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## Highly selective synthesis of hematite nanoparticles for solid-phase determination of deltamethrin in aqueous samples

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### ABSTRACT

Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) nanoparticles was selectively synthesized by the sol-gel pyrolysis method and used for preconcentration of Deltamethrin from aqueous samples. Parameters affected on the particle size of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> such as: iron salt and poly vinyl alcohol concentration, pyrolysis temperature and ratio of water-ethanol were investigated and optimized by the on at a time method.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles prepared under optimized conditions were used as a sorbent for solid phase extraction of Deltamethrin and parameters affected extraction were studied and optimized. A HPLC–UV method was used for the determination of Deltamethrin. The method had an LOD of 1 ppb Deltamethrin, and a linear calibration curve in the range of 1 ppb to 1000 ppb. Finally, the proposed method applied for the determination of Deltamethrin in environmental samples successfully.

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### KEYWORDS

Hematite;  
Nanoparticle;  
Solid-phase extraction;  
Sol-Gel;  
Deltamethrin;  
Pesticides.

### 1. INTRODUCTION

Metallic oxides having different shapes and sizes receive considerable attention due to their theoretical as well as technological applications<sup>[1-8]</sup>. Nanoparticles, which are the perfect building blocks for some complex and composite shaped nanomaterials, can form nanoclusters, nanowires, nanobelts, nanotubes and dendrite structures<sup>[9-12]</sup>. Over the years researchers have employed different routes to facilitate large-scale synthesis of nanostructured materials, like Cao and Zhu et al.<sup>[13,14]</sup> who used a hydrothermal process to achieve the same. Similarly, organometallic precursors<sup>[15]</sup>, emulsion liquid membrane systems<sup>[16]</sup>, reverse micelle methods<sup>[17,18]</sup>, solid template method<sup>[19]</sup>, chemical vapour deposition<sup>[20]</sup>, vapour-liquid-solid methods and sol-gel technique<sup>[21,22]</sup> have also been used.

Fe<sub>2</sub>O<sub>3</sub> has long been recognized in catalysis, magnetic and biomedical applications<sup>[23-26]</sup>. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is one of the most important, stable, non-toxic, nature-friendly and corrosion-resistant metal oxides. It is an n-type semiconductor with optical band gap (E<sub>g</sub>) of 2.1 eV and possesses extensive applications in pigments, magnetic devices and as anticorrosive agents, catalysts, gas sensors and as photoanodes for photo-assisted electrolysis<sup>[27-35]</sup>. It can be prepared from various techniques, e.g., hydrothermal, sol-gel, pyrolysis, microwave synthesis<sup>[36-39]</sup>. A number of earlier reports<sup>[13,40-42]</sup> have dealt with the formation and growth mechanism of different nano and microstructures of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> such as nanospheres, nanorods, nanowires, nanotubes, spindles, cage like structures, cubes, etc. Pu et al, in a not so early report<sup>[41]</sup>, used capping agent-surfactant CTAB and showed that concentration varia-

tion of the precursor could lead to controlled variation of size and morphology of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

Wen et al.<sup>[42]</sup> synthesized vertically aligned nanobelts and nanowires arrays of iron oxide by direct thermal oxidation of iron substrates under the flow of O<sub>2</sub>, whereas Liu et al.<sup>[43]</sup> employed different surfactant assistance, like aqueous butanol solution as the solvent and carbamide as the base to produce  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanotubes and nanorods. Chueh et al.<sup>[10]</sup> synthesized uniform  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires by a vapour-solid process. In addition to this, Morales et al.<sup>[44]</sup> showed that synthesis of hematite particles in the presence of a magnetic field along the c axis resulted in a greater axial ratio (6.5) than those formed in the absence of a magnetic field (6.0).

Use of nanometer-sized particles (nanoparticles, NPs) for sample extraction in chemical analysis is gaining research interest<sup>[45-47]</sup>. Compared with micrometer-sized particles used for solid-phase extraction (SPE), NPs offer a significantly higher surface. The greater ratio of area-to-volume promises much greater extraction capacity and efficiency. Another advantage of NPs is that NPs' surface functionality can be easily modified to achieve selective sample extraction or cell collection<sup>[48-50]</sup>.

Determination of trace level pesticides in aquatic environment is very important due to their intense use in agriculture and to their persistence as well<sup>[51-52]</sup>. Deltamethrin pesticides (herbicides) are among the most heavily used pesticides today. Deltamethrin structure has been shown in SCHEME 1.

Analytical methods often used for the determination of Deltamethrin in environmental water samples typically include derivatization followed by HPLC with Ultra Violet detection (HPLC/UVD) or HPLC with

mass spectrometric detection (HPLC-MS). The Deltamethrin procedure is often tedious and skill-demanding. More convenient HPLC-UV methods have also been developed. In these methods, an extraction/enrichment step, e.g. SPE, was normally needed prior to HPLC-UV determination because of the extremely low concentration level of pesticides in water samples.

Iron oxides such as Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> NPs are the most popular nanomaterials used for Extraction, preconcentration and purification of biological and chemical analytes were carried out using these. Fe<sub>2</sub>O<sub>3</sub> has two stable phases including  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Hematite) and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (Magemite). The experimental findings showed that the neutral and modified pesticides exhibited a strong affinity to Fe<sub>2</sub>O<sub>3</sub> NPs mediated by the combination of hydrophobic and multiple electrostatic interactions.

The aim of this work was to develop a simple and selective method for preparing of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and develop a NP-based SPE of small organic molecules for HPLC-UV analysis, which, to the best of our knowledge, has never been reported before. In the NP-based extraction procedure, the NPs were collected after extraction either elute sample in cartridge by some solution same methanol and acetonitrile which use for large volume samples. A NP-based SPE method was developed to extract pesticides from water samples. In the procedure, at first synthesis of Fe<sub>2</sub>O<sub>3</sub> NPs with sol-gel method and estimation of parameters and then use Fe<sub>2</sub>O<sub>3</sub> NPs as SPE in apply to collect the pesticides analyte. Fe<sub>2</sub>O<sub>3</sub> NPs with a chemically modified surface were used for enriching/extracting pesticides.

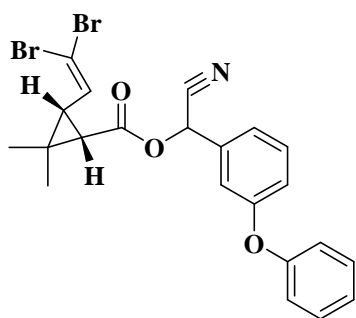
## 2. EXPERIMENTAL

### 2.1. Chemicals and reagents

Deltamethrin, iron (III) Sulfate, Polyvinyl Alcohol, Methanol, Ethanol, Acetonitrile, and hydrochloric acid were purchased from Merck Company and were used without any further purification. A stock solution (1000 ppm) from Deltamethrin was prepared in methanol. Double-distilled water was used throughout the work.

### 2.2. Instrumentals

Scanning electron microscopy (SEM) XL30 model with platinum coating from Oxford Company and X-



SCHEME 1: Molecular structure of deltamethrin

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ray diffraction (XRD) Xpert diffractometer ( $\lambda = 0.1541$  nm) CuK $\alpha$  were used for sample characterization. Milli-Q (Millipore Corp., Bedford, MA) water system was used. The HPLC system consisted of a pump (K-1001), an auto injector equipped with a 100  $\mu$ L sampling loop (Triathlon), an on-line degasser (D-14163), and a UV-detector (2600) from KNAUER (Berlin, Germany) equipped with AC<sub>18</sub> reversed-phase column (300mm  $\times$  5mm i.d.) was used for sample analysis. The HPLC system was controlled by Chromgate software (product of KNAUER). Mobile phase water, containing 0.2% Acetic acid (pH=3) and acetonitrile (22:78) at flow rate of 1ml/min and wavelength of 247 nm was used.

### 2.3. Preparation of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NP procedure

There are a number of methods adopted for the synthesis of nanoparticles: the sol-gel technique, inverse micelle, exfoliation by polymerization, and biomimetic synthesis are some of the techniques used for producing nanoparticles of metals (Au, Pt, Pd, Co, Fe). Sol-gel technique was used for ferrous oxide synthesis by reaction of ferrous sulfate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) salt and polyvinyl alcohol (PVA) in a hydro alcoholic solution. After make a mix of hydroalcoholic solution ferrous sulfate and PVA added to that slowly and was heated to 70°C to make sol. Then sample was heated to 90°C to make gel. Finally, gel put in to oven for about 6 hours to pyrolysis the sample to yield Fe<sub>2</sub>O<sub>3</sub>. After synthesis of Fe<sub>2</sub>O<sub>3</sub> nanoparticle, load them as sorbent in SPE column.

### 2.4. Fe<sub>2</sub>O<sub>3</sub> NP-based SPE procedure

100mg of NPs of Fe<sub>2</sub>O<sub>3</sub> was added in a glass column and used same polyethylene filters before and af-

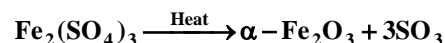
ter that for hold them in the column. Before used as SPE, conditioning of them was performed with acetonitrile and water and then sample solution containing Deltamethrin passed through cartridge. Then SPE was eluted with 1 ml acetonitrile. The solution was filtered through a 0.45  $\mu$ m syringe filter and 50  $\mu$ L injected into the HPLC-UVD system for analysis without further purification.

## 3. RESULTS AND DISCUSSION

In this paper, we describe preparation of Fe<sub>2</sub>O<sub>3</sub> NP and its application for solid-phase extraction of the pesticide (Deltamethrin) extraction and determination with HPLC.

### 3.1. Synthesis of Fe<sub>2</sub>O<sub>3</sub> nanoparticle

At the proposed synthesis method, the gel network rigidity controls the morphology and particle size of the synthesized sample to make a uniform nanostructured Fe<sub>2</sub>O<sub>3</sub>. In the gel structure, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> salt was homogeneously dispersed among polymeric network. Because of gel network rigidity, the dispersed ions in the gel network can not alter their positions. Therefore, during the pyrolysis of the gel's outer layers, the iron sulfate of the burnt layers grew Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> nanoparticles. Finally, iron sulfate nanoparticles were calcinated to form  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NPs. The chemical equation is as follows:



In this method, the amount of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, PVA, the mixed solvent composition, and

the pyrolysis temperature have an considerable effect on the composition, morphology, and particle size of the sample. The degree of these effects was optimized by the "one at a time" method.

At first step of synthesis optimization, Fe<sub>2</sub>O<sub>3</sub> NPs were prepared at iron (III) sulfate range of 0.25, 0.5, 1, 2, 4, 6 and 8% wt while the other parameters were kept constant (PVA=6% wt, pyrolysis temperature=550°C, water-ethanol ratio=40-60). The obtained results showed that 1% wt of iron (III) sulfate had sufficient homogeneity and good particle size (Figure 1).

PVA in the range of 1, 3, 6, 9 and 12% wt was used separately for Fe<sub>2</sub>O<sub>3</sub> NP preparation at constant conditions (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>=1% wt, Temperature=550°C, water-ethanol ratio=40-60) according to section 2.4.

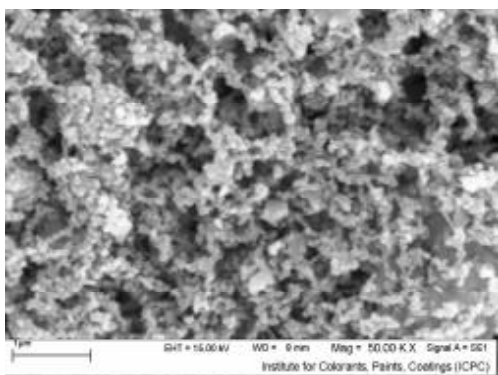


Figure 1: SEM image of Fe<sub>2</sub>O<sub>3</sub> NPs synthesized at 1% wt iron (III) sulfate

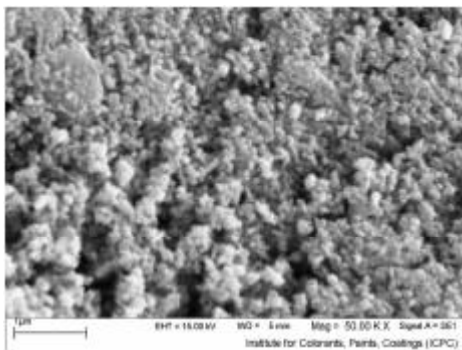


Figure 2: SEM image of sample was synthesized at 6% wt PVA

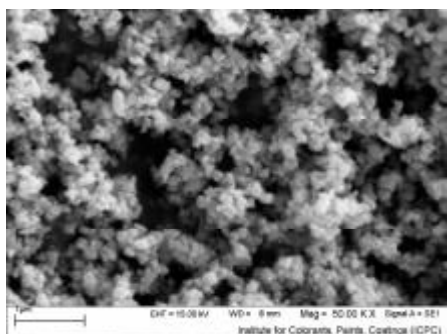


Figure 3: SEM image of sample was synthesized at 50-50 ratio of water-ethanol

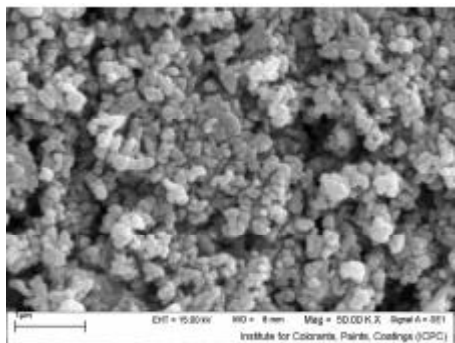
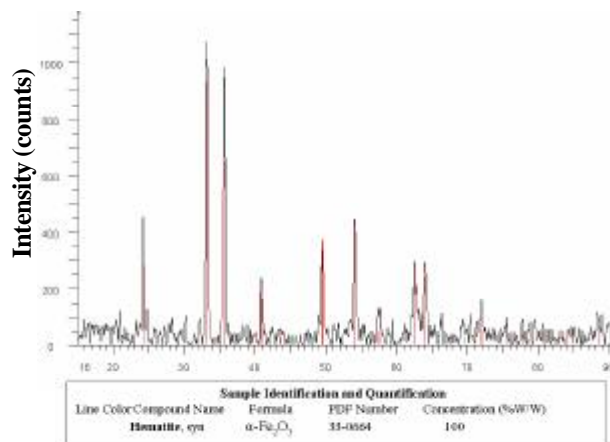


Figure 4: SEM image of  $\text{Fe}_2\text{O}_3$  NPs synthesized at pyrolysis temperature of  $650^\circ\text{C}$

The results showed 6% wt PVA is sufficient to obtain a uniform morphology and smaller particles of hematite (Figure 2).

Some different water-ethanol ratios of 0-100, 20-80, 40-60, 50-50, 60-40, 80-20 and 100-0 were separately used for synthesizing of  $\text{Fe}_2\text{O}_3$  while the other conditions were constant ( $\text{Fe}_2(\text{SO}_4)_3 = 1\%$  wt, PVA = 6% wt and Temperature =  $550^\circ\text{C}$ ) and water-ethanol ratio = 50-50). All samples were characterized by SEM studies. The obtained results revealed that the water-



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Figure 5: X-ray diffraction pattern of  $\alpha\text{-Fe}_2\text{O}_3$  nano particles

ethanol ratio of 50-50 is a suitable composition for the sol solvent. Figure 3 shows the SEM image of the sample prepared at 6% wt PVA. As it is seen from Figure 3, this amount of PVA makes more uniform structure for the  $\text{Fe}_2\text{O}_3$  NPs.

Temperature of pyrolysis was studied in the range of  $450, 550, 650, 750, 850, 950^\circ\text{C}$ . In these experiments, all samples were characterized by SEM and XRD. SEM studies showed that the pyrolysis temperature of  $650^\circ\text{C}$  is the best to obtain uniform nanostructure with the smaller particles (Figure 4).

The purity of the prepared  $\text{Fe}_2\text{O}_3$  nanoparticles was examined using X-ray diffraction. The XRD pattern of the final powder which synthesized at pyrolysis temperature of  $650^\circ\text{C}$  was shown in Figure 5.

Based on SEM image and XRD pattern, the synthesized sample at optimum conditions (1% wt  $\text{Fe}_2(\text{SO}_4)_3$ , 6% wt PVA, water-ethanol ratio of 50:50 and pyrolysis temperature of  $650^\circ\text{C}$ ) had uniform nanoparticles with a particle diameter of  $25 \pm 3$  nm in very fine powder form.

### 3.2. Extraction of Deltamethrin with $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles

100 mg of  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles was packed in glass syringe (5 ml). Before used as SPE, conditioning of the column (cartridge) was performed with acetonitrile and water. The sample solution containing Deltamethrin passed through cartridge. Then SPE was eluted with 1 ml acetonitrile. The solution eluted from SPE was filtered through a  $0.45\mu\text{m}$  syringe filter and

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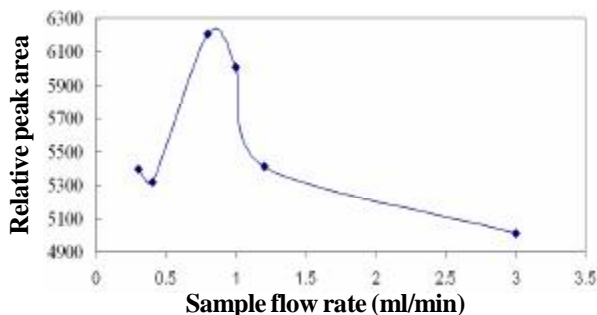


Figure 6: Effect of sample flow rate on the recovery of deltamethrin by  $\text{Fe}_2\text{O}_3$  NP-based solid phase extraction

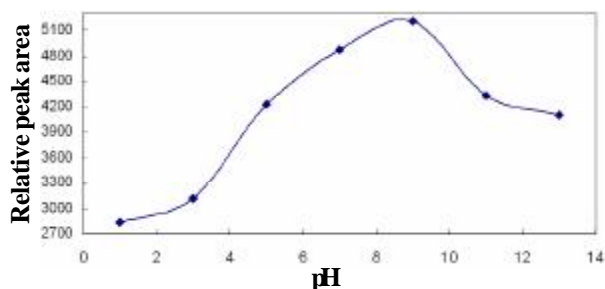


Figure 7: Effect of solution temperature on the recovery of deltamethrin by  $\text{Fe}_2\text{O}_3$  NP-based solid phase extraction

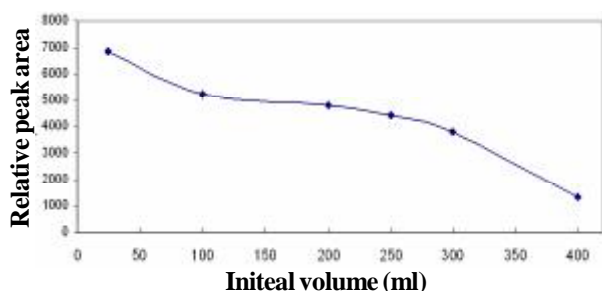


Figure 8: Effect of sample solution pH on the recovery of deltamethrin by  $\text{Fe}_2\text{O}_3$  NP-based solid phase extraction

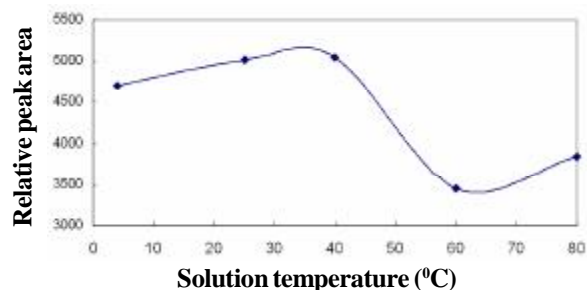


Figure 9: Effect of initial sample volume on the recovery of deltamethrin by  $\text{Fe}_2\text{O}_3$  NP-based solid phase extraction

50  $\mu\text{L}$  injected into the HPLC–UVD system for analysis without further purification. In this system, there are some effective parameters including flow rate of sample

solution, initial temperature of sample solution, initial pH of sample solution, and initial sample volume which their effect on the extraction efficiency were investigated.

### 3.2.1. Effect of sample flow rate

Six samples with same conditions were passed from cartridge at 6 different flow rates of 0.3, 0.4, 0.8, 1, 1.2 and 3 ml/min. Figure 6 shows the effect of sample flow rate on the extraction efficiency. As it is obvious in figure 6, maximum extraction efficiency is seen for the sample flow rate of 0.8 ml/min. At lower flow rates, adsorbed species of frontier sample band can be desorbed by following sample bands. At higher flow rates, contact time of analyte with sorbent ( $\text{Fe}_2\text{O}_3$ ) is low so that adsorption efficiency is decreased.

### 3.2.2. Effect of pH

The adsorption of Deltamethrin on  $\text{Fe}_2\text{O}_3$  NPs was studied in the pH range of 1 to 13. The results of effect of pH on the recovery of the Deltamethrin were shown in figure 7.

It can be seen that maximum recovery was found in the pH range of 9. For understanding of pH effect, the adsorption mechanism for Deltamethrin should be explained. As it has been previously reported<sup>[9]</sup>, the surface of iron oxide nanoparticles is hydrolyzed to form hydroxyl groups in aqua's solution. Deltamethrin can be bonded to the surface of  $\text{Fe}_2\text{O}_3$  by hydrogen bonds. At lower pH, donor atoms of Deltamethrin (O and N) get proton to form positive sites so that the hydrogen bond capacity is decreased and consequently, Deltamethrin adsorption. At solution pHs higher than 9, hydroxyl groups of sorbent can be ionized and their hydrogen bonding possibility with donor atoms of Deltamethrin (O and N) is decreased.

### 3.2.3. Effect of initial sample volume

In order to explore the possibility of concentrating low concentration of analytes from large volumes, the effect of sample volume on the retention of analyte was also investigated. For this purpose, 25, 100, 200, 250, 300 and 400 mL of the sample solutions containing same total Deltamethrin of 0.25  $\mu\text{g}$  was passed through cartridge. Finally, the cartridge was eluted with 1 mL acetonitrile and, analyzed with HPLC. The results are shown in figure 8. As it is seen from figure 8, the proposed sorbent can adsorb Deltamethrin from big solu-

tion with low content. The obtained results show the high capacity of  $\alpha\text{-Fe}_2\text{O}_3$  for the preconcentration of Deltamethrin.

### 3.2.4. Effect of initial sample temperature

In order to obtain maximum efficiency, initial temperature of sample solutions was changed and, the effect of temperature on the final HPLC signal counts was studied. Figure 9 shows the temperature dependency of Deltamethrin extraction. Kinetic of Adsorption and desorption of Deltamethrin on the surface of  $\alpha\text{-Fe}_2\text{O}_3$  is increased when the solution temperature increased from 5 to 40°C. At higher temperatures, kinetic rate of desorption is more than adsorption so that the extraction efficiency is decreased.

### 3.3. Analytical performance and application

Detection limit (LOD) of the proposed method for the determination of Deltamethrin was obtained 1 ppb. Linear calibration curve was obtained in the range of 1 to 1000 ppb (seven points) for Deltamethrin to general procedure extraction ( $r^2 > 0.99$ ). The proposed method was applied for the determination of Deltamethrin in tap water and the recovery was obtained above 90% with relative standard deviation (%RSD) lower than 8%.

## 4. CONCLUSIONS

Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) nanoparticles can be selectively synthesized by a simple PVA-based sol-gel pyrolysis method. Extraction of small organic molecules such as Deltamethrin pesticides from large volume samples can be effectively performed using  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles as extract agent. Adsorbed species was eluted from SPE cartridge by small volume of acetonitrile. The eluted Deltamethrin was analyzed by HPLC-UV method. The proposed method was successfully used for the determination of Deltamethrin in tap water.

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## REFERENCES

- [1] L.Diamandescu, D.Mihaila-Tarabasanu, N.Popescu-Pogrion, A.Totovina, I.Bibicu; *Ceram.Int.*, **25**, 689 (1999).
- [2] P.Camargo, G.Nunes, G.Friedermann, D.Evans, G.Leigh, G.Tremiliosi-Filho, E.L.de Sa, A.Zarbin, J.Souares; *Mater.Res.Bull.*, **38**, 1915 (2003).
- [3] X.Xu, J.Gueo, Y.Wang; *Mater.Sci.Eng.B*, **77**, 207 (2000).
- [4] F.Kulikov, A.Vanetsev, G.Murav'eva, A.Iinskii, N.Oleinikov, Y.Tretyakov; *Inorg.Mater.*, **39**, 1074 (2003).
- [5] T.S.Ahmadi, Z.L.Wang, T.C.Green, A.Henglein A, M.A.Elsayed; *Science*, **272**, 1924 (1996).
- [6] S.Sun, C.B.Murray, D.Weller, L.Folks, A.Moser; *Science*, **387**, 1989 (2000).
- [7] Z.L.Wang; *Adv.Mater.*, **12**, 1295 (2000).
- [8] X.Jiang, Y.Xia; *J.Am.Chem.Soc.*, **125**, 16176 (2003).
- [9] L.Manna, E.C.Scher, A.P.Alivisatos; *J.Am.Chem.Soc.*, **122**, 12700 (2000).
- [10] Y.L.Chueh, M.W.Lai, J.Q.Liang, L.J.Chou, Z.L.Wang; *Adv.Funct.Mater.*, **16**, 2243 (2006).
- [11] Y.Zhang, H.Jia, X.Luo, X.Chen, D.Yu, R.Wang, *J.Phys.Chem.B*, **107**, 8289 (2003).
- [12] Q.Li, V.Kumar, Y.Li, H.Zhang, T.J.Marks, R.P.H.Chang; *Chem.Mater.*, **17**, 1001 (2005).
- [13] M.Cao, T.Liu, S.Gao, G.Sun, X.Wu, C.Hu, Z.L.Wang; *Angew.Chem.Int.Edn, Communications*, **44**, 2 (2005).
- [14] L.P.Zhu, H.M.Xiao, X.M.Liu, S.Y.Fu; *J.Mater.Chem.*, **16**, 1794 (2006).
- [15] K.W.Chang, J.J.Wu; *Adv.Mater.*, **16**, 545(2000).
- [16] L.Liu, Q.S.Wu, Y.P.Ding, H.J.Liu, J.Y.Qi, Q.Liu; *Aust.J.Chem.*, **57**, 219 (2004).
- [17] J.Jin, K.Hashimoto, S.I.Ohkoshi; *J.Mater.Chem.*, **15**, 1067 (2005).
- [18] M.D.Mukadam, S.M.Yusuf, P.Sharma, S.K.Kulshrestha; *J.Magn.Magn.Mater.*, **1401**, 272 (2004).
- [19] D.Miser, E.Shin, M.Hajaligol, F.Rasouli; *Appl.Catal.A*, **258**, 7 (2004).
- [20] J.Chatterjee, Y.Haik, C.Chen; *J.Magn.Magn.Mater.*, **257**, 113 (2003).
- [21] D.Kim, Y.Zhang, W.Voit, K.Rao, J.Kehr, B.Bjelke, M.Muhammed; *Scripta Mater.*, **44**, 1713 (2001).
- [22] K.Woo, H.Lee; *J.Magn.Magn.Mater.*, **272-276**, e1155 (2004).
- [23] D.T.Mitchell, S.B.Lee, L.Trofin, N.Li, T.K.

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- Nevanen, H.Soderlund, C.R.Martin; J.Am.Chem. Soc., **124**, 11864 (2002).
- [24] Z.Zhang, B.Q.Wei, P.M.Ajayan; Appl.Phys.Lett., **79**, 4207 (2001).
- [25] C.Gong, D.Chen, X.Jiao, Q.Wang; J.Mater.Chem., **11**, 1844 (2002).
- [26] K.Kanie, A.Muranatsu; J.Am.Chem.Soc., **125**, 11578 (2005).
- [27] P.Chauhan, S.Annapoorni, S.K.Trikha; Thin Solid Films, **346**, 266 (1999).
- [28] M.Fukazawa, H.Matuzaki, K.Hara; Sens. Actuators.B, **13**, 521 (1993).
- [29] J.S.Han, T.Bredow, D.E.Davey, A.B.Yu, D.E. Mulcahy; Sens.Actuators.B, **75**, 18 (2001).
- [30] E.Comini, V.Guidi, C.Frigeri, I.Ricco, G.Sberveglieri; Sens.Actuators.B, **77**, 16 (2001).
- [31] T.Ohmori, H.Takahashi, H.Mametsuka, E.Suzuki; Phys.Chem.Chem.Phys., **2**, 3519 (2000).
- [32] S.N.Frank, A.J.Bard; J.Phys.Chem., **81**, 1484 (1977).
- [33] B.C.Faust, M.R.Hoffmann, D.W.Bahnemann; J.Phys.Chem., **93**, 6371 (1989).
- [34] W.Weiss, D.Zscherpel, R.Schlögl; Catal.Lett., **52**, 215 (1998).
- [35] J.W.Gues; Appl.Catal., **25**, 313 (1986).
- [36] H.C.Zeng; J.Mater.Chem., **16**, 649 (2006).
- [37] C.Burda, X.Chen, R.Narayanan, M.A.El-Sayed; **105**, 1025 (2005).
- [38] W.U.Huynn, J.J.Dittmer, A.P.Alivisatos; Science, **295**, 2425 (2002).
- [39] L.H.Mattoussi, B.O.Dabbousi, E.L.Thomas, M.G. Bawendi, M.F.Rubner; J.Appl.Phys., **83**, 7965 (1998).
- [40] Y.M.Zhao, Y.H.Li, R.Z.Ma, M.J.Roe, D.G. McCartney, Y.Q.Zhu; Small, **2**, 422 (2006).
- [41] Z.Pu, M.Cao, J.Yang, K.Huang, C.Hu; Nanotechnology, **17**, 799 (2006).
- [42] X.Wen, S.Wang, Y.Ding, Z.L.Wang, S.Yang; J.Phys.Chem.B, **109**, 215 (2005).
- [43] L.Liu, H.Z.Kou, W.Mo, H.Liu, Y.Wang; J.Phys.Chem.B, **110**, 15218 (2006).
- [44] M.Ocana, M.P.Morales, C.J.Serna; J.Colloid Interface Sci., **171**, 85 (1995).
- [45] A.S.Nair, T.Pradeep; J.Nanosci.Nanotech., **7**, 1 (2007).
- [46] A.Kaur, U.Gupta; E.J.Chem., **5**, 930 (2008).
- [47] M.A.Xiaoguo, H.Bei., C.Meiqing; Rare Metals, **26**, 541 (2007).
- [48] X.Zhao, Y.Shi, T.Wang, Y.Cai, G.Jiang; J.Chrom.A, **1188**, 7 140 (2008).
- [49] M.Valcarcel, S.Cardenas, B.M.Simonet, Y.Moliner-Martínez, R.Lucena; Trends Anal.Chem., **27**, (2008).
- [50] T.Zhou, C.A.Lucy; J.Chrom.A, **1213**, 78 (2008).
- [51] Y.Chen, Z.Guo, X.Wang, C.Qiu; J.Chrom.A, **1184**, 7191 (2008).
- [52] S.Wang, P.Zhao, G.Min, G.Fang.; J.Chrom. A, **1165**, 7166 (2007).