



# Anhydride functionalised calcium ferrite nanoparticles: A new selective magnetic material for enrichment of lead ions from water and food samples



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## ARTICLE INFO

### Article history:

Received 9 April 2014

Received in revised form 9 July 2014

Accepted 11 August 2014

Available online 20 August 2014

### Keywords:

Calcium ferrite nanoparticles

Food samples

Lead

Preconcentration

## ABSTRACT

In this research a sonochemistry route for manufacture of uniform nanocrystalline  $\text{CaFe}_2\text{O}_4$  and its anhydride functionalisation were reported. The potential of raw and modified material as a magnetically separable sorbent in selective enrichment of lead ions from water and food samples is outlined. This material was characterised using FT-IR, XRD, SEM and VSM techniques. The SEM and VSM results indicated that the calcium ferrite nanoparticles are sphere-like particles possessing superparamagnetic properties with an average diameter of 40 nm. Various analytical parameters, including pH, contact time, type and concentration of eluent, adsorption capacity, sample volume and interference of ions, were optimised. Following a modification by anhydride, calcium ferrite selectivity toward lead ions was raised more than twofold compared to the unmodified nanoparticles. Finally a pre-concentration procedure was applied for determination of trace Pb(II) in canned tuna fish, canned tomato paste, parsley, milk and well-water samples with satisfactory results.

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## 1. Introduction

Solid-phase extraction (SPE) is the most common pre-treatment method for sample matrix simplification and pre-concentration of trace amounts of analyte in samples (Poole & Poole, 2002). SPE has become a powerful method compared to preparation techniques such as liquid–liquid extraction (Amorim & Ferreira, 2005), cloud point extraction (Liang & Yang, 2010) and co-precipitation (Soylak & Tuzen, 2008) due to its simplicity, cost-effectiveness, lower organic solvent consumption, high enrichment factor and ability to be coupled with different detection methods (Liang, Liu, & Guo, 2005; Suleiman, Hu, Pu, Huang, & Jiang, 2007). In SPE, one influential factor on precision and sensitivity is the material used as adsorbent. A suitable solid phase for SPE technique should be stable, insoluble, should have appropriate active groups, good regenerability and qualitative sorption (Huang & Hu, 2008).

Various types of adsorbents such as ion-imprinted and mesoporous materials, activated carbon, carbon nanotubes, resins and nanoparticles (Afkhami, Saber-Tehrani, Bagheri, & Madrakian, 2011; Esen et al., 2009; Ghaedi, Montazerzohori, Nejati Biyareh, Mortazavi, & Soyлак, 2013; Hernandez-Morales et al., 2012; Lian et al., 2005; Soyлак, Elci, & Dogan, 1996; Tuzen, Soyлак, & Elci,

2005) have been used as solid sorbent in SPE. Among the aforementioned sorbents the nanoparticles (NPs) have received a major focus because of their large surface area, ability to functionalise with different chemical groups and small size, which lead to improvement in sensitivity, selectivity and rapidity in SPE methods (Kaur & Gupta, 2009). Despite these merits, nanoparticles possess some drawbacks. For instance, high back-pressure in column dynamic extraction mode and the need to centrifuge and filter in static batch mode have made this method rather time consuming (Mehdinia, Roohi, & Jabbari, 2011).

In order to prevent such difficulties, magnetic solid-phase extraction (MSPE), in which magnetic nanoparticles (MNPs) are used instead of nanoparticles, was developed (Safarikova & Safarik, 1999). The superparamagnetic behaviour of magnetic nanoparticles, which only can be magnetised in the presence of magnetic field, allow the separation and pre-concentration in SPE to be faster and simpler (Hu, Lo, & Chen, 2005). Additionally, chemical stability and biocompatibility are other characteristics that make these particles potentially useful for a broad range of applications (Khanna & Verma, 2013a).

The most conventional MNPs used directly as adsorbents or supports in separation and pre-concentration procedure are iron oxides comprised from  $\text{Fe}_3\text{O}_4$  (magnetite),  $\gamma\text{-Fe}_2\text{O}_3$  (maghemite) and spinel-ceramic ferrites with  $\text{MFe}_2\text{O}_4$  structure (M: Mn, Co, Cu, Ni, Ca, Zn) (Ensafi, Rabiei, Rezaei, & Allafchian, 2013;

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Mashhadizadeh, Amoli-Diva, Shapouri, & Afrouzi, 2014; Parsons, Lopez, Peralta-Videa, & Gardea-Torresday, 2009; Stefanova, Georgieva, Kmetov, & Roman, 2012; Suleiman, Hu, Peng, & Huang, 2009; Wang, Li, Wang, Zhao, & Jiang, 2012). Ceramic ferrites have been investigated in recent years for their high magnetic permeability, chemical and corrosive stability (Hu, Lo, & Chen, 2007; Ren et al., 2012). Among them,  $\text{CaFe}_2\text{O}_4$  shows remarkable characteristics, such as high thermal stability, which makes it applicable over a wide temperature range. It also possesses lower saturation magnetisation properties compared to the other ferrites that deter aggregation and expedite dispersion in aqueous solution (Candeia, Bernardi, Longo, Santos, & Souza, 2004) resulting in more contact and shorter equilibrium time.

In comparison with other ferrites such as  $\text{MnFe}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4$ , calcium ferrite has a significant advantage; it is biocompatible and eco-friendly due to the presence of  $\text{Ca}^{2+}$  instead of heavy metals (Khanna & Verma, 2013b). There are several reports on usage of  $\text{CaFe}_2\text{O}_4$  as a pigment, an anode in lithium batteries, adsorbent of hydrogen sulfide, and solid catalyst but none on its use for the separation and pre-concentration of organic and inorganic materials.

Heavy metals potentially can accumulate in different organs and be the cause of severe diseases and disorders, due to their non-biodegradability and persistence (Cheng, He, Peng, & Hu, 2012; Soyлак, Elci, Akkaya, & Dogan, 2002). These elements, which generally are derived from various industrial activities, are major sources of air, water, and food pollution. Another source is contamination caused during storage or processing (Parkar & Rakesh, 2014). Lead is a highly toxic heavy metal, even at low concentration causing damage to the kidneys as well as the nervous, haematological and cardiovascular systems (Castro-Gonzalez & Mendez-Armenta, 2008; Liu et al., 2011; Shah, Soyлак, Kazi, & Afridi, 2012). Therefore, the accurate and precise determination of heavy metals in food and environmental samples is important.

A number of studies have determined lead ions using different magnetic nanoparticles, but to the best of our knowledge, there is no report on analytical application of  $\text{CaFe}_2\text{O}_4$  magnetic NPs as solid sorbents for extraction and determination of lead ions from complex matrices. Like other MNPs,  $\text{CaFe}_2\text{O}_4$  suffers from lack of sufficient selectivity towards target analytes; hence, the modification of the surface of MNPs with a suitable coating is necessary. Also, the modification can improve chemical stability of MNPs. Therefore, in the current study a sonochemistry route was applied to manufacture a uniform nanocrystalline  $\text{CaFe}_2\text{O}_4$ . Moreover, the performance of anhydride modified calcium ferrite as a biocompatible and eco-friendly sorbent for pre-concentration of trace lead prior to its determination by flame atomic absorption spectrometry (FAAS) was outlined. Finally, this method was applied for the analysis of water and food samples.

## 2. Experimental

### 2.1. Reagents and solutions

All chemicals used in this work were analytical grade and were used without any purification.  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2$ , 3-aminopropyl-triethoxysilane (APTES), sodium hydroxide and  $\text{Pb}(\text{NO}_3)_2$  were purchased from Merck (Darmstadt, Germany) and phthalic anhydride (PA) was purchased from Sigma (St. Louis, MO). Stock solutions ( $1000 \text{ mg L}^{-1}$ ) of  $\text{Pb}(\text{II})$  were supplied from  $\text{Pb}(\text{NO}_3)_2$ . Standard stock solutions ( $1000 \text{ mg L}^{-1}$ ) of other elements were prepared from their salts. The solutions of lead were prepared in distilled water and 1%  $\text{HNO}_3$ . Working standard solutions of lower concentration were prepared on a daily basis

using appropriate dilution. HCl and  $\text{NH}_3$  aqueous solutions were used to adjust pH.

### 2.2. Apparatus

Lead determination was performed by an atomic absorption spectrometer AA-400 (Varian Australia Pty Ltd., Musgrave, Victoria, Australia), equipped with deuterium background correction lamp and air-acetylene flame. The Pb hollow cathode lamp (Varian) was used as the radiation source at 217 nm. The lamp current and slit width were operated at 5 mA and 1 nm, respectively. A scanning electron microscope (SEM), KYKY-EM3200 (Madell Technology Corporation, Ontario, CA) was employed to characterise magnetic nanoparticles. X-ray powder diffraction (XRD) measurements were performed using a STADI-MP (STOE & Cie, GmbH, Darmstadt, Germany) with monochromatised  $\text{Cu K}\alpha$  radiation. Fourier-transform infrared spectra (FT-IR) were measured with an Equinox 55 (Bruker Optik GmbH, Ettlingen, Germany) with ATR method over the wavelength of  $400\text{--}4000 \text{ cm}^{-1}$ . Magnetisation measurement was performed using a vibration sample magnetometer (VSM) (Model 7400, Lake Shore Cryotronics, Inc., Westerville, OH). Magnetic separation was done by a magnet with 1.31 magnetic field. A pH-meter model 781 from Metrohm (Herisau, Switzerland) with glass combination electrode was used for pH adjustment.

### 2.3. Procedure

#### 2.3.1. Preparation of magnetic $\text{CaFe}_2\text{O}_4$ nanoparticles (MNPs)

$\text{CaFe}_2\text{O}_4$  nanoparticles were synthesised by ultrasonic-assisted chemical co-precipitation method (Wu et al., 2011). Briefly,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (10.0 g) and  $\text{Ca}(\text{NO}_3)_2$  (1.25 g) were dissolved in 100 mL distilled water using an ultrasonic bath at  $80^\circ\text{C}$ . Then 20 mL of NaOH (3.0 M) were added as co-precipitant into the mixture. The colour of the bulk solution changed immediately from orange to brown. The solution was kept in an ultrasonic bath for 30 min at  $80^\circ\text{C}$ , then collected with filter paper and washed with distilled water several times. The final product (MNPs) was dried at  $80^\circ\text{C}$  for 4 h followed by further heating for 1 h at  $300^\circ\text{C}$  and stored for subsequent modification.

#### 2.3.2. Preparation of modified $\text{CaFe}_2\text{O}_4$ nanoparticles

An amount of 2.0 g of synthesised  $\text{CaFe}_2\text{O}_4$  powder was added to 30 mL toluene followed by addition of 2 mL of APTES. The suspension was refluxed at  $50^\circ\text{C}$  for 12 h. After cooling to room temperature amine-coated MNPs were washed with ethanol three times and then dried. In the subsequent step the amine-functionalised  $\text{CaFe}_2\text{O}_4$  was added to the solution of 1.0 g of PA in 50 mL ethanol and was stirred for 4 h at room temperature. The final modified solid adsorbent ( $\text{CaFe}_2\text{O}_4\text{-APTES-PA}$ ) was separated by magnet field and washed three times with ethanol then air-dried overnight.

### 2.4. Procedure of magnetic solid-phase extraction

The adsorption of lead ion on modified  $\text{CaFe}_2\text{O}_4$  was performed using a batch technique under ambient conditions. Initially, 30 mg of modified  $\text{CaFe}_2\text{O}_4$  nanoparticles were added into 50 mL of aqueous solution containing various amounts (0.005–4.5 mg) of  $\text{Pb}^{2+}$  ions. The pH value of the mixture was adjusted approximately to 6.5 by adding 1.0 M HCl and 1.0 M  $\text{NH}_3$  solutions. Then, the solution was shaken for 10 min to ensure sufficient interaction between MNPs and metal ions. After equilibrium the solid mass was magnetically separated from the mixture and the supernatant was decanted. Finally the separated solid was shaken with 3 mL of 1.0 M  $\text{HNO}_3$  solution and the analyte in the eluent was determined by FAAS.

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