Zinc(II)-doped Manganese Ferrite Nanoparticles as an Efficient Magnetic Adsorbent for Cadmium Extraction from Water Samples

Hossein Abdolmohammad-Zadeh* and Zahra Ayazi

Department of Chemistry, Faculty of Sciences, Azarbaijan Shahid Madani University, 35 km Tabriz-Marageh Road,
P. O. Box: 53714-161, Tabriz 5375171379, Iran

In this work, an effective and simple method was utilized for the synthesis of zinc(II)-doped manganese ferrite magnetic nanoparticles ($Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs). The prepared $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPS was studied and characterized by Fourier transform infrared spectroscopy, field emission scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction spectroscopy and Brunauer-Emmett-Teller analysis. The prepared $Zn_{0.2}Mn_{0.8}Fe_2O_4$ nanomaterial was applied as an applicable magnetic nano-sorbent for solid-phase extraction of cadmium(II) (Cd(II)) ions. The enriched Cd(II) ion was desorbed from the surface of the MNPs using a diluted HNO_3 solution, and quantified by flame atomic absorption spectrometry. The influential variables, including the adsorbent mass, sample volume, pH, extraction time, and desorption conditions were investigated and optimized. Based on the method validation, the limit of detection for the developed method was 0.03 ng ml^{-1} and the calibration curve is linear in the range of 0.1-30.0 ng ml^{-1}. The method's repeatability based on intra-day and inter-day precisions are 1.9% and 3.3%, respectively. For evaluation of the method accuracy, a certified reference material, natural waters, and industrial wastewater samples were analyzed.

Keywords: Magnetic solid-phase extraction, Nano-sorbent, Zinc(II)-doped manganese ferrite, Cadmium; Water and industrial wastewater samples, Flame atomic absorption spectrometry

INTRODUCTION

Sample preparation consists of an extraction or separation step in the analysis processes in which not only the desired analyte is separated from the sample matrix, but also the pre-concentration is performed. It plays an essential role in the accuracy, and limit of detection, especially, when the measurement of trace amounts of the analyte/s is required. Continued efforts for developing new sample preparation methods have been led to the development of methods which are fast, easy, inexpensive, and reliable, applying the least amount of adsorbent.

Magnetic solid-phase extraction (MSPE) as a new format of SPE uses magnetic nanoparticles (MNPs) as nano-sorbent leading to a facile and fast extraction of analyte/s from the complex matrices with a satisfactory adsorption efficiency [1,2]. One of the main advantages of MSPE is that the nano-sorbent can be easily and rapidly isolated from the sample solution by applying a permanent magnet, while in SPE methods, the adsorbent should be separated by filtration, centrifugation or passing through a column [3,4]. MNPs have attracted much attention in scientific societies due to their superparamagnetic nature and their unique chemical and physical properties such as high dispersion, high surface-to-volume ratio and large relative surface area, leading to enhanced adsorption capacity.

Different spinel MNPs with a general chemical formula of AB_2O_4, such as $CoFe_2O_4$, $MnFe_2O_4$, $MgFe_2O_4$, $NiFe_2O_4$, have been used as magnetic nano-sorbents up to now [5-7]. Manganese ferrite ($MnFe_2O_4$) possessing the specific

*Corresponding author. E-mail: h.abdol@azaruniv.ac.ir

saturation magnetization of 40 emu g^{-1}, can be easily isolated from the solution using an external magnetic field [8-12]. Additionally, it is chemically stable and synthesized easily using inexpensive materials. Therefore, the application of $MnFe_2O_4$ MNPs as a nano-sorbent can combine the high adsorption capability of iron oxide and manganese oxide along with its complete and convenient isolation by applying a magnetic field in water treatment processes. Different methods including sol-gel [13], co-precipitation [14,15], combustion [16,17], hydrothermal synthesis [18], and micelle routes [19] have been employed for the synthesis of ferrite NPs under mild conditions. The synthesized MNPs using these methods exhibit good chemical homogeneity and high purity [20]. It has been reported that Zn^{2+} doping in the manganese ferrite structure leads to a considerable decrease in the crystallite size values due to the smaller ionic radius of Zn^{2+} (0.68 Å) than Mn^{2+} (0.75 Å). In addition, it has been found that the surface area and the porosity of $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs are enhanced by the increase in Zn^{2+} doping level, because of the decrease in the crystallite size and the bulk density [21]. Therefore, it is expected that this MNPs can exhibit high extraction capability toward the target analyte. However, to the best of our knowledge, so far, there is no report in the literature based on the application of $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs in the sample preparation procedures.

Our goal in this research is to synthesis $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs via a simple co-precipitation method and use it as an effectual adsorbent for MSPE of Cd(II) ion from aquatic samples. Cadmium is one of the few elements that have no structural role in the human body. Cadmium and its soluble species, are toxic even at very low concentrations, and are accumulated in the organs and the environment [22,23]. Therefore, the determination and control of its concentration in different samples is a significant subject to research. After successful synthesis of $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs and its characterization, the effect of important parameters influencing the MSPE efficiency was studied applying one variable at a time procedure.

EXPERIMENTAL

Reagents and Standards

Zinc nitrate hexahydrate $(Zn(NO_3)_2.6H_2O)$, cadmium nitrate tetrahydrate $(Cd(NO_3)_2.4H_2O)$, ferric chloride hexahydrate $(FeCl_3.6H_2O)$, manganese chloride tetrahydrate $(MnCl_2.4H_2O)$, hydrochloric acid, sodium dihydrogen phosphate, sodium hydroxide, and acetone were all purchased from Merck (Darmstadt, Germany). Cd(II) stock solution at the concentration level of 1000 µg ml^{-1} was prepared in deionized water and was stored in the refrigerator at 4 ℃. The working solutions were prepared daily, by diluting the appropriate volume of the stoke solution with the deionized water.

Instrumentation

Cd(II) ions have been determined by applying a flame atomic absorption spectrometer model SpectrAA 220 (Varian, Australia), which was equipped with an air-acetylene flame and a hollow cathode lamp using a deuterium background corrector. The source wavelength was 279.5 nm, which was applied with a current intensity of 1.5 mA. A magnetic heater stirrer (Corning, America) was employed in the MNPs synthesis procedure. A Metrohm pH meter model 827 (Switzerland) with a combined glass-calomel electrode was applied to adjust the pH of aqueous solutions.

To study and identify the various present functional groups in the structure of MNPs, a Bruker Fourier transform infrared spectrometer (Germany) was applied. A Bruker D8 Advance X-ray diffractometer (Germany) was applied for recording the XRD spectra of the prepared $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs. Cu-K_α radiation with the wavelength of 0.154 nm was applied as the X-ray source applying an acceleration voltage of 40 kV. A field emission scanning electron microscope (FESEM, MIRA3 TESCAN, Czech Republic) was used to study the surface characteristics, morphology, and elemental analysis of the synthesized $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs. Zeta potential determinations were performed with a HORIBA Scientific Analyzer (model SZ-100, Japan). Nitrogen adsorption-desorption isotherms, surface area, pore size distribution, and pore volume were determined using a BEISORP MINI II (BEL Japan, Inc.) analyzer. The pore radius (r_p) distribution was analyzed by the Barrett-Joyner-Halenda (BJH) model using the adsorption branch of isotherms. For isolation and phase separation of MNPs from the solution, a permanent magnet of Nd-Fe-B (10,000 G) was used. A Pars Azma mechanical stirrer (Iran) was

employed for agitating the solutions during the extraction and a CONICA ultrasonic bath (Italy) was applied for dispersion or dissolution of desired chemicals in the solution.

Preparation of $Zn_{0.2}Mn_{0.8}Fe_2O_4$ NPs

The $Zn_{0.2}Mn_{0.8}Fe_2O_4$ NPs were synthesized by the co-precipitation method [21] as follows: Appropriate amounts of $Zn(NO_3)_2.6H_2O$, $MnCl_2.4H_2O$ and $FeCl_3.6H_2O$ were added to deionized water. The obtained solution was heated up to 70 ℃, while stirring with a magnetic stirrer. Then, NaOH solution (6 M) was added to the solution to increase its pH. The produced sediment particles were collected at the beaker bottom, and the supernatant was decanted. The obtained precipitate was rinsed with distilled water several times to eliminate its impurities. The resulting precipitate was washed with acetone and placed in the furnace at 500 °C for 5 h and then was used as a nano-sorbent.

MSPE Condition

To perform MSPE of Cd(II) ion, 200 mg of magnetic zinc-doped manganese ferrite NPs were added into a 200 ml of real sample solution or working standard solution containing Cd(II) ion in phosphate buffer (0.1 M, pH 7.5), and the resulted mixture was mechanically stirred for 15 min. After complete adsorption of Cd(II) ion onto the adsorbent, the nano-sorbent particles were collected by applying a permanent magnet in the beaker bottom and the solution was overflowed. The pre-concentrated Cd(II) ion onto the $Zn_{0.2}Mn_{0.8}Fe_2O_4$ nano-sorbent was desorbed by the addition of 2 ml of nitric acid solution (0.6 M) to the nano-sorbent for 15 min. Finally, the desorbed Cd(II) ion was separated from the adsorbent and transferred to a microtube and measured by FAAS.

RESULTS AND DISCUSSION

Characterization of $Zn_{0.2}Mn_{0.8}Fe_2O_4$

The mixed ferrite of $Zn_{0.2}Mn_{0.8}Fe_2O_4$ was synthesized through the co-precipitation method at 70 °C. The purity and structure of the synthesized mixed ferrite were studied using X-ray diffraction spectroscopy. Figure 1 displays the XRD spectrum of the prepared $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs. The existence of characteristic diffraction peaks at certain 2θ
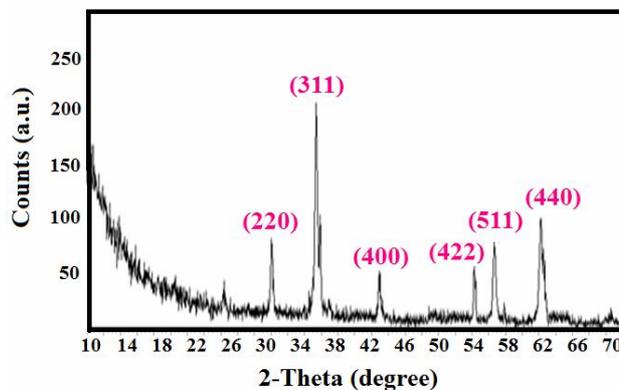
Fig. 1. XRD pattern of the prepared $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs.

values 30°, 35.3°, 43°, 54.4°, 56.6° and 62.3°, related to (220), (311), (400), (422), (511) and (440) planes confirms that the synthesized MNPs are single-phase with a cubic spinel structure, and there is no characteristic peak from the impurities. Zinc doping into manganese ferrite structure decreases the network constant, which can be due to the distribution of zinc cation on both tetrahedral and octahedral sites. Zn cation is randomly allocated in the octahedral and tetrahedral cavities, but its tendency to occupy the tetrahedral sites is higher than the octahedral site [21]. The XRD pattern of the synthesized $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs was compared with magnetite (Fe_3O_4) NPs and $MnFe_2O_4$ NPs according to the published data. It has been reported that the characteristic peaks of Fe_3O_4 NPs are observed at 2θ of 30.1°, 35.5°, 43.1°, 53°, 57.4° and 62.6° which correspond to the Bragg reflections from (220), (311), (400), (422), (511), and (440), respectively, match well with those from the Joint Committee on Powder Diffraction Standards for magnetite (JCPDS No. 19-0269) [24]. For $MnFe_2O_4$, the peaks for the mentioned diffraction planes are located at 2θ = 30.2°, 35.5°, 43.2°, 53.6°, 57.0°, and 62.7°, respectively (well matched with JCPDS No. 074-2403) [25]. According to this comparison, it is clear that the characteristics diffraction plane of cubic spinel structure of Fe_3O_4 NPs is observed for all MNPs with an insignificant shift in peaks location. Additionally, for the main diffraction peaks of $Zn_{0.2}Mn_{0.8}Fe_2O_4$ including (311), (440) and (511), there is a small shift to less 2θ values, due to the zinc doping into the $MnFe_2O_4$ structure, which has good agreement with the previous reports [21].
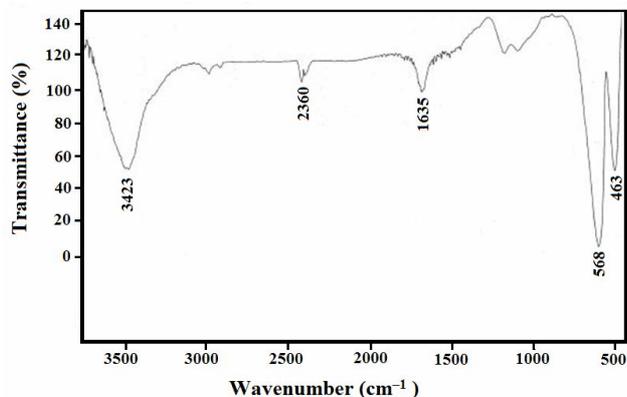
Fig. 2. FTIR spectrum of the synthesized $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs.

Fig. 4. EDX analysis of the synthesized nanosorbent.

Fig. 3. (a) and (b) The field emission-scanning electron micrograph of the prepared magnetic adsorbent in different magnifications.
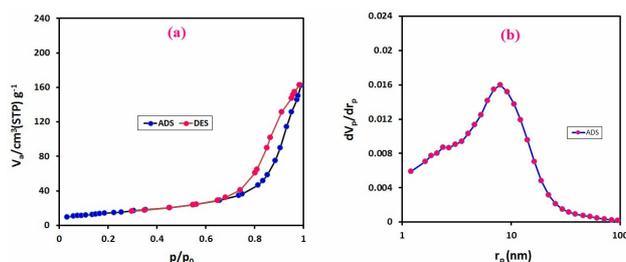
Fig. 5. (a) Nitrogen adsorption/desorption isotherm, and (b) pore size distribution curve of the synthesized nanosorbent.

The FT-IR was applied to determine the nature and also to approve the presence of various functional groups in the structure of a sample. Figure 2 shows the FT-IR spectrum of $Zn_{0.2}Mn_{0.8}Fe_2O_4$. Accordingly, it is observed that there are two important peaks in the structure of all spinel ferrites due to the metal-oxygen bond. The peak at 568 cm^{-1} is related to the O-Fe vibration in the tetrahedral cavity, and the observed peak at 463 cm^{-1} is due to the O-Fe vibration in the octahedral cavity. The peak at 1635 cm^{-1} corresponds to the H_2O bending vibration, which has been absorbed by $Zn_{0.2}Mn_{0.8}Fe_2O_4$ after calcination. The broad band observed at 3423 cm^{-1} is ascribed to the stretching vibration of O-H bond.

FE-SEM images of $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs are represented in Fig. 3 with different magnifications. Accordingly, the structure of these MNPs is cumulative of cubic and quasi-cubic crystals with a diameter range of 15-64 nm. Additionally, the synthesized MNPs have exhibited a porous morphology, in which the NPs are slightly interconnected and aggregated. The EDX analysis was also employed to study the composition of $Zn_{0.2}Mn_{0.8}Fe_2O_4$. The results that are given in Fig. 4, confirm the presence of Zn, Mn, Fe and O elements in the composition of the nanosorbent.

The nitrogen adsorption/desorption isotherm and the corresponding pore-size distribution curve of the synthesized $Zn_{0.2}Mn_{0.8}Fe_2O_4$ are shown in Fig. 5. As shown in Fig. 5a, the isotherm is found to be of type IV classification with an H1 hysteresis loop in the range between 0.65 and 1.0 relative pressure (P/P°), which is typical of mesoporous solid. In addition, the pore-size distribution was confirmed by the corresponding Barrett-

Table 1. The Pore Structure Parameters of Fe_3O_4, $MnFe_2O_4$ and $ZnMnFe_2O_4$ NPs

Samples	Average pore size (nm)	Pore volume ($cm^3 g^{-1}$)	Specific surface area ($m^2 g^{-1}$)
Fe_3O_4	45.584	0.1081	25.89
$MnFe_2O_4$	32.211	0.1986	39.13
$ZnMnFe_2O_4$	19.337	0.2503	51.78

Joyner-Halenda (BJH) pore-radius distribution curve as shown in Fig. 5b. The specific surface area, average pore size and pore volume of the studied samples are listed in Table 1.

Extraction Optimization

Extraction efficiency of $Zn_{0.2}Mn_{0.8}Fe_2O_4$ toward Cd(II). To study the effect of zinc doping on the structure of manganese ferrite and also to illustrate the higher performance of manganese ferrite in comparison with magnetite NPs, the extraction efficiencies of these three MNPs toward Cd(II) ion were compared. According to the obtained results presented in Fig. 6, the $MnFe_2O_4$ shows higher extraction capability for Cd(II) compared with Fe_3O_4 MNPs, which may be because of internal and surface pores, induced by displacement of Fe^{3+} ions from tetrahedral to octahedral sites in the spinel ferrite structure as a result of Mn^{2+} doping in Fe_3O_4 structure. Additionally, it is clear that zinc doping into the structure of $MnFe_2O_4$ MNPs has led to the highest extraction recovery, due to the enhancement of the specific surface area raising from the decrease of the bulk density and the crystallite size (Table 1). Consequently, $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs were selected as an effectual nano-sorbent for MSPE of Cd(II) ions.

Choice of eluent. After selecting the appropriate adsorbent for the analyte separation and enrichment using MSPE, it is required to use the suitable solvent/solution for the thorough desorption of the trapped analyte on the nano-sorbent to achieve the highest extraction efficiency. Considering the fact that, electrostatic attraction is the main mechanism for adsorption of Cd(II) ions by the synthesized nano-sorbent, therefore, the acidic solutions were applied to change the surface charge of $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs to be
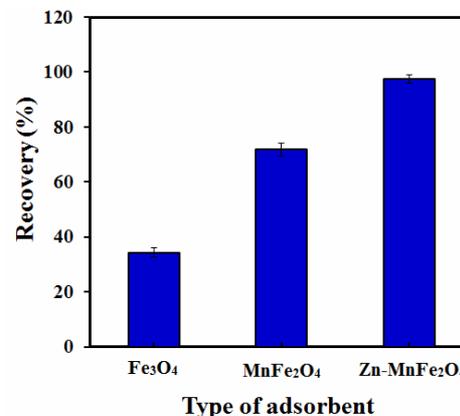
Fig. 6. Comparison of the extraction capability of various synthesized nano-sorbents toward Cd(II) ion. Experimental conditions: Sample volume; 100 ml, Amount of the adsorbent; 250 mg, pH; 6, Extraction time; 20 min.

positive, leading to a repulsive interaction between nano-sorbent surface and Cd(II) ions. Herein, various solutions such as sulfuric acid, hydrochloric acid, nitric acid, acetic acid, and citric acid were studied. According to the results shown in Fig. 7a, nitric acid has led to complete desorption of the Cd(II) species trapped by the adsorbent. Therefore, it was selected as an effective eluting solution for further examinations.

Desorption solution concentration. By selecting nitric acid as the desorption solution, its concentration was also evaluated in the concentration range of 0.01 to 0.1 M. According to the results shown in Fig. 7b, complete desorption of Cd(II) ions from $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs was achieved applying 0.06 M nitric acid, and the extraction recovery was constant applying higher concentration of nitric acid. Hence, 0.06 M HNO_3 was used as the best concentration for the rest of the experiments.

The volume of desorption solution. Considering the desorption process, it is necessary to apply the lowest possible volume of nitric acid solution with complete desorption ability to obtain a high enrichment factor and sensitivity. In this regard, different volumes of HNO_3 solution (0.06 M) ranging from 1 to 5 ml were used for desorption of loaded Cd(II) ions on the adsorbent. According to the results displayed in Fig. 7c, enhancing the
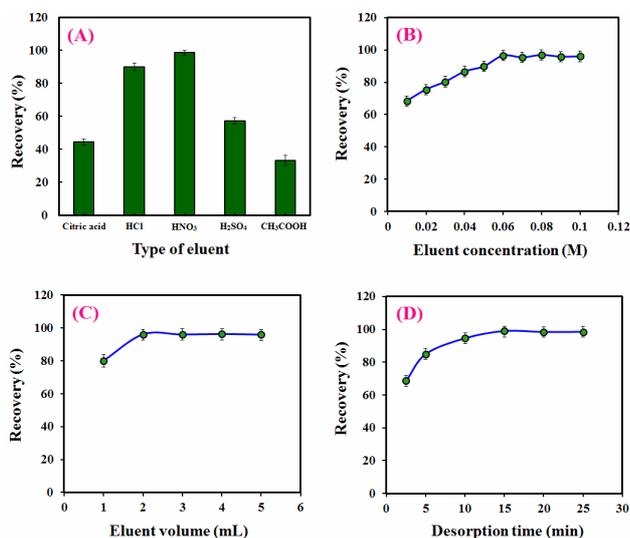
Fig. 7. Effect of different parameters on the desorption process; (a) elution solution, (b) eluent concentration, (c) desorption solution volume, and (d) elution time. Experimental conditions: (a) Sample volume; 100 ml, Amount of the adsorbent; 250 mg, pH; 6, Extraction time; 20 min, Desorption time; 20 min, Eluent concentration; 0.1 M, Eluent volume; 2 ml, (b) Sample volume; 100 ml, Amount of the adsorbent; 250 mg, pH; 6, Extraction time; 20 min, Desorption time; 20 min, Eluent volume; 2 ml, (c) Sample volume; 100 ml, Amount of the adsorbent; 250 mg, pH; 6, Extraction time; 20 min, Desorption time; 20 min, Eluent concentration; 0.06 M, and (d) Sample volume; 100 ml, Amount of the adsorbent; 250 mg, pH; 6, Extraction time; 20 min, Eluent concentration; 0.06 M, Eluent volume; 2 ml.

volume of HNO_3 solution has led to increaseing of the extraction recovery up to 2 ml, and after that, the extraction recovery has remained almost constant. When low volumes of the eluent were applied, the desorption cannot be completely performed and a fraction of the trapped analyte remained on the surface of the nano-sorbent. By increasing its volume up to a certain volume, complete desorption was achieved and after that more increase in eluent volume led to the dilution of the analyte and decreasing of analytical method's sensitivity. Therefore, 2 ml of HNO_3 solution was applied for further experiments to reach the highest

enrichment factor.

Elution time. Desorption time is another effective parameter influencing the desorption efficiency, which its effect should be evaluated to reach a complete elution process during a minimum elution time. For this purpose, after extraction of Cd(II), the elution was carried out using 2 ml of 0.06 M HNO_3 during various desorption times (2.5 to 25 min). Considering the results displayed in Fig. 7d, it is clear that, by increase of desorption time up to 15 min, the extraction recovery was increased and after that, the extraction recovery remained constant. As is expected, enhance of elution time leads to the progress of proton absorption by nano-sorbent and desorption of Cd(II) ions. Therefore, it seems that 15 min of elution time is enough for the complete elution of Cd(II) ion from $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs, and more increase of the desorption time has no significant effect on the extraction recovery.

The pH effect. The pH of the sample solution is another important factor affecting the MSPE, which should be investigated for Cd(II) extraction. The pH of the sample solution should guarantee the nano-sorbent stability and also lead to the highest possible extraction recovery. The pH of the sample solution can influence not only the surface charge density of the nano-sorbent but also can affect the form of the analyte. In this investigation, the pH of the sample solution was changed in the range of 4 to 10. At pH values lower than 4.0, as the $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs surface is positively charged, and it does not have the ability to adsorb Cd(II) ions due to the electrostatic repulsive interactions; while at higher pH values, the surface of the MNPs is negatively charged and the electrostatic attraction between the $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs surface and Cd(II) ions can lead to successive extraction of Cd(II) ions. As shown in Fig. 8, the zeta potential of the synthesized $Zn_{0.2}Mn_{0.8}Fe_2O_4$ nanosorbent is -62.1 mV at pH 7.5. It is worth noting that, by more increase of pH value, the extraction recovery is decreased due to the cadmium hydroxide formation in alkaline media. Considering the results displayed in Fig. 9a, the highest extraction recovery was obtained around pH 7-8. Accordingly, the pH of 7.5 was applied as the optimum pH value and adjusted by 0.1 M phosphate buffer.

Nano-sorbent amount. Another effective factor influencing the extraction recovery in the MSPE methods is
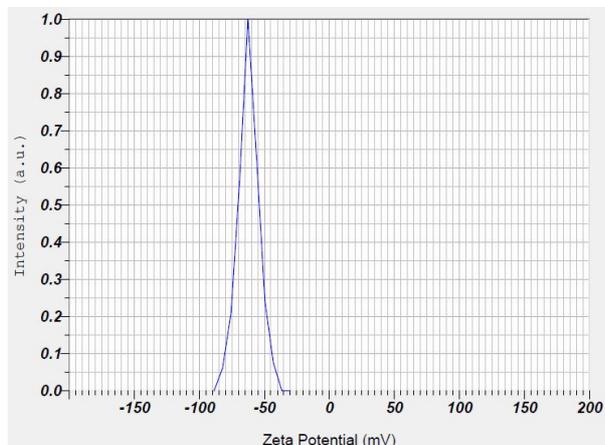
Fig. 8. Zeta potential diagram of the synthesized $Zn_{0.2}Mn_{0.8}Fe_2O_4$ nanosorbent.

the mass of adsorbent applied for the extraction. Generally, the SPE technique is an equilibrium-based process similar to the chromatography methods, in which the distribution constant is very high, leading to complete retention of analyte/s onto the adsorbent/sorbent. According to Nernst's distribution law based on the distribution of a solute in the organic/sorbent and in the aqueous phases [26], by the increase of the sorbent amount, the concentration of loaded analyte on/in the sorbent decreases, leading to progress of equilibrium in a way to extract more analytes on/into the sorbent. On the other hand, the value for the distribution constant is closely proportional to the tendency of the sorbent toward the target analyte, showing the sorbent's capability to extract the target analyte/s. Applying a more efficient sorbent with high distribution constant and high sorptive capacity leads to reaching the exhaustive extraction by applying a low amount of the sorbent. Herein, in order to investigate the effect of adsorbent mass on the extraction recovery, various amounts of $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs ranged from 50 to 400 mg were studied. The obtained results showed that 200 mg of the MNPs has led to complete extraction of Cd(II) ion, and higher amounts of the MNPs have not improved the extraction recovery (Fig. 9b). Thus, 200 mg of $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs was chosen as the appropriate amount to reach the maximum extraction efficiency for Cd(II) ion.

Extraction time. Extraction time is another important parameter affecting the extraction recovery by creating the opportunity for the analyte/s to interact with the adsorptive

sites of the adsorbent. One of the significant advantages of MSPE methods over common SPE methods is simple and rapid isolation of nano-sorbent from the sample solution after performing the extraction and elution process by applying an external magnetic field, without using time-consuming centrifugation or filtration process, leading to a fast, simple and easy extraction procedure. Herein, to study the influence of extraction time on the extraction recovery, the experiments were performed for various contact times varied from 5 to 25 min applying optimum value for the other investigated parameters. As depicted in Fig. 9c, the extraction efficiency is reached its maximum value using 15 min of contact time and there is no improvement in extraction recovery after this time. Therefore, 15 min was applied as the optimum value for the further examinations.
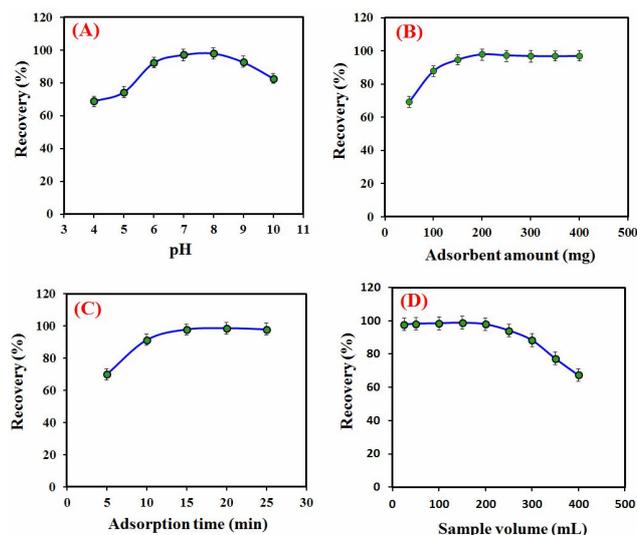
Fig. 9. Effect of different factors on the extraction recovery, (a) pH effect, (b) effect of sorbent mass, (c) effect of extraction time, and (d) effect of sample volume. Experimental conditions: (a) Sample volume; 100 m., Amount of the adsorbent; 250 mg, Extraction time; 20 min, Desorption time; 15 min, Eluent concentration; 0.1 M, Eluent volume; 2 m., (b) Sample volume; 100 m., pH; 7.5, Extraction time; 20 min, Desorption time; 15 min, Eluent concentration; 0.06 M, Eluent volume; 2 m., (c) Sample volume; 100 m., Amount of the adsorbent; 200 mg, pH; 7.5, Desorption time; 15 min, Eluent concentration; 0.06 M, Eluent volume; 2 mL, and (d) Amount of the adsorbent; 200 mg, pH; 7.5, Extraction time; 15 min, Desorption time; 15 min, Eluent concentration; 0.06 M, Eluent volume; 2 m.

Sample volume. To evaluate the enrichment factor (EF) and the possibility of extraction of target analytes with trace concentrations from large sample volumes, one can study the sample volume to find the highest sample volume applicable for the developed MSPE method. In this regard, it was investigated by spiking a similar amount of Cd(II) ion into different sample volumes ranging from 25 to 400 ml. The obtained solutions with different concentrations and volumes were extracted by contacting 200 mg of the nano-sorbent with the Cd(II) solution at the pH of 7.5 for 15 min. The elution step was then performed by the addition of 2 ml HNO_3 solution (0.06 M) to the analyte-loaded nano-sorbent for 15 min. According to the obtained data represented in Fig. 9d, the complete extraction of the analyte is possible applying sample volumes up to 200 ml, but at higher volumes, the extraction efficiency is decreased. Therefore, 200 ml of the sample solution was selected as the best value for the rest of the experiments. Considering the fact that the extraction recovery is close to 100%, the sample volume is 200 ml and the optimum desorption solution volume is 2 ml, EF was calculated to be 100.

Adsorption capacity. For determining the adsorption capacity of $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs, 200 mg of this MNPs was contacted with Cd(II) ions present in 200 ml aqueous solution with the concentration of 0.1 to 50 µg ml^{-1} and pH of 7.5 (phosphate buffer, 0.1 M). To ensure reaching the equilibrium state for Cd(II) ion between two phases, the beaker content was mechanically agitated for 30 min and then $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs were separated using an external magnetic field. Afterward, the loaded Cd(II) ions were desorbed from the adsorbent using 2 ml of 0.06 M HNO_3 and the concentration of Cd(II) ion was determined using FAAS. The adsorbent capacity (q) for Cd(II) ion has been estimated applying the following equation:

$$q = \frac{(C_0 - C_t)\,V}{m} \tag{1}$$

in which, C_0 and C_t are the analyte initial and equilibrium concentration, respectively, V is the sample volume and m is the amount of the adsorbent. According to the results, the adsorption capacity for $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs toward Cd(II) ion was calculated to be 29.68 mg g^{-1}.

The prepared nano-sorbent reusability. Generally,
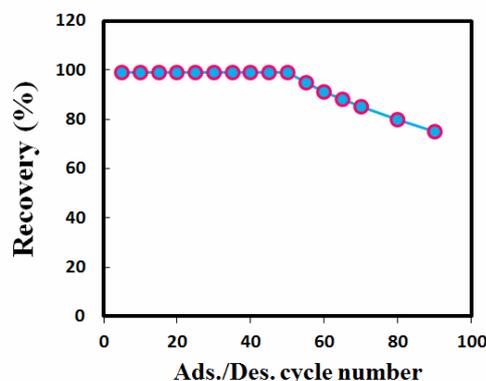
Fig. 10. Effect of adsorption/desorption cycle times on recovery of Cd(II) ions by the synthesized $Zn_{0.2}Mn_{0.8}Fe_2O_4$ nanosorbent.

one of the key parameters indicating the quality of the nano-sorbent is the adsorbent stability and reusability, because an adsorbent with high stability can be applied for more extraction and desorption cycles leading to less consumption nano-sorbent, cost-effective and environmental-friendly process. For this purpose, two criteria should be evaluated: carry-over effect and extraction capability of the adsorbent toward Cd(II) ion. To evaluate the carry-over effect, the adsorbent was washed with 2 ml of 0.06 M HNO_3 and 10 ml of deionized water at three steps, respectively, after each extraction process, and the washed nano-sorbent was eluted to desorb the remained Cd(II) ion on the nano-sorbent. According to the experimental results, no memory effect was observed which is promising to use the adsorbent for the subsequent extraction. On the other hand, according to the results displayed in Fig. 10, the prepared nano-sorbent is exhibited high chemical stability during 50 cycles of extraction without any decrease in the Cd(II) extraction efficiency and magnetic properties of the nano-sorbent.

The effect of interferences. For investigating the selectivity of the MSPE method based on the application of $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs, the effect of co-existing ions in the real samples on Cd(II) extraction and determination was studied. In this regard, interfering ions with different concentration ratios were added to the aqueous solution of Cd(II) ions with a concentration of 15 ng ml^{-1} and the resulted solution was extracted applying the developed

Table 2. Tolerance Limits of Potentially Interfering Ions in the Determination of 15 ng ml^{-1} Cd(II) Ion

Interfering ions	Interfering ion to analyte weight ratio
Na$^+$, K$^+$, Li$^+$, Fe^{3+}, Ca^{2+}, F$^-$, Cl$^-$, PO$_4^{3-}$, Mg^{2+}, NO$_3^-$, CH$_3$COO$^-$	>1000:1
CO$_3^{2-}$, CrO$_4^{2-}$, Ag$^+$	800:1
Cu^{2+}, Mn^{2+}	500:1
Co^{2+}, Ni^{2+}	300:1
Zn^{2+}, Pb^{2+}, Hg^{2+}	100:1
Cr^{3+}	10:1

MSPE method. For an interfering ion, the highest concentration ratio which causes the variance of the extraction recovery of the target analyte less than ± 5% is defined as the tolerance limit. If the interference effect for one coexisting ion is observed, its concentration ratio in relation to the analyte concentration is gradually reduced up to eliminate the interference effect. The tolerance limits of the studied co-existing ions are tabulated in Table 2. As can be seen, the presence of co-existing ions has no significant interference effect in the determination of Cd(II) ion, with the exception of Cr^{3+}. The interference effect of Cr^{3+} can be overcome by its oxidation with 0.005 M H$_2$O$_2$ to give CrO$_4^{2-}$. As it is clear the tolerance limit was resulted at high concentration ratio for almost of investigated ions, indicating the insignificant interfering effects of the co-existent ions in the determination of Cd(II) ion. This level of selectivity can be assigned to the inability of Zn$_{0.2}$Mn$_{0.8}$Fe$_2$O$_4$ MNPs to adsorb the anionic and cationic species, and this property lets to measure the trace concentrations of Cd(II) ion in various real samples without any interference effect.

Analytical figures of merit. After evaluation of effects of important parameters affecting the extraction recovery and optimizing them, the figures of merit for the developed MSPE method was evaluated in the terms of limit of detection (LOD), method's linear dynamic range (LDR), its accuracy and precision. To examine the method's linearity, 200 ml of Cd(II) working standard solutions at different concentration levels, were extracted applying Zn$_{0.2}$Mn$_{0.8}$Fe$_2$O$_4$ MNPs under optimized extraction and

desorption procedure (each point of concentration was examined with three replication). Then, the calibration plot was depicted applying average results, which is linear in the range of 0.1 to 30.0 ng ml^{-1} with a satisfactory correlation coefficient (0.9984). LOD for the developed MSPE-FAA method was estimated by the equation of LOD = 3S$_b$/m, in which S_b is the standard deviation of results corresponding to the several replicated experiments applying blank sample and m denotes the calibration curve slope. After analysis of the blank sample in 5 replication, LOD was estimated to be 0.03 ng ml^{-1}. To assay the repeatability of the method, intra-day and inter-day precisions of the developed method were investigated by performing 5 replicates for measurement of Cd(II) ion with a concentration of 15 ng ml^{-1} in one day and 5 days, respectively. Accordingly, the relative standard deviation percentage (RSD%) was calculated to be 3.3% and 1.9% for inter-day and intra-day precisions, respectively.

The evaluation of the accuracy of the developed MSPE method was performed by analysis of the standard sample, NIST SRM 1643e, containing specific concentration of Cd(II) ion (6.6568 ± 0.073 ng ml^{-1}). Accordingly, the concentration of Cd(II) ions was measured to be 6.54 ± 0.26 ng ml^{-1}, which fits well with the real concentration of Cd(II) ion in the standard sample. The obtained results were statistically analyzed applying t-test and the result revealed that there is no considerable difference between the real concentration in certified sample and the resulted concentration at confidence level of 95%, confirming the high accuracy of the developed method.

The analytical figure of merit for the developed MSPE-FAA method was compared with the other published researches [27-32] by comparison of the limit of detection, linear dynamic range, enrichment factor, and precision. According to Table 3, the developed method has a lower limit of detection and wider LDR in comparison with some researches based on SPE-AAS, but the methods are based on the application of high-performance liquid chromatography-ultraviolet variable wavelength detector [28,30] have lower LOD values. In these methods, the extracts have been completely evaporated under N$_2$ flow and dissolved by the addition of a low volume of the solvent leading to a concentrated final extract and higher sensitivity and lower LOD values. The developed method's precision

Table 3. Comparison of the Analytical Performance of the Developed Method with the other Reported Researches for the Determination of Cd(II)

Method	Sample	LOD (ng ml^{-1})	LDR (ng ml^{-1})	RSD (%)	EF	Ref.
SPE-FAAS[a]	Water and food samples	0.42	2.1-75	3	100	[27]
MSPE-HPLC-VWD[b]	Water samples	0.016	0.05-200	1.5	250	[28]
MMR-FBA-GFAAS[c]	Edible oils	0.006	0.05-1 (ng g^{-1})	3.3	9	[29]
MSPE-HPLC-VWD	Water samples	0.011	0.05-200	2.3	100	[30]
IIP-SPE-ETAAS[d]	Sea food	0.21	1.65-30	9	12.5	[31]
SPE-FAAS	Water samples	0.2	1-20	5.1	250	[32]
MSPE-FAAS	Water samples	0.03	0.1-30.0	1.9	100	This research

[a]Solid phase extraction-flame atomic absorption spectrometry. [b]Magnetic solid phase extraction high performance liquid-phase chromatography-ultraviolet variable wavelength detector. [c]Magnetic-mechanical robotic-flow-batch analyzer-graphite furnace atomic absorption spectrometer. [d]Ion imprinted polymer-solid phase extraction-electrothermal atomic absorption spectrometry.

is better in comparison to some cases and is comparable with the rest of them. As a result, the developed MSPE-FAA method can be regarded as an effectual analytical method for the measurement of Cd(II) ions due to its low LOD, wide LDR, and good precision.

For evaluating the applicability and efficiency of the developed MSPE method for Cd(II) ion measurement, it was applied for pre-concentration, separation, and measurement of Cd(II) ion in 200 ml of different water samples, without and with spiking a determined concentration of Cd(II) ion into different samples. In this regard, different real water samples including spring water and tap water were collected from Azarshahr (East Azarbaijan province, Iran), well water and river water were collected from Miandoab (West Azarbaijan province, Iran), and two industrial wastewater samples were collected from Azarshahr and Maragheh (East Azarbaijan province, Iran). The collected samples were filtered (with the exception of tap water) and stored in a refrigerator up to use without further pretreatment process. The matrix effect on the performance of the extraction was investigated by calculation of the recovery percentage of Cd(II) ion and the

obtained data are reported in Table 4. The high values for relative recovery confirmed that the developed MSPE-FAA method can be applied for the determination of Cd(II) ion in real samples with high accuracy and insignificant matrix effect.

CONCLUSIONS

A novel magnetic adsorbent based on $Zn_{0.2}Mn_{0.8}Fe_2O_4$ NPs was synthesized *via* a facile co-precipitation method and used as an efficient adsorbent for the selective extraction of Cd(II) ion from aqueous samples. It resulted that $MnFe_2O_4$ MNPs exhibits higher extraction efficiency in comparison to Fe_3O_4 MNPs. Additionally, doping zinc into the $MnFe_2O_4$ MNPs structure causes an enhancement in the extraction capability due to the decrease of the values of the crystallite size and enhance of the specific surface area. The $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs are easily separated after the extraction process applying an external magnetic field and it is not required to perform any additional column passing, filtration or centrifugation of the sample solution, leading to the convenience and fast extraction procedure. Additionally,

Table 4. Determination of Cd(II) ion in Several Water Samples and a Certified Reference Material

Samples	Added (ng ml^{-1})	Found (ng ml^{-1})	Recovery (%)
Spring water[a]	-	2.1 ± 0.1	-
	10.0	11.9 ± 0.4	98.0
	20.0	21.6 ± 0.3	97.5
Well water[b]	-	1.7 ± 0.1	-
	10.0	11.6 ± 0.3	99.0
	20.0	22.1 ± 0.5	102.0
Tap water[a]	-	-	-
	10.0	9.6 ± 0.3	96.0
	20.0	19.9 ± 0.4	99.5
River water[b]	-	-	-
	10.0	9.6 ± 0.1	96.0
	20.0	19.6 ± 0.2	98.0
Wastewater 1[c]	-	6.5 ± 0.1	-
	10.0	16.7 ± 0.3	102.0
	20.0	26.0 ± 0.4	97.5
Wastewater 2[d]	-	8.3 ± 0.2	-
	10.0	18.2 ± 0.4	99.0
	20.0	28.3 ± 0.5	100.0

	Certified value (ng ml^{-1})	Assayed value (ng ml^{-1})	Relative error (%)
NIST SRM 1643e	6.6568 ± 0.073	6.54 ± 0.26	-1.75

[a]Obtained from local source, Azarshahr, Iran. [b]Obtained from local source, Miandoab, Iran. [c]Obtained from industrial wastewater of glass manufacturing factory, Maragheh, Iran. [d]Obtained from industrial wastewater of dye manufacturing factory, Shahid Salimi Industrial Area, Tabriz, Iran.

one of the major advantages of the prepared adsorbent is its stability and reusability making it applicable for at least 50 cycles of extraction/elution process. The analytical figure of merit for the developed method confirms that the $Zn_{0.2}Mn_{0.8}Fe_2O_4$ MNPs is a proper magnetic nano-sorbent for extraction of Cd(II) ion. Furthermore, the developed MSPE method is selective, reproducible, accurate, cost-effective and efficient for the extraction of Cd(II) ions from various real samples.

REFERENCES

[1] K. Aguilar-Arteaga, J.A. Rodriguez, E. Barrado, Anal. Chim. Acta 674 (2010) 157.

[2] E. Öztürk Er, G. Dalgıç Bozyiğit, Ç. Büyükpınar, S. Bakırdere, Crit. Rev. Anal. Chem. 9 (2020) 1.

[3] H. Abdolmohammad-Zadeh, Z. Ayazi, Z. Naghdi, J. Magn. Magn. Mater. 488 (2019) 165311.

[4] M.A. Karimi, A. Hatefi-Mehrjardi, S.Z. Mohammadi, A. Mohadesi, M. Mazloum-Ardakani, A.A. Kabir, M. Kazemipour, N. Afsahi, Int. J. Environ. Anal. Chem. 92 (2012) 1325.

[5] P.A. Vinosha, P.A. Vinosha, A.C. Preetha, B. Xavier, G.F. Nirmala, A. Manikandan, A. Dinesh, Y. Slimani, M. Almessiere, A. Baykal, J. Supercond. Nov. Magn. 34 (2021) 995.

[6] N. Tara, S.I. Siddiqui, G. Rathi, S.A. Chaudhry, A.M. Asiri, Curr. Anal. Chem. 16 (2020) 14.

[7] R. Asadi, H. Abdollahi, M. Gharabaghi, Z. Boroumand, Adv. Powder Technol. 31 (2020) 1480.

[8] W. Tang, Y. Su, Q. Li, S. Gao, J.K. Shang, Water Res. 47 (2013) 3624.

[9] R. Wu, R. Wu, J. Qu, J. Chem. Technol. Biotechnol. 80 (2005) 20.

[10] K.-W. Jung, S. Lee, Y.J. Lee, Bioresour. Technol. 245 (2017) 751.

[11] V. Stefanova, D. Georgieva, V. Kmetov, I. Roman, A. Canals, J. Anal. Atom. Spectrom. 27 (2012) 1743.

[12] K.L. Bhowmik, A. Debnath, R.K. Nath, S. Das, K.K. Chattopadhyay, B. Saha, J J. Mol. Liq. 219 (2016) 1010.

[13] S. Chakrabarty, S. Bandyopadhyay, M. Pal, A. Dutta, Mater. Chem. Phys. 259 (2021) 124193.

[14] N. Kaur, M. Kaur, Process. Appl. Ceram. 8 (2014) 137.

[15] H. Bagheri, O. Zandi, A. Aghakhani, Anal. Chim. Acta 692 (2011) 80.

[16] A.B. Naik, P.P. Naik, S.S. Hasolkar, D. Naik, Ceram.

Inter. 46 (2020) 21046.

[17] A.T. Dhiwahar, M. Sundararajan, P. Sakthivel, C.S. Dash, S. Yuvaraj, J. Phys. Chem. Solids 138 (2020) 109257.

[18] S. Fayazzadeh, M. Khodaei, M. Arani, S. Mahdavi, T. Nizamov, A. Majouga, J. Supercond. Nov. Magn. 33 (2020) 2227.

[19] T. Ahmad, K.V. Ramanujachary, S.E. Lofland, A.K. Ganguli, J. Chem. Sci. 118 (2006) 513.

[20] Y.-K. Sun, I.-H. Oh, Indust. Engin. Chem. Res. 35 (1996) 4296.

[21] D. Varshney, K. Verma, A. Kumar, Mater. Chem. Phys. 131 (2011) 413.

[22] J.O. Duruibe, M.O.C. Ogwuegbu, J.N. Egwurugwu, Inter. J. Phys. Sci. 2 (2007) 112.

[23] P. Bhattacharya, S.H. Frisbie, E. Smith, R. Naidu, G. Jacks, B. Sarkar, Handbook of Heavy Metals in the environment. Marcell Dekker Inc., New York, 2002, p. 147.

[24] Z.M. Khoshhesab, Z. Ayazi, Z. Farrokhrouz, Anal.

Methods 8 (2016) 4934.

[25] B. Sahoo, S.K. Sahu, S. Nayak, D. Dhara, P. Pramanik, Catal. Sci. Technol. 2 (2012) 1367.

[26] A. Andrade-Eiroa, M. Canle, V. Leroy-Cancellieri, V. Cerdà, TrAC Trends Anal. Chem. 80 (2016) 641.

[27] M. Tuzen, S. Sahiner, B. Hazer, Food Chem. 210 (2016) 115.

[28] Y. Yuan, Y. Wu, H. Wang, Y. Tong, X. Sheng, Y. Sun, X. Zhou, Q. Zhou, J. Hazard. Mater. 386 (2019) 121658.

[29] I.S. Barreto, S.I.E. Andrade, F.A.S. Cunha, M.B. Lima, M.C.U. Araujo, L.F. Almeida, Talanta 178 (2018) 384.

[30] Q. Zhou, M. Lei, Y. Liu, Y. Wu, Y. Yuan, Talanta 175 (2017) 194.

[31] M.C. Barciela-Alonso, V. Plata-Garcia, A. Rouco-Lopez, A. Moreda-Pineiro, P. Bermejo-Barrera, Microchem. J. 114 (2014) 106.

[32] H. Parham, N. Pourreza, N. Rahbar, J. Hazard. Mater. 163 (2009) 588.