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Facile synthesis of cysteine functionalized magnetic graphene oxide nanosheets: Application in solid phase extraction of cadmium from environmental sample

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ABSTRACT

A facile method for synthesis of cysteine functionalized magnetic graphene oxide nanosheets is introduced. In comparison with other metal ions, cysteine has more affinity to coordinate with cadmium, therefore, the modified graphene oxide nanosheets were used as a selective sorbent for solid-phase extraction and determination of trace cadmium in different food samples (rice, wheat, milk and shrimp). Satisfactory recoveries were obtained by using 0.8 mg mL^{-1} of sorbent in a pH range of 5–9. The results showed good adsorption capacities (24.39–30.30 mg g^{-1} at 298–328 K) of the adsorbent with the high selectivity toward cadmium ions. The process was relatively fast and the equilibrium was established within 5 min and its kinetics followed the pseudo-second order mechanism. The best interpretation for the equilibrium data was given by Langmuir isotherm and the thermodynamic parameters showed that the adsorption process was spontaneous, endothermic and chemical in nature.

1. Introduction

Heavy metals contamination is known to be a significant problem, which threatens the environment and human life. The main threats to human health from heavy metals are associated with exposure to lead (Pb), cadmium (Cd), mercury (Hg) and arsenic (As) [1–3]. Cd and its compounds are highly toxic and exposure to this metal is known to cause cancer and targets the body's cardiovascular, renal, gastrointestinal, neurological, reproductive and respiratory systems [4–6]. It is considered more toxic than either lead or mercury. The most common sources of Cd toxicity are foods such as rice and wheat which are grown in soil contaminated by sewage sludge, super phosphate fertilizers and irrigation water. Ocean fish such as tuna, codfish and haddock concentrate within their tissues relatively large amounts of Cd. Therefore, the effective removal of Cd from the environmental, biological and food samples has been a crucial issue related to the quality of human life.

Several analytical methods including inductively coupled plasma optical emission spectrometry, inductively coupled plasma-mass spectrometry, flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry and graphite furnace atomic absorption spectrometry, have been proposed for the determination of Cd in various matrices [7–17]. However, the direct determination of this metal in real samples with above techniques was very difficult in most cases, because of matrix effect and low existing level. Under these circumstances, in order to determine trace levels of Cd a separation and enrichment step prior to the determinations may be beneficial. For this purpose, several methods have been applied, including, liquid–liquid extraction, cloud point extraction, liquid-phase microextraction and solid-phase extraction [18–23]. Among these techniques, solid-phase extraction (SPE) as a popular technique for achieving separation and preconcentration of metal ions in environmental samples has been developed and widely used because of its high enrichment factor, simple operation, minimal cost, reusability of the adsorbent and the ability to combine with different detection techniques whether in on-line or off-line mode [23–26]. In this sense, graphene, a single layer of sp^2 bonded carbon atoms in a two-dimensional hexagonal lattice, has been attracted more attentions due to its physico-chemical properties, such as a large surface area, high dispersibility and hydrophilicity [27–29]. However, it is easy to aggregate, which will lead to great reduction in the surface area and the adsorption. Therefore, chemical modification of graphene is imperative. In comparison with

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graphene, graphene oxide (GO) has oxygen containing groups such as epoxides, hydroxyl, carboxyl, and carbonyl on its surface. These functional groups may serve as binding sites for metal ions. However, unfunctionalized GO doesn't have enough selectivity for efficient removal of heavy metals and also, the oxygen-containing functional groups cannot provide strong coordination with metals ions. In order to further improve selectivity and adsorption properties, various graphene-based nanocomposites have been fabricated by chemical modification of GO [30–34]. Moreover, it is difficult to separate graphene or GO from aqueous solution via traditional centrifugation and filtration method because of its small particle size. Therefore, magnetic graphene based adsorbents that facilitate separation by magnetic field have begun to be used in the field of environmental remediation [35–40].

Owing to the exceptional characteristics of amino acids (such as: relatively high affinity to metal ions, biocompatibility, structural flexibility and durability and also, significantly lower material and manufacturing cost) these compounds can be used as a suitable ligand in extraction of heavy metals from different media [41–43]. Cysteine, a nonessential, water-soluble, sulfur-containing amino acid with three functional groups (—SH, —NH_2,—COOH), has a strong tendency to coordinate with Cd^{2+} ions [44,45]. Herein, we report the synthesis, characterization and application of cysteine functionalized magnetic GO (Cys-MGO) nanosheets as a selective sorbent for solid-phase extraction and determination of Cd in rice, wheat, milk and shrimp samples.

2. Experimental

2.1. Apparatus and reagents

Graphite powder (diameter <150 mm and purity 99.99% trace metals basis, Sigma–Aldrich Co.) and cysteine (purity 97%, Sigma–Aldrich Co.) were used to prepare the cysteine functionalized graphene oxide. Other chemicals used in this study were purchased from Merck Chemical Co. with analytical grade and were used without further purification. Ultrapure water (Millipore) was used throughout the whole experiments.

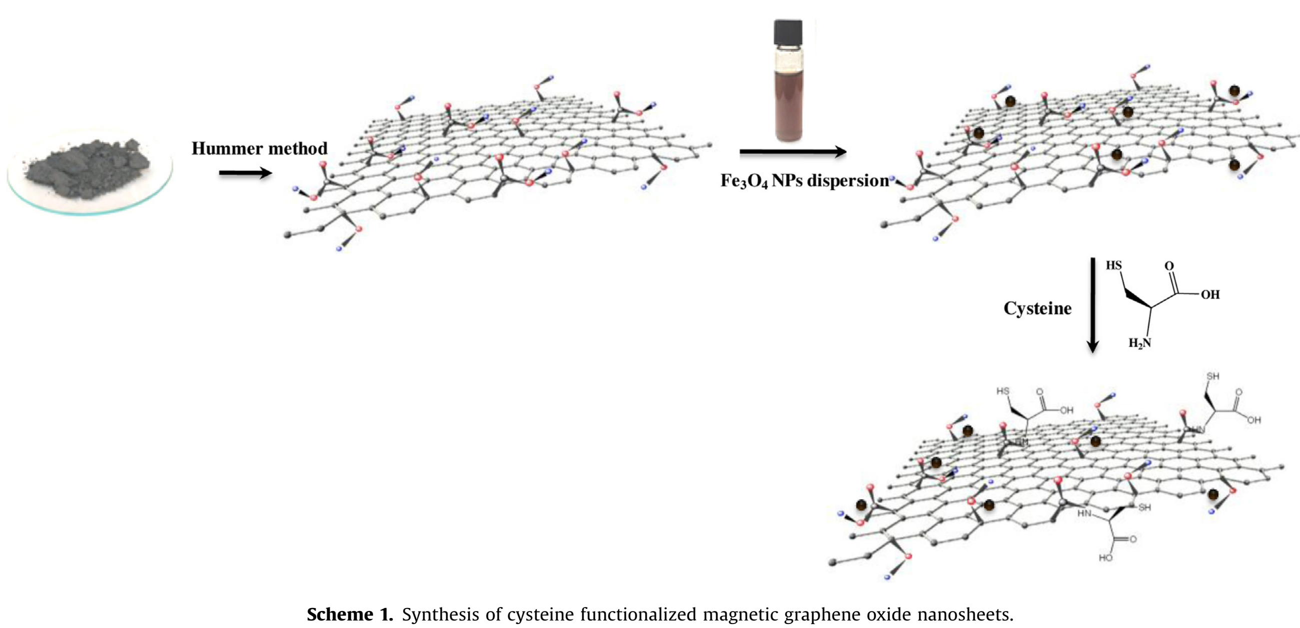
The structure and morphology of cysteine functionalized magnetic GO nanosheets were characterized by X-ray diffraction (XRD-D8, BRUKER) and transmission electron microscopy (TEM-CM10, Philips). Magnetic properties were investigated by using a vibrating sample magnetometer (VSM) with an applied field between −10,000 and 10,000 Oe at room temperature (MDKF, Iran). Thermogravimetric analyses (TGA) were carried out with thermogravimetric analyzer (STA 503, Bahr, Germany) at a heating rate of 10 °C/min under N_2 flow (10 mL/min). ICP-OES spectrometer (Thermo Scientific, IRIS Intrepid II, USA) were used for measuring the concentrations of elements. Microwave digester (Milestone, Japan) was used to digest the samples and temperature was controlled by use of an ATC-400CE inner temperature sensor probe.

2.2. Synthesis of cysteine functionalized magnetic GO nanosheets

Graphite oxide was synthesized using the harsh oxidation of graphite according to the modified Hummers method [46]. Briefly, graphite powders (1 g) were sonicated in concentrated H_2SO_4 (22 mL) for 30 min. while keeping the temperature below 20 °C by using an ice bath, $KMnO_4$ (3 g) was gradually added with stirring. The mixture was then stirred at 35 °C for 2 h. The resulting solution was diluted by adding 50 mL of water under vigorous stirring and was kept for 15 min. The reaction was terminated by adding 150 mL of distilled water followed by 10 mL of 30% H_2O_2 solution. The graphite oxide precipitate was separated by centrifugation, washed repeatedly with 5% HCl solution and then with distilled water until the pH of the solution became neutral and was kept in an oven at 80 °C for 48 h to complete drying.

Magnetic GO (MGO) nanosheets were fabricated according to Han et. al [47]. First, graphite oxide (100 mg) was dispersed in deionized water under sonication for 1 h for the exfoliation of the graphitic oxide into a GO monolayer. At the same time, 100 mg of Fe_3O_4 MNPs which were prepared via the co-precipitation method [48], were suspended in 0.1 M HNO_3 solution (100 mL). Next, the obtained positive surface charge Fe_3O_4 MNPs was added to the GO dispersion under sonication. After 1 h, the resulting nanocomposites were collected by using an external magnet and dried at 60 °C in vacuum oven.

Cys-MGO nanosheets were synthesized by facile and green procedure [49]. Briefly, MGO (100 mg) was dispersed in distilled water (100 mL) and 10 mL of cysteine solution (20 mg mL^{-1}) then was added. After addition an equimolar amount of NaOH, the mixture was sonicated for 1 h at room temperature. The resulting nanocomposite was centrifuged, washed well with H_2O/EtOH



Scheme 1. Synthesis of cysteine functionalized magnetic graphene oxide nanosheets.