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Microwave assisted carbon modification of magnetite nanoparticles, used for solid phase extraction of trace elements

D. H. Sánchez[1], D. L. Georgieva[2*], V. J. Kmetov[2], V. M. Stefanova[2]

[1]*University of Alicante; PO Box 99, 03080 Alicante, Spain*

[2]*Department of Analytical chemistry and computer chemistry, University of Plovdiv,*
24 "Tzar Assen" Str., Plovdiv 4000, Bulgaria

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The carbon encapsulated magnetic nanoparticles (MNPs) have high potential as a sorbent for solid phase extraction (SPE) of organic and inorganic compounds. Carbon is an excellent material for MNPs core-shell modification due to its chemical stability, biocompatibility, and possibility for further surface modification. This coating improves the stability of magnetic nanoparticles and introduces new surface properties that could facilitate their application.

A new microwave-assisted procedure for carbon coating of magnetite nanoparticles by hydrothermal route is presented. The Fourier transform infrared spectroscopy with attenuated total reflection (ATR-FTIR) was used for surface characterization of produced Fe_3O_4@C NPs.

The carbon coated nanoparticles were tested as sorbent for SPE of V, Cr, Co, Ni, Cu, Zn, Cd, Tl and Bi from model solutions. The inductively coupled plasma quadrupole mass spectrometer (ICP-MS) was used for SPE optimization studies.

Key words: *magnetic nanoparticles, MW-assisted carbon coating, SPEIntroduction*

The magnetic nanoparticles MNPs are attractive new material as a sorbent for solid phase extraction of different compounds [1, 2]. Compared to other nano-sized materials the use of MNPs allows to simplify the extraction process and saves time as a result of their isolation from the sample matrix by an external magnetic field. For the purpose of magnetic assisted SPE, iron oxides nanoparticles (Fe_3O_4 and Fe_2O_3 [2]) or different types of ferrites ($MnFe_2O_4$ [3], $CoFe_2O_4$ [4]) are commonly used. The application of bare MNPs for extraction of trace elements is limited, due to their instability in acidic solutions [3]. One approach to overcome this drawback is to protect the magnetic core with resistant layer (commonly SiO_2) [5]. Carbon is also excellent material for MNPs core-shell modification due to its chemical stability, biocompatibility, and possibility of further surface modification. Carbon coating improves the stability of magnetic nanoparticles, but also introduces new surface properties, that could facilitate their application or further modification.

Carbon encapsulated magnetic materials were previously used for SPE of trace elements [6, 7], organophosphorus pesticides [8], polycyclic aromatic hydrocarbons (PAHs) [9, 10], etc.

The synthesis of MNPs@C is attracting a lot of attention and interests from scientists and a few strategies were reported to prepare MNPs@C [1]. Different synthesis routes of carbon-coating, are reported including arc discharge [11], thermal chemical vapour condensation (TCVC) [12], pyrolysis [13], and hydrothermal reactions [14–17]. The latter does not require special reagents (the carbon precursor usually is glucose), but a special equipment (autoclaves) is needed and it consumes time (3 to 14h) and energy.

According to Wang *et al* [17] for effective construction of carbon layer on magnetite nanoparticles, a preliminary modification with oleic acid is required. The authors compared TEM images of the products from classical hydrothermal reaction with glucose where Fe_3O_4 nanoparticles were added in absence of any additional surface modification and after oleic acid treatment. Authors declare that according to TEM characterization Fe_3O_4 nanoparticles without any surface modification cannot be incorporated into carbon sphere and the final product mainly consists two kinds of particles, ones is carbon nanospheres and the others are free Fe3O4 nanoparticles [17].

In the present work, a new route for MW assisted hydrothermal synthesis of carbon-coated Fe_3O_4 nanoparticles is investigated. Two types of magnetic cores (bare and oleic acid stabilised) were studied as precursors for Fe_3O_4@C NPs production.

MATERIALS AND METHODS

Reagents

All reagents were analytical or suprapur reagent-grade. Ferric chloride ($FeCl_3{\cdot}6H_2O$), ferrous

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[*] To whom all correspondence should be sent.
E-mail:georgieva@uni-plovdiv.net

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chloride ($FeCl_2 \cdot 4H_2O$), were used for NPs synthesis, as well as Glucose monohydrate ($C_6H_{12}O_6 \cdot H_2O$), Oleic acid and 2-(2,4-Dihydroxy-phenylazo) thiazole (TAR), were used for surface modification. All were purchased from Sigma Aldrich Company (Milwaukee, WI, USA). Other reagents, including ammonia solution (25%) for magnetic NPs precipitation; KCl for pH zero charge determination; and HNO_3 (65%) for model solution conservation and carbon encapsulated NPs stability test, were from Merck (Darmstadt, Germany). Double distilled water was used for the preparation of all solutions.

After appropriate dilution, ICP multi-element standard solution 28 elements 100 mg L^{-1} (CPA, Bulgaria), was used for SPE procedure optimization. Single element solution of Rh 10 mg L^{-1} (Fluka Chemie GmbH, Buchs, Switzerland) was used as internal standard during ICP-MS determination.

Instrumentation

An inductively coupled plasma quadrupole mass spectrometer ICP-MS Agilent 7700 (Tokyo, Japan) with octopole reaction system (He collision gas flow 4.0 mL min^{-1}) was used for SPE optimization studies. The instrumental parameters were as follow: RF power 1.5 kW; plasma, auxiliary and nebulizer Ar gas flow rates: 15 L min^{-1}; 0.9 L min^{-1} and 0.95 L min^{-1} respectively; sample flow rate 0.34 mL min^{-1}; MicroMist nebulizer. Fifteen isotopes: ^{51}V, ^{53}Cr, ^{59}Co, ^{60}Ni, $^{63,65}Cu$, $^{66,68}Zn$, $^{111,114}Cd$, ^{205}Tl, $^{206,208}Pb$, ^{209}Bi and ^{103}Rh (as internal standard) were monitored at 1 point per mass peak with 100 ms acquisition time with five replicates for each measurement.

For characterization of carbon coated magnetic NPs, ATR-FT-IR Bruker Vertex 70 (Bruker Corporation, Germany) and FAAS Perkin Elmer 4000 were used. A microwave system MDS ETHOS One (Milestone Inc.) was used for magnetite nanoparticles carbon encapsulation.

A permanent NdFeB magnet, N45, Ni-Cu-Ni (P188/5-45-30-N) was used for phase separation during SPE tests.

Magnetic NPs synthesis

The magnetic NPs were produced by co-precipitation of a mixture containing Fe^{2+} ion and Fe^{3+} in basic media according previously optimised procedure [3]. Produced nanoparticles were stored as suspensions in double distilled water (10 g L^{-1} Fe_3O_4 NPs)

Magnetic NPs modification

1. Oleic acid modification

The modification with oleic acid was used as preliminary step before the carbon coating according to the modified procedure proposed from Zhang *et al.* [17]. Briefly into 30 mL of magnetite nanoparticles suspension, 0.5 mL of oleic acid and 0.3 mL of ammonia solution (25%) were added dropwise at 80^0C under vigorous stirring for 30 min. The oleic acid-stabilized Fe_3O_4 nanoparticles were separated by centrifugation (6000 rpm, 2 hours) and washed with water three times and once with ethanol.

2. Preparation of carbon encapsulated magnetite nanoparticles ($Fe_3O_4@C$)

Both type magnetite nanoparticles (bare and oleic acid modified) were tested as a precursor for carbon modified magnetic material production. Modification procedure was based on microwave assisted hydrothermal reaction in aqueous solution of glucose. The reaction mixtures were prepared by suspending 0.3 g of magnetite nanoparticles (bare or oleic acid modified) in 10 ml, 5 mol L^{-1} glucose solution in water. Prepared suspensions were subjected to microwave treatment under the following conditions: MW power 180 W; reaction mixture heated in 4 steps - 100ºC, 130ºC, 170ºC and 200ºC. For the first three steps, 2 min were set to reach the specified temperature and 2 min to hold on. For the last step (200ºC) 5 min were set as ramp time, and the samples were treated at for one hour. After cooling, the carbon modified nanoparticles were washed with double distilled water and stored as water suspension.

Estimation of pH zero charge of the carbon coated magnetite nanoparticles

The pH zero charge of the produced $Fe_3O_4@C$ NPs was determined by pH drift method [7]. For this estimation 30 ml of 0.1 mol L^{-1} KCl solution was used and initial pH_i was adjusted from 2-10 by addition of diluted HNO_3 or NaOH solutions. The adjusted pH solutions were transferred to conical test tube containing 0.1 g of carbon coated NPs. The suspensions were shaken and allowed to equilibrate for 24 h. After treatment the MNPs were separated by permanent magnet and the pH in supernatant solution (pH_f) were measured again. The difference between initial and final pH values (ΔpH) was plotted against pH_i. The pH point zero charge (pH_{PZC}) was identified as the cross point of the fitted line with the abscissa.

Evaluation the potential of new carbon coated magnetite nanoparticles as sorbents for SPE of elements

The solid phase extraction procedure was performed in a batch mode. The optimization of SPE was carried out using model solutions (10 μg L^{-1}), prepared by dilution of multi-element standard.

Approximately 200 mg of the modified nanoparticles were transferred into a conical test tube. Afterwards the model solution of tested elements was added and pH was adjusted to 8. The extraction of metal ions was performed by continuous shaking for 30 min.

The carbon modified MNPs with adsorbed analytes were separated by a permanent magnet for 5 min and the supernatant solution was decanted. The obtained solution was then stabilised with HNO_3 (0.1% v v^{-1}) and was subjected to ICP-MS analysis.

RESULTS AND DISCUSSION

Characterisation of carbon modified Fe_3O_4 nanoparticles

The ATR-FT-IR technique was employed for characterisation of carbon modified nanoparticles. The spectra obtained for unmodified and carbon encapsulated (with and without oleic acid modification) dried Fe_3O_4 nanoparticles are presented on Fig. 1

The intensive peaks at 1700 cm^{-1} and 1060 cm^{-1} observed on Figure 1 illustrate the presence of C=O in modified samples. The peaks from 2800 to 2980 cm^{-1} are ascribed to C-H vibration. The region at 1000–1300 cm^{-1} is assigned to O-H bending and C=O stretching vibrations. The broad band at 3100–3700 cm^{-1} comes from the stretching vibrations of O-H. The obtained results are consistent with those reported by Zhang *et al* [10] for carbon coated magnetite nanoparticles obtained by classical hydrothermal reaction. The ATR-IR examination proved the presence of carbon as a result from MW assisted modification procedure, but results are not indicative for a formation of compact carbon layer surrounding the magnetic core.

One indirect test for the efficiency of encapsulation of Fe_3O_4 nanoparticles with a protective carbon layer is to examine their stability in acidic medium. All produced MNPs (bare and modified) were exposed to the action of nitric acid (1 mol L^{-1}) for 15 min and then the content of dissolved iron was determined by FAAS. The results presented as mass of dissolved iron per gram sorbent are given in Table 1.

From the results presented in Table 1, it can be concluded that preliminary modification with oleic acid is necessary for successful encapsulation of magnetic core with carbon. The $Fe_3O_4@C$ produced after modification of magnetite with oleic acid show the best stability in acidic medium.

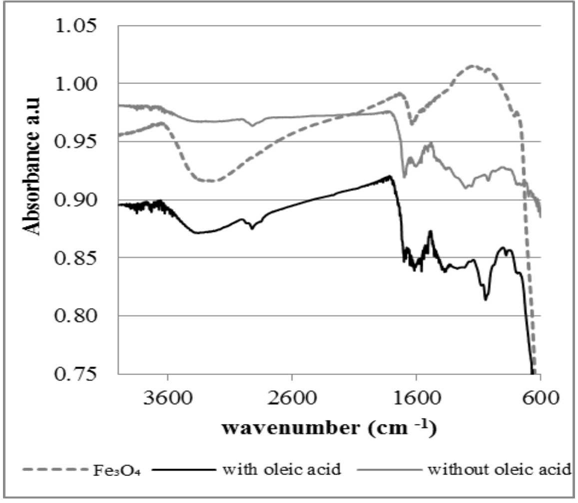

Fig. 1 ATR-FTIR spectra of unmodified and modified $Fe_3O_4@C$ NPs

Table 1. Stability of nanoparticles in acidic medium

Sample	mass dissolved Fe in mg per 1g nanoparticles mg g^{-1}
Unmodified Fe_3O_4 NPs	117
$Fe_3O_4@C$ without oleic acid modification	84
$Fe_3O_4@C$ with oleic acid modification	18

The mass of dissolved Fe reduced by factors of 6.5 to 4.66, compared to the bare material and directly carbonised nanoparticles respectively. The observed positive effect of oleic acid on the stabilisation of carbon layer is in agreement with the results reported by Wang *et al* [17]. All further experiments were performed with $Fe_3O_4@C$ produced after MNPs treatment with oleic acid.

The pH zero charge (pH_{PZC}) of studied $Fe_3O_4@C$ NPs was found to be 4.8. This result additionally proves the successful formation of carbon layer because the obtained here value is close to the reported by Pyrzynska *et al* (pH_{PZC} ~ 4 for carbon composites [7]). While the existing data of bare Fe_3O_4 NPs indicate the pH_{PZC} ~7 [2].

Evaluation of $Fe_3O_4@C$ NPs applicability as a sorbent for SPE of elements

The evaluation of new $Fe_3O_4@C$ NPs as a potential sorbent for magnetic assisted SPE of elements was accomplished varying two parameters: (i) pH of the extraction medium and (ii) quantity of nanoparticles used for the extraction.

The extraction degree E% (Eq. 1) was used as an estimator for the sorption effectiveness. For calculation of E%, model solutions (with 10 μg L^{-1}

initial analyte concentrations) were subjected to solid phase extraction with Fe_3O_4@C NPs and the residual concentration of elements in the aqueous phase after extraction were measured by ICP-MS.

$$E\,(\%) = \frac{Q_i\,(initial) - Q_S\,(residual)}{Q_i\,(initial)} \cdot 100 \qquad (1)$$

where: E% is the extraction degree; $Q_{initial}$ is the analyte quantity in the model solution; $Q_{residual}$ is the final analyte quantity in residual aqueous phase after SPE.

Study of the pH influence on extraction degree

The solution pH is a parameter influencing on NPs surface charge and affects the sorption capabilities of carbon. At pH values above pH_{PZC}, the negative charge of carbon layer promotes the adsorption process due to the electrostatic attraction between metallic cations and nanoparticles, and vice versa when the pH of the solution is less than corresponding pH_{PZC} - repulsion between positively charged NPs and metal ions is expected to decrease the extraction degree.

The effect of pH on the extraction degree of target metal ions was assessed in the pH range from 4 to 10 (Fig. 2).

As it is seen from Fig. 2, at pH=4 the extraction is not effective for most of the studied elements with exception of Bi and Tl. The extraction of Cr is slightly favourable at pH=4 and decreases at higher pH values. An explanation of this phenomenon is the possibility used multi-elemental standard to contain chromium in its highest oxidation state (6+) which under the specified experimental conditions could form an oxo-anion. Unfortunately the documentation, provided by the producer, includes certified values for concentrations of the elements with corresponding uncertainties, but the certificate does not contain information about the oxidation state of elements.

For the whole tested pH range the extraction degrees for V and Pb are below 45 %. Best performance for all other studied element is obtained when pH of the model solution was set in the pH interval form 6 to 8. Lowering of the extraction degrees for all elements (with an exception of Tl) were observed at pH=10. Considering the fact, that all studied metal ions (except Tl) are able to form stable negatively charged complexes with hydroxide, the observed trend can be explained with an electrostatic repulsion between $M(OH)_{xn}^{-}$ and the negatively charged MNPs.

Optimization of the sorbent amount

In comparison to classical sorbents used in SPE, the nanoparticles possess significantly higher surface, therefore the amount needed for extraction of analytes should be much lower. The quantity of Fe_3O_4@C NPs was varied at levels 5, 10, 20 and 30 mg (Fig. 3).

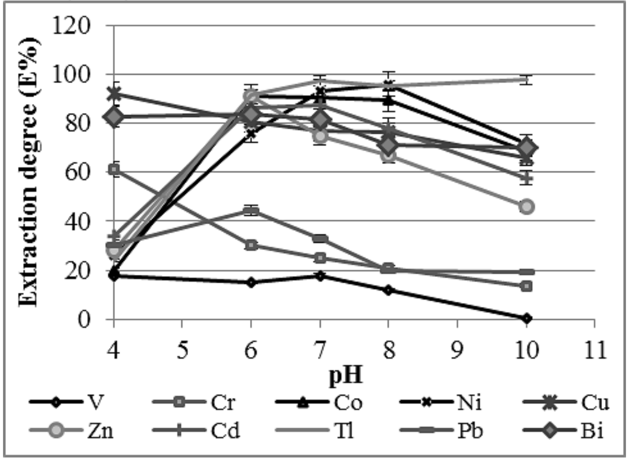

Fig. 2 Effect of solution pH on the extraction degree of metal ions collected on Fe_3O_4@C NPs. *Other conditions: 200 mg NPs;* $C_A = 10\ \mu g\ L^{-1}$; $V_A = 50$ *mL.*

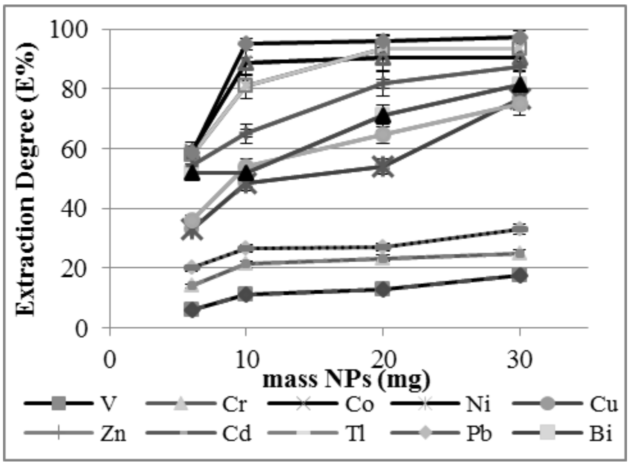

Fig. 3 Effect of the amount of sorbent on the extraction degree of analytes on Fe_3O_4@C NPs. *Other conditions: pH=7;* $C_A = 10\ \mu g\ L^{-1}$; $V_A = 50$*mL.*

Extraction degrees higher than 80% were achieved only for Ni, Co and Tl using at least 10 mg of NPs. Further increase of the mass of sorbent leads to an improvement of E% for all elements with exception of Tl, Co and Cr. For most of the elements (except from Cu, Zn and Bi) a uniform extraction is reached when mass of carbon modified NPs is above 20 mg. The mass of carbon modified nanoparticles needed for SPE of studied elements is at least twice higher compared to quantity of unmodified Fe_3O_4 NPs (10 mg) used for group extraction of 9 elements as APDC complexes [3]. This can be explained by the extensively increase of nanoparticles size during carbon modification which reduces the surface/mass ratio.

CONCLUSIONS

A new MW assisted procedure with a hydrothermal reaction with glucose was developed for production of carbon encapsulated magnetite nanoparticles (Fe_3O_4@C). The preliminary modification of magnetic cores with oleic acid leads to improvement of modification procedure. Further development of the modification procedure in the direction of formation of thin and thick carbon layer, respectively, would reduce the consumption of sorbent.

In comparison with classical hydrothermal route, the proposed procedure is fast, simple and easy for implementation.

The synthesised Fe_3O_4@C NPs are promising sorbent for magnetically assisted dispersive SPE of Co, Ni, Cu, Zn, Cd, Tl and Bi.

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НОВА МИКРОВЪЛНОВО ПОДПОМОГНАТА ПРОЦЕДУРА ЗА ПОЛУЧАВАНЕ НА ВЪГЛЕРОД-МОДИФИЦИРАНИ МАГНЕТИТНИ НАНОЧАСТИЦИ С ЦЕЛ ПРИЛОЖЕНИЕТО ИМ ЗА ТВЪРДОФАЗНА ЕКСТРАКЦИЯ НА ЕЛЕМЕНТИ

Д. Санчес[1], Д. Георгиева[2*], В. Кметов[2], В. Стефанова[2]

[1] Университет Аликанте, Испания, PO Box 99, 03080 Аликанте, Испания

[2]Пловдивски Университет „Паисий Хилендарски", Катедра аналитична химия и компютърна химия,
*ул. Цар Асен, 24, 4000 Пловдив, *E-mail: georgieva@uni-plovdiv.net*

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(Резюме)

Предложен е нов подход за получаване на въглерод модифицирани магнетитни наночастици, чрез хидротермична реакция с глюкоза, проведена в лабораторна микровълнова система. Изследвана е възможността за изграждане на въглероден слой върху немодифицирани и на третирани с олеинова киселина Fe_3O_4 наночастици. Получените нови материали са охарактеризирани с инфрачервена спектрометрия с пълно вътрешно отражение (ATR FTIR), изследвана е стабилността им в кисела среда. Установено е че за успешно изграждане на защитен слой от въглерод върху магнитното ядро е необходима предварителна модификация с олеинова киселина.

Изследван е потенциала на получените нови материали за магнитно подпомогната твърдофазна екстракция на V, Cr, Co, Ni, Cu, Zn, Cd, Tl, Pb и Bi от моделни разтвори. Проследено е влиянието на киселинността на разтворите и количеството на наночастиците върху ефективността на екстракцията на изследваните елементи.

***Ключови думи:** въглерод-модифицирани магнитни наночастици, МВ подпомогната модификация, твърдофазна екстракция*