic groups, and the mix was stirred 2h [19]. The modified GO was separated from the suspension using centrifugation cycles and washed with water. The etilendiamine (EDA) was coupled in situ with GO through the carboxylic groups of the modified GO using DCC as a coupling agent. The suspension was stirred for 48 h at 50°C. Finally, GO-EDA was separated from the suspension using centrifugation cycles and washed with water.

The prepared GO-EDA sheets were then made magnetic by adding slowly a 35 ml aqueous solution of mixed $FeCl_3 \cdot 6H_2O$ (1.10 g) and $FeCl_2 \cdot 4H_2O$ (0.43 g) into the GO suspension (300 mg of GO-EDA in 200 mL) at 80 °C, and then 5 mL of 30 % ammonia solution was added quickly for the co-precipitation of Fe_3O_4 nanoparticles on GO sheets in N_2 atmosphere. After being rapidly stirred for 45 min, the resultant Fe_3O_4 decorated GO suspension was cooled to room temperature and separated from the solution with the aid of external permanent magnet, washed with deionized water and kept in ethanol for further functionalization.

3. RESULTS AND DISCUSSION

3.1 Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra shows two characteristic broad bands appeared at 3423 cm^{-1} and 3368 cm^{-1} corresponding to structural O–H (−COOH and –COH) stretching vibrations of GO. Other peaks at 1714 cm^{-1} and 1699 cm^{-1} were associated with C=N stretching vibration of imine bond. The spectrum also showed peaks at 632 and 588 cm^{-1} due to Fe-O stretching vibrations. The peaks at 1130 and 1412 cm^{-1} were assigned to C=S stretching, and confirm the immobilization of DPTH onto GO sheets. In DPTH (2) spectrum a band at 1206 cm^{-1} associated with (C-O-C) as stretching was also assigned, not being found in DPTH (1). That confirms the addition of ClCH$_3$COONa to the structure in order to increase the amount of –COOH functional group over the GO sheet (modified GO).

3.2 Transmission electronic microscopy (TEM)

The surface morphology of the prepared materials (DPTH(1) and DPTH(2)) was characterized by TEM. TEM images showed that Fe$_3$O$_4$ nanoparticles are disorderly dispersed onto a GO sheets with an approximate diameter of 13 nm (fig. 2A, 2B).
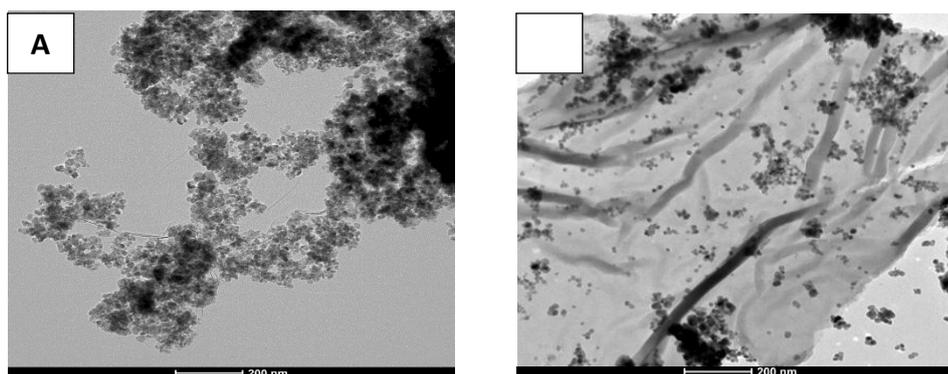
FIGURE 2 TEM images of A) DPTH(1) and B) DPTH(2) with a scale of 200 nm.

3.3 Elemental analysis and X-ray photoelectronic spectroscopy (XPS)

CNHS elemental analysis confirmed the incorporation of S in DPTH with 0.33% and 2.02% of S in DPTH(1) and DPTH(2), respectively. Furthermore, the higher amount of S in DPTH(2) indicated the better functionalization of this resin.

TABLE 1 Elemental composition of the materials.

Sample	% C	% S	% N	% Fe
1-DPTH	8.681	0.121	0.657	51
2-DPTH	27.046	1.087	4.638	46

The surface composition of DPTH(1) and DPTH(2) was studied by XPS. The XPS spectrum at the sulphur energy showed two oxidation states in both materials (Fig. 3) due to the presence of a C=S bond tautomeric equilibrium (C=S/C-SH) [6]. In the case of DPTH(2) (Fig. 3B) the peak situated in a

lower bind energy (C-SH bond) clearly present a higher intensity in comparison with the equivalent peak in DPTH(1) (Fig. 3A). It can be concluded that the tautomeric equilibrium is displaced to the tautomeric C-SH form when the materials are synthesized by method 2. The main explanation for this fact is the presence of electronic interactions between the π-π system of GO and the aromatic system of the functional groups, favouring the tautomer with the most extended electronic system. This effect is stronger when the DPTH are close to the GO sheet, as in the case of the functionalization through the -COOH groups of the GO sheet (method 2). In method 1, the functional groups are attached to the MNPs, resulting in a greater distance between the electronic systems.
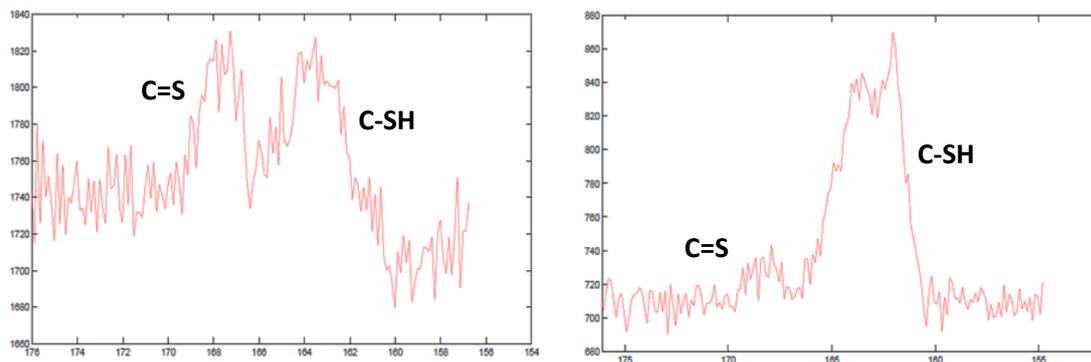
FIGURE 3 XPS spectra of DPTH(1) (A) and DPTH(2) (B).

3.4 Study of absorption capacity of magnetic functionalized materials

The capacity of adsorption toward to 10 elements was studied. The sorption capacity of the resin was determined in batch by ICP-MS. The results were showed in Tables 2A and 2B. From these results could be stablished that a greater amount of heavy metals was absorbed by DPTH(2) at the two pHs. Noble metals were adsorbed more effectively at acid pH for the two resins.

TABLE 2 Capacity of adsorption of resins at (A) pH 5 and (B) pH 8.

pH 5 (A)	DPTH(1) (mg/g)	DPTH(2) (mg/g)	pH 8 (B)	DPTH(1) (mg/g)	DPTH(2) (mg/g)
Co	0.03	0.00	Co	0.03	0.27
Ni	0.02	0.00	Ni	0.01	0.28
Cu	0.00	0.18	Cu	0.00	0.27
Cd	0.00	0.09	Cd	0.00	0.44
Hg	0.29	0.46	Hg	0.26	0.17
Pb	0.03	0.40	Pb	0.03	0.21
Pd	0.49	0.21	Pd	0.32	0.05
Ag	0.23	0.39	Ag	0.04	0.11
Pt	0.46	0.31	Pt	0.25	0.00
Au	0.33	0.32	Au	0.46	0.00

4. CONCLUSIONS

In this paper two mechanisms for the functionalization and coupling of magnetic nanoparticles and graphene oxide (MNPs-GO) were discussed. For the synthesis of DPTH by the method 1, silica covered MNPs were functionalized and after, were dispersed on GO. For DPTH method 2 synthesis, MNPs were coprecipitated into GO-EDA sheets and after, the functionalization of these sheets was conducted. The new materials were characterized, and the capacity of adsorption towards 10 elements were studied (transition and noble metals). Finally, it can be concluded that the best yields were obtained with the second procedure of synthesis. Besides, DPTH (2) showed higher capacity of adsorption for the studied elements.

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