An Innovative Nanosorbent Based on ZnO@Ag₂O@Fe₃O₄ Nanocomposite- for Extraction and Preconcentration of Cd(II) Ions from Water Samples

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In this study, a ZnO@Ag₂O@Fe₃O₄ nanocomposite as an innovative magnetic solid phase extraction agent is introduced. The structural and morphological properties of the as-prepared nano-sorbent were characterized using X-ray diffraction analysis, Fourier transform infrared spectroscopy, field emission scanning electron microscopy and nitrogen adsorption–desorption techniques. The synthesized magnetic nano-sorbent was applied for extraction and pre-concentration of Cd(II) ions from water samples. The as-prepared nano-sorbent with the magnetism property was easily manipulated by a magnet. Factors affecting the extraction of the Cd(II) ions from aqueous solutions were investigated and optimized conditions were reported. Under optimum conditions, linear concentration range of 0.1-10 ng ml^{-1} with a correlation coefficient of 0.9918 was obtained for Cd(II) ions. The detection limit and enrichment factor for cadmium are 0.03 ng ml^{-1} and 200, respectively. The intra- and inter-day relative standard deviations (at 4 ng ml^{-1} Cd(II) ion concentration and n = 6) were found to be 1.8 and 2.6%, respectively. The maximum sorption capacity of the nano-sorbent for cadmium was 48 mg g^{-1}. The accuracy of the method was checked by the analysis of the standard reference material NIST SRM 1643e, and successfully applied to determine cadmium in several water and wastewater samples with relative recovery values in the range of 98-102% for the spiked samples.

Keywords: ZnO@Ag₂O@Fe₃O₄ nanocomposite, Magnetic nano-sorbent, Cadmium, Flame atomic absorption spectrometry, Water samples

INTRODUCTION

Recently, pollution of the natural waters by heavy metal has caught considerable attention. Among heavy metals, cadmium (Cd) not only causes the pollution, but also is considered as a risk factor for people's health [1]. Cd(II) ion is classified as the sixth most toxic material jeopardizing human's health. Through the food chain system (*i.e.* soil-plant-animal-human), Cd(II) ion is transferred into animals and human beings, causing the vulnerability of vital body organs such as liver, kidney tissues and brain [2]. According to the World Health Organization endorsement, the maximum allowable concentration for Cd(II) ions in drinking water is 3 μg l^{-1} [3].

Flame atomic absorption spectrometry (FAAS), as an analytical method, has been widely used for determination of metals in various fields including environmental, food and pharmaceutical analyses. However, sample pretreatment is an important step in a whole analytical process, especially in the monitoring of trace amounts of analytes in complex matrices [4]. Among various applied sample pretreatment procedures, the mostly used method is solid phase extraction (SPE), which provides many advantages such as low consumption of organic solvents, high enrichment factor, high recovery, safety with

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considering hazardous samples and *in situ* or online coupling with various analytical methods [5]. The choice of the adsorbent in SPE procedures is a crucial point since it can control the analytical factors such as selectivity and capacity. Several materials have been used as adsorbent for SPE procedure, such as active carbon, metal oxide nanoparticles (NPs), nanocomposites (NCs), inorganic materials, *etc.* [6-12]. Among these reported adsorbents, the metal oxides with high surface area and specific affinity for adsorption of heavy metal from aqueous samples have illustrated a promising performance in practical and industrial applications. ZnO as a remarkable metal oxide for material sciences has been paid much attention due to the nontoxic, multifunctional and unique properties such as ultraviolet absorbent, varistors, photocatalyst, gas sensor, photodetector, LED applications, surface acoustic wave devices, antivirus agent and so on [13]. In addition, ZnO nanostructures can be used as sorbents in sample preparation process which have some advantages including low cost, environmental abundance, ease of preparation in various shapes and sizes, monotonous surface morphology, environmental friendliness, high stability in harsh media and special adsorption properties [14]. In comparison with the metal oxides based on a single metal, the binary oxides and nanocomposites with two or more metals may provide an improved performance for heavy metal extraction/pre-concentration from contaminated water samples [15].

On the other hand, due to the mesoporous nature of Ag_2O nanomaterials [6], the use of silver oxide nanoparticles can be very useful for improving the selectivity and adsorption capacity. Thus, Ag_2O decorated ZnO nanoparticles may be used as a proper sorbent in SPE. Furthermore, the presence of Fe_3O_4 NPs as magnetic components into as-prepared nanocomposite enables us to obtain a magnetic SPE agent with recyclability property for several times. In this case, the obtained nanocomposite can be easily collected from the solution using a magnet and reused. As we know, there is no report on the application of the $ZnO@Ag_2O@Fe_3O_4$ nanocomposite in magnetic solid phase extraction (MSPE) procedure. Accordingly, in this research, a $ZnO@Ag_2O@Fe_3O_4$ nanocomposite as a novel SPE agent is synthesized for extraction and pre-concentration of Cd(II) ions from water samples.

EXPERIMENTAL

Reagents and Solutions

All reagents were of analytical grade and deionized water was obtained from Serum Sazi Shahid Ghazi Co. (Tabriz, Iran). $ZnO@Ag_2O@Fe_3O_4$ nanocomposite precursors, *i.e.*, $Zn(NO_3)_2.6H_2O$, $AgNO_3$, $FeCl_3.6H_2O$, $FeCl_2.4H_2O$, NaOH, polyethylene glycol (PEG) and ammonia solution, and $Cd(NO_3)_2.4H_2O$, sodium dihydrogen phosphate, all used organic solvents, and all salts employed for the interferences studies were purchased from Merck (Darmstadt, Germany). Stock solution (1000 mg l^{-1}) of Cd(II) ion was prepared by dissolving the proper amount of its nitrate salt in the deionized water and working standard solutions were prepared by suitable dilution of the stock solution.

Apparatus and Instruments

A FAAS model SpectrAA 220 (Varian, Australia) equipped with a Cd hallow cathode lamp and an air/acetylene burner was used for the Cd determination. The instrumental parameters included: wavelength; 279.5 nm, band pass; 1 nm, lamp current; 1.5 mA; acetylene flow rate of 1.5 $l min^{-1}$ and air flow rate of 3.5 $l min^{-1}$.

A MIRA3 (TESCAN, Czech Republic) field emission scanning electron microscope (FESEM) was used to study the morphological properties of the nano-sorbent. To study the structural properties of the as-synthesized nano-sorbent, powder X-ray diffraction (XRD) measurements were performed at room temperature by employing a D8 Advance (Bruker, Germany) instrument with Cu-K$_\alpha$ radiation (1.54 Å). In addition, a Fourier transform infrared spectrometer model Vector 22 (Bruker, Germany) was employed to study the functional groups of the nano-sorbent by recording the FT-IR spectra in the range of 4000-400 cm^{-1}. Magnetic properties of the sorbent were measured by a vibrating sample magnetometer model 3886 (AGFM/VSM, Iran). Nitrogen adsorption-desorption isotherms, Brunauer-Emmett-Teller (BET) surface area, and Barret-Joyner-Halenda (BJH) pore volume were measured by a BEISORP analyzer (BEL Japan, Inc.) at 77 K, and data analysis software version 6.1.0.4.

A pH-meter model 827 (Metrohm Ltd., Switzerland)

equipped with a glass-combined electrode was used to determine the pH values. An ultrasonic bath (SONICA, Italy) was used to disperse the nano-sorbent in sample solutions. Hot plate stirrer model 1000 (Jenway, U.K.), an electrical furnace model EX.1200-30L (Exciton, Iran) and Selecta Lab centrifuge model Tl320 were used during the magnetic SPE agent preparation process. A shaker (Pars Azma, Iran) and an electronic analytical balance model PB303 (Mettler Toledo, Switzerland) were also used in this work.

Synthesis of the Nano-sorbent

Synthesis of the ZnO nanoparticles. ZnO nanoparticles were prepared using the procedure described in elsewhere [16] with some modifications. Briefly, 100 ml of 0.1 M zinc solution was obtained by dissolving an appropriate amount of $Zn(NO_3)_2.6H_2O$ in deionized water. Then, 125 ml of 1 M NaOH solution was slowly added into the vigorously stirred solution during 25 min. The resultant mixture was centrifuged at 4000 rpm for 5 min, and then washed several times with deionized water. The obtained nanoparticles were dried in an oven at 80 °C.

Synthesis of the ZnO@Ag₂O nanocomposite. ZnO@Ag₂O nanocomposite was synthesized by a simple chemical precipitation method [17]. In brief, 0.4 g of as-prepared ZnO nanoparticles was dispersed in 100 ml of water, and 2 g of PEG-400 was added into the mixture. Subsequently, the mixture was stirred for 30 min after adding 1.8 g AgNO₃ salt. Then, 0.2 M NaOH solution was added dropwise into the mixture to reach the final pH value of around 14. The obtained nanocomposite was washed with deionized water for several times followed by a filtration and drying at 90 °C.

Synthesis of the ZnO@Ag₂O@Fe₃O₄ nanocomposite. A simple *in situ* chemical precipitation method was used for the preparation of ZnO@Ag₂O@Fe₃O₄ nanocomposite [18]. For this purpose, 80 mg of the synthesized ZnO@Ag₂O nanocomposite was dispersed in 250 ml deionized water to form well-disperse suspension. Then, 80 mg of FeCl₂.4H₂O and 216 mg of FeCl₃.6H₂O were added and stirred for 10 min at 50 °C. Afterward, 1 ml of NH₃ solution was added dropwise into the mixture and kept on reacting for 40 min at 50 °C. Finally, the obtained magnetic nanocomposite was collected with a magnet, washed with

deionized water and dried in an oven.

Sample Preparation

Real samples including tab water, underground water, river water, and treated effluent collecting from local sources were chosen for the analysis. The samples were filtered from the blue band filter paper and analyzed through the procedure given in "General procedure" section.

General Procedure

200 mg of the as-prepared ZnO@Ag₂O@Fe₃O₄ nanocomposite was placed in a beaker. Afterward, 400 ml of standard or sample solution containing Cd(II) ions in the range of 0.1-10 ng ml^{-1} (pH 7) was transferred into the beaker. Under mechanical stirring of the samples for 20 min, the extraction/adsorption of Cd(II) ions onto the sorbent was proceed. Then, the sorbent was isolated with a Nd-Fe-B (10,000 G) magnet (6.0 mm × 6.0 mm × 3.0 mm) and the clear supernatant was poured away. To desorb the extracted analyte, the isolated sorbent was eluted with 2.0 ml of 1.5 M acetic acid solution with the aid of a mechanical shaking for 10 min. Finally, the nano-sorbent was collected by a magnet, and the eluate solution containing the concentrated cadmium ions was transferred into a vial for FAAS analysis.

RESULTS AND DISCUSSION

Choice of Adsorbent

To find the suitable adsorbent for extraction the Cd(II) ions from aqueous solutions, the as-synthesized adsorbents, ZnO NPs, Fe₃O₄ NPs, ZnO@Fe₃O₄ NC, ZnO@Ag₂O NC and ZnO@Ag₂O@Fe₃O₄ NC, were individually tested. According to Fig. 1, the analyte recovery is not significant in the case of bare Fe₃O₄ NPs, but it is about 50% for ZnO NPs. However, the recovery of the analyte on the ZnO@Ag₂O NC is the highest (>98%). Compared to ZnO NPs, the ZnO@Ag₂O NC demonstrated a superior performance for extraction/pre-concentration of Cd(II) ions. It may be attributed to the mesoporous nature of Ag₂O nanoparticles [6], which improves the selectivity and adsorption capacity of the nanocomposite due to high surface area. As shown in Fig. 1, there is no obvious
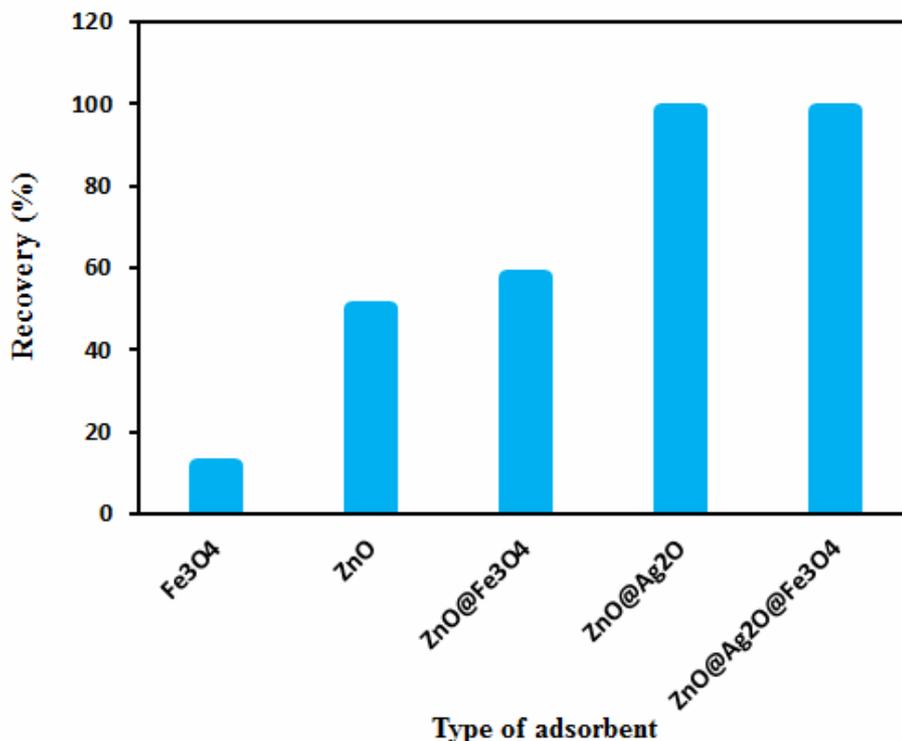
Fig. 1. Effect of adsorbent type on the extraction efficiency of Cd(II) ions.

variation in the recovery values with incorporation of Fe_3O_4 NPs as magnetic components. Accordingly, $ZnO@Ag_2O@Fe_3O_4$ nanocomposite was used as an adsorbent for the next experiments.

Characterization of $ZnO@Ag_2O@Fe_3O_4$ Nanocomposite

The crystal structure of the obtained sorbent was characterized by X-ray diffraction (XRD). Figure 2 shows the XRD patterns of ZnO NPs, $ZnO@Ag_2O$ NC and $ZnO@Ag_2O@Fe_3O_4$ NC. The characteristic diffraction peaks of ZnO consisting the (100), (002), (101), (102), (110), (103), (112), (004) and (202) facets (JCPDS No.65-3411) can be seen in Fig. 2a. As shown in Fig. 2b, in XRD pattern of $ZnO@Ag_2O$ nanocomposite, the new diffraction peaks are appeared at $2\theta = 32.8°$, $38.1°$ and $54.9°$ that respectively correspond to crystal plates of (111), (200) and (220) in Ag_2O with cubic system (JCPDS No.41-1104), confirming that the ZnO and Ag_2O NPs coexist in the composite structure. After magnetizing the nanocomposite

with Fe_3O_4 NPs, the new peaks were appeared at the Bragg angles of about 30.36, 35.48, 46.28, 54.6, 57.1 and 62.88 (Fig. 2c) that are respectively attributed to the (220), (311), (400), (422), (440) and (511) facets of the cubic spinel crystal planes of Fe_3O_4 (JCPDS No. 19-0629), confirming the existence of Fe_3O_4 NPs in the synsized nano-sorbent. X'pert highscore program was used for more identification of diffraction peaks in the as-prepared materials and the obtained peak lists are given in Fig. 3. The line marked with "•", "*" and "×" are indexed to the ZnO, Ag_2O and Fe_3O_4 nanoparticles, respectively. The peak lists of $ZnO@Ag_2O@Fe_3O_4$ nanocomposite clearly demonstrate the co-existence of ZnO, Ag_2O and Fe_3O_4 diffraction peaks in the as-prepared nanocomposite.

To characterize the surface functional groups of the sorbent, the infrared absorption spectroscopy was employed. Figure 4 shows the FT-IR spectra of ZnO NPs, $ZnO@Ag_2O$ NC and $ZnO@Ag_2O@Fe_3O_4$ NC in the region from 400 to 4000 cm^{-1}. For the ZnO nanoparticles three absorption regions can be observed in Fig. 4a. The broad
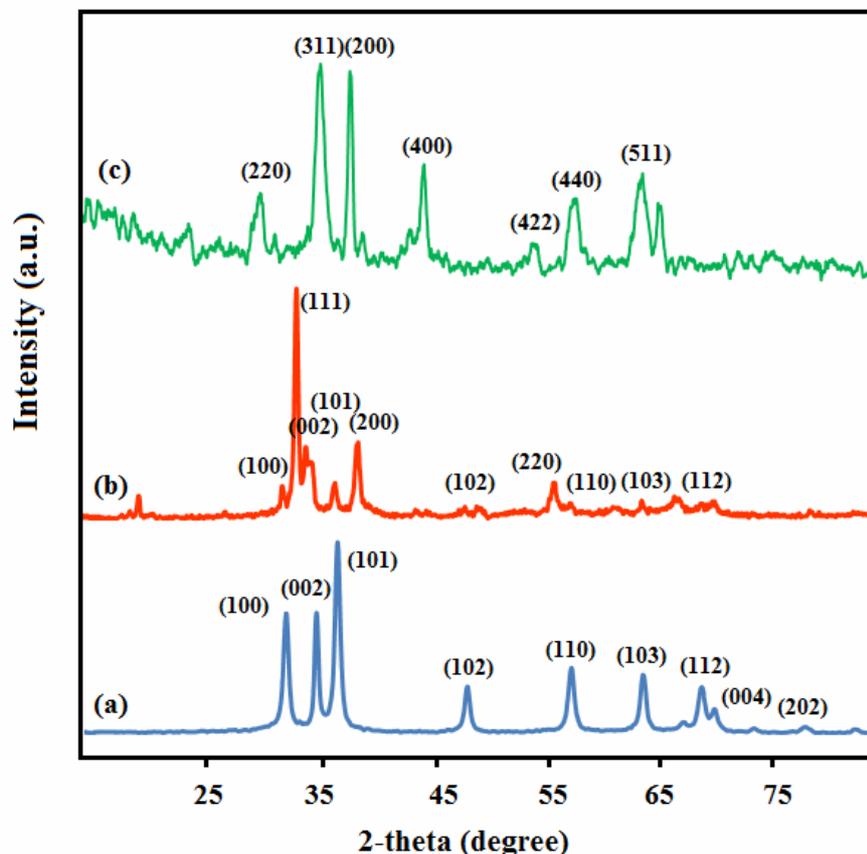
Fig. 2. XRD patterns of the (a) ZnO NPs, (b) ZnO@Ag$_2$O NC and (c) ZnO@Ag$_2$O@Fe$_3$O$_4$ NC.

peaks at 3000-3500 cm^{-1} and 1384 cm^{-1} are attributed to the stretching and bending vibrations of O-H of the water adsorbed physically, respectively [19]. The band arising from the absorption of atmospheric CO$_2$ on metal cations can be observed at 1500 cm^{-1} in the FT-IR spectrum [20]. Moreover, the vibrational band observed at 572 cm^{-1} is also the characteristic peak of Zn-O [21]. According to the literature, the FT-IR spectrum of pure Ag$_2$O powder contains the bands at 460, 530, 650 and 951 cm^{-1} and a broad peak in the range of 2800-3500 cm^{-1} [22]. As can be seen from FT-IR spectrum of ZnO@Ag$_2$O NC (Fig. 4b), the band in the region of 3000-3500 cm^{-1} is extended and two obvious peaks are observed at 660 cm^{-1} and 895 cm^{-1} which could be attributed to the Ag$_2$O components in ZnO@Ag$_2$O NC. Due to vicinity the stretching vibration of Ag-O band at 530 cm^{-1}, the characteristic peak of Zn-O is broadened and shifted to low wavenumber indicating the

interactions between the ZnO and Ag$_2$O nanoparticles [23]. The FT-IR spectrum of ZnO@Ag$_2$O@Fe$_3$O$_4$ is shown in Fig. 4c. Fe-O bond stretching vibration around 594 cm^{-1} can be seen in the FT-IR spectrum of the ZnO@Ag$_2$O@Fe$_3$O$_4$ NC. Due to the overspread of spectra in region 500-700 cm^{-1}, the vibrational band of Zn-O at 551 cm^{-1} has been covered.

Field emission scanning electron microscopy (FESEM) was employed to obtain some information about the size and morphology of the as-prepared SPE agent. FESEM image of ZnO@Ag$_2$O@Fe$_3$O$_4$ NC is shown in Fig. 5. It can be seen that the obtained NC has a nearly uniform distribution in size, and the average diameter of ZnO@Ag$_2$O@Fe$_3$O$_4$ NC was less than 50 nm.

The nitrogen adsorption-desorption isotherms of ZnO@Ag$_2$O@Fe$_3$O$_4$ NC are shown in Fig. 6. Figure 6 shows that the isotherms exhibit a typical hysteresis of a
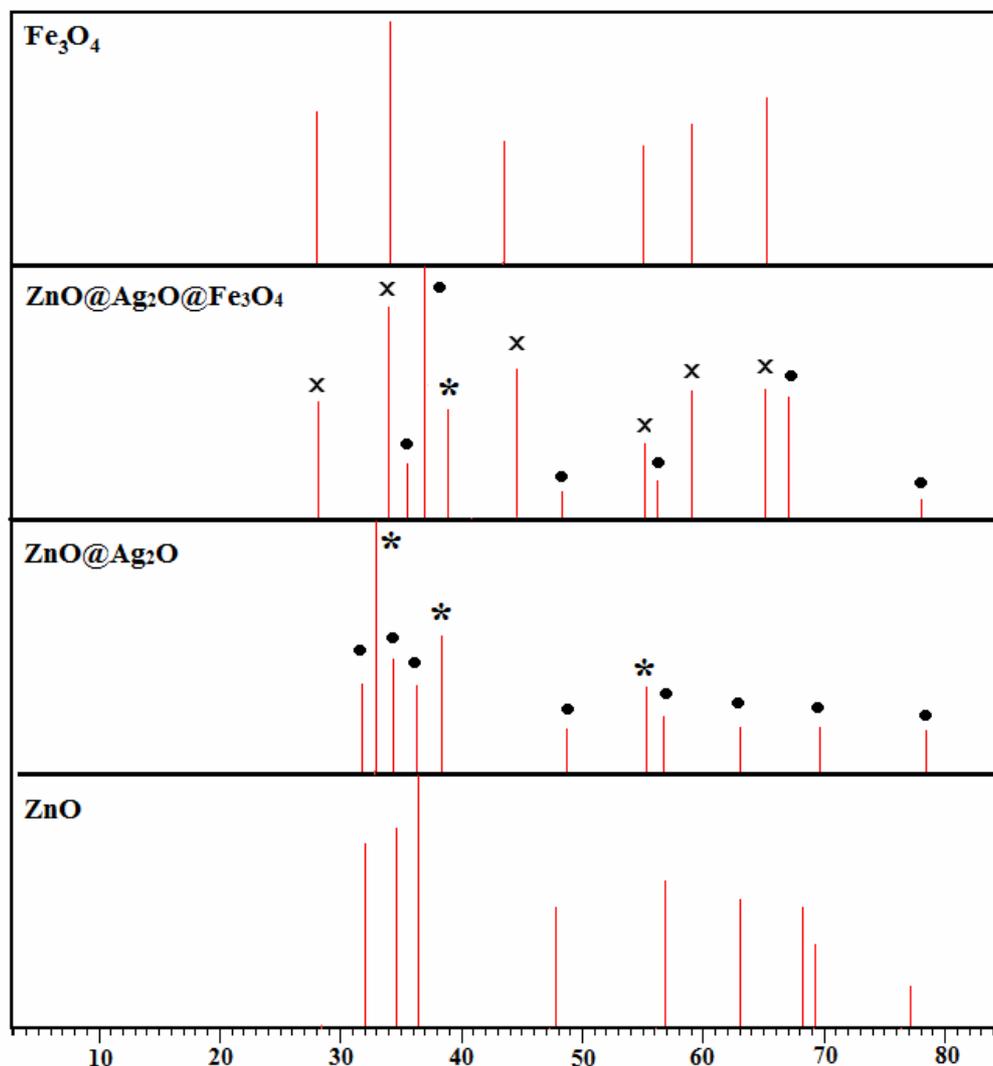
Fig. 3. Diffraction peak lists of the ZnO NPs, ZnO@Ag$_2$O NC, ZnO@Ag$_2$O@Fe$_3$O$_4$ NC and Fe$_3$O$_4$ NPs obtained by X'pert highscore program.

mesoporous system [24], indicating that ZnO@Ag$_2$O@Fe$_3$O$_4$ NC contains mesoporous structures. According to BET analysis, the total specific surface area is 114.96 m^2 g^{-1}, which is a relatively large value, demonstrating the porous structure of as-prepared nanocomposite. The multimodal pore-size distribution is further confirmed by its corresponding pore-radius distribution curve as shown in inset of Fig. 6. According to the BJH theory, the total pore volume and mean pore diameter are 0.2312 cm^3 g^{-1} and 2.10 nm, respectively.

The magnetic property of the as-prepared ZnO@Ag$_2$O@Fe$_3$O$_4$ NC was also studied with a vibrating sample magnetometer (VSM). Figure 7 shows the plot of room temperature magnetization (M) versus magnetic field (H) (hysteresis loop) of the synthesized ZnO@Ag$_2$O@Fe$_3$O$_4$ NC. As can be seen from Fig. 7, the saturation magnetization of ZnO@Ag$_2$O@Fe$_3$O$_4$ NC is 58.55 emu g^{-1}. This magnetic nanocomposite can be
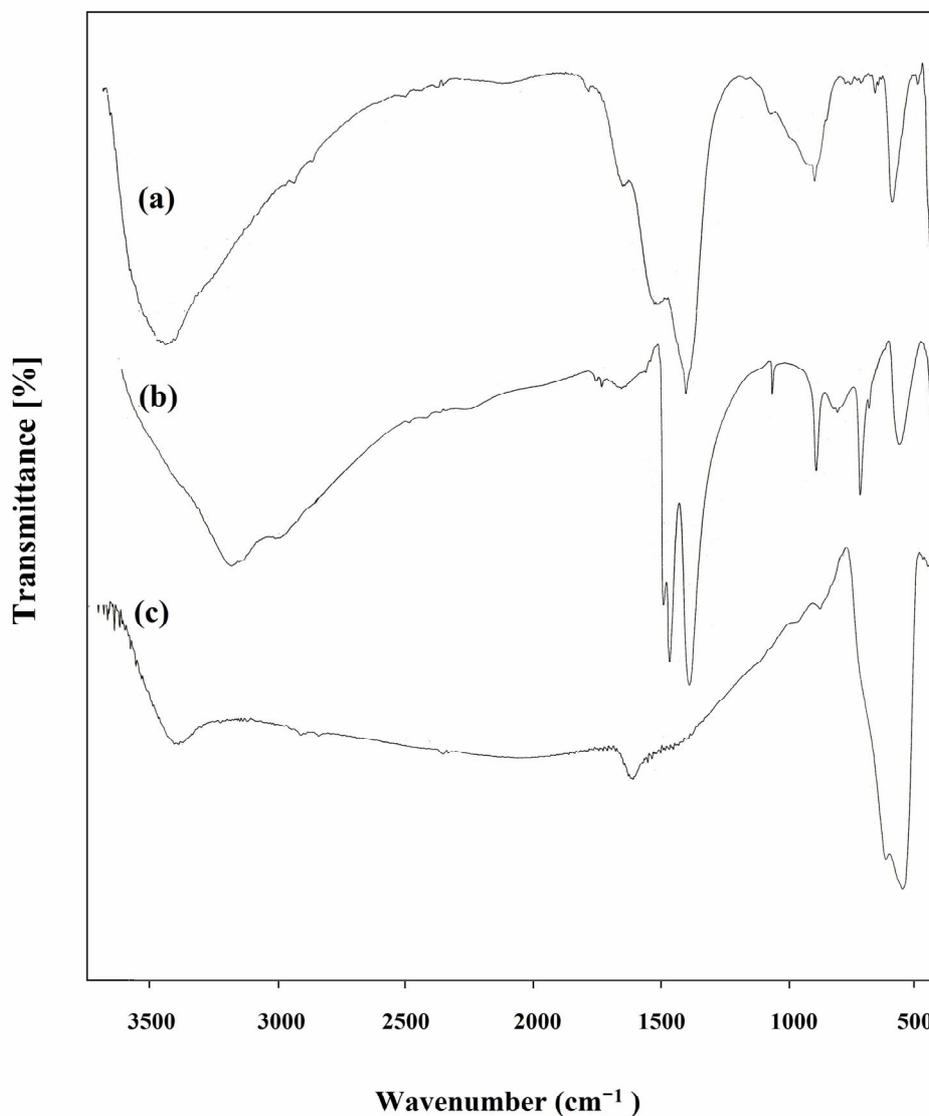
Fig. 4. FT-IR spectrum of the (a) ZnO NPs, (b) ZnO@Ag₂O NC and (c) ZnO@Ag₂O@Fe₃O₄ NC.

separated from the solution easily and rapidly by a magnet due to the relatively large saturation magnetization. Additionally, there is no hysteresis in the magnetization with both remanence and coercivity, indicating that the magnetic nano-sorbent is superparamagnetic.

Optimization of Magnetic Solid Phase Extraction Conditions

To achieve the maximum capability of the magnetic

SPE agent for selective Cd(II) ions pre- concentration, the method was optimized for various effective parameters such as pH, amount of the sorbent, sample volume and elution conditions. The recovery percentage, calculated from the amount of Cd(II) ion eluted from the ZnO@Ag₂O@Fe₃O₄ NC and its amount in the starting sample, was considered as an analytical signal. A 4 ng ml^{-1} Cd(II) ion solution was used for all measurements and each reported data is the mean of three experiments.
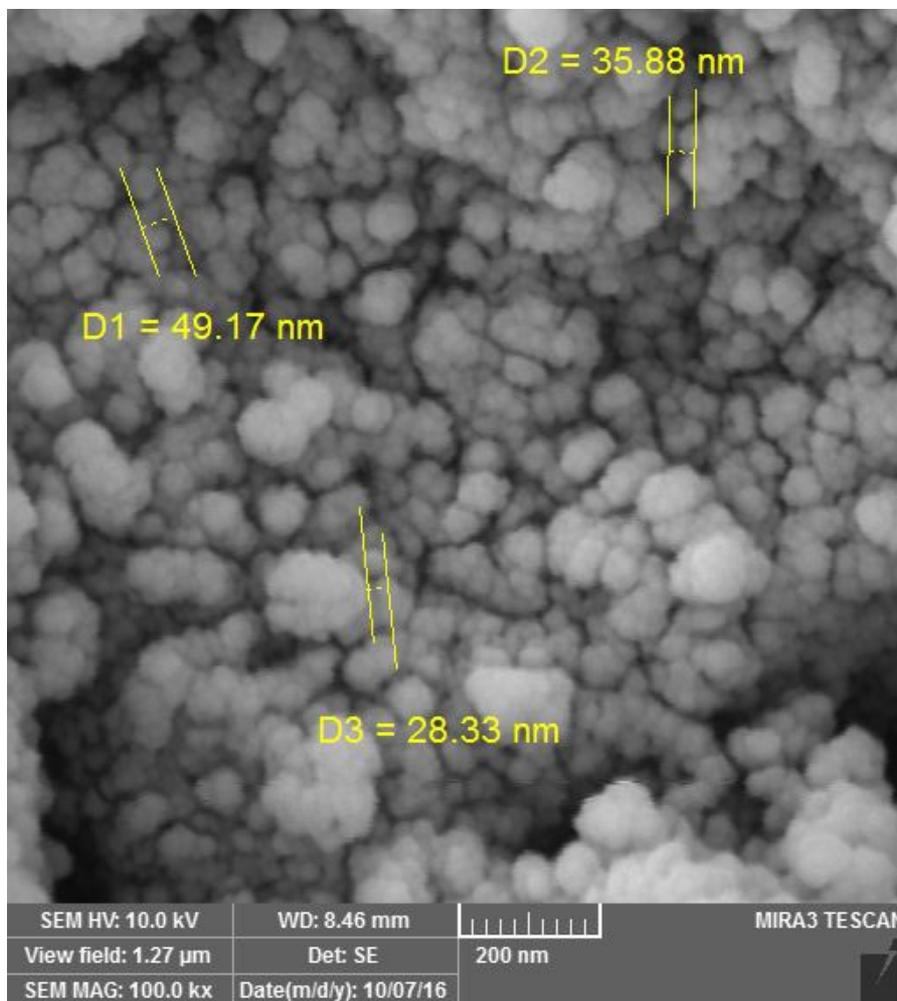
Fig. 5. FESEM image of the ZnO@Ag$_2$O@Fe$_3$O$_4$ NC.

Effect of pH

As well known, in SPE studies, pH has a crucial effect on the surface charge of nano-sorbent [25]. pH$_{pzc}$ of the synthesized ZnO@Ag$_2$O@Fe$_3$O$_4$ NC, estimated by so-called pH drift method [26], is around 6. Accordingly, the nanocomposite surface is negatively charged when the pH value is above 6 and positively charged when the pH value is below 6. The effect of pH on the adsorption of the as-prepared sorbent toward Cd(II) ions was studied in the pH range from 4-12. It can be seen from Fig. 8 that Cd(II) ions are adsorbed quantitatively (recovery higher than 98%) on magnetic ZnO@Ag$_2$O nanocomposite in the pH range of 5-8. The positive charge of the nanocomposite surface at pH

<5 leads to weak adsorption of the Cd(II) ions on the nano-sorbent surface, so, the recovery values are decreased. At pH > 8, however, the recovery values decrease due to precipitation of Cd(II) ion as hydroxide forms. Furthermore, it has been reported that heavy metal ions may form many polynuclear species in alkaline media [27]. Therefore, to reach the maximum extraction efficiency, pH 7 was selected as an optimum value and the phosphate buffer solution (0.1 M) was used for this purpose.

Effect of Amount of the Nano-sorbent

To test the effect of amount of the nano-sorbent on the pre-concentration of Cd(II) ions, the extraction was

236
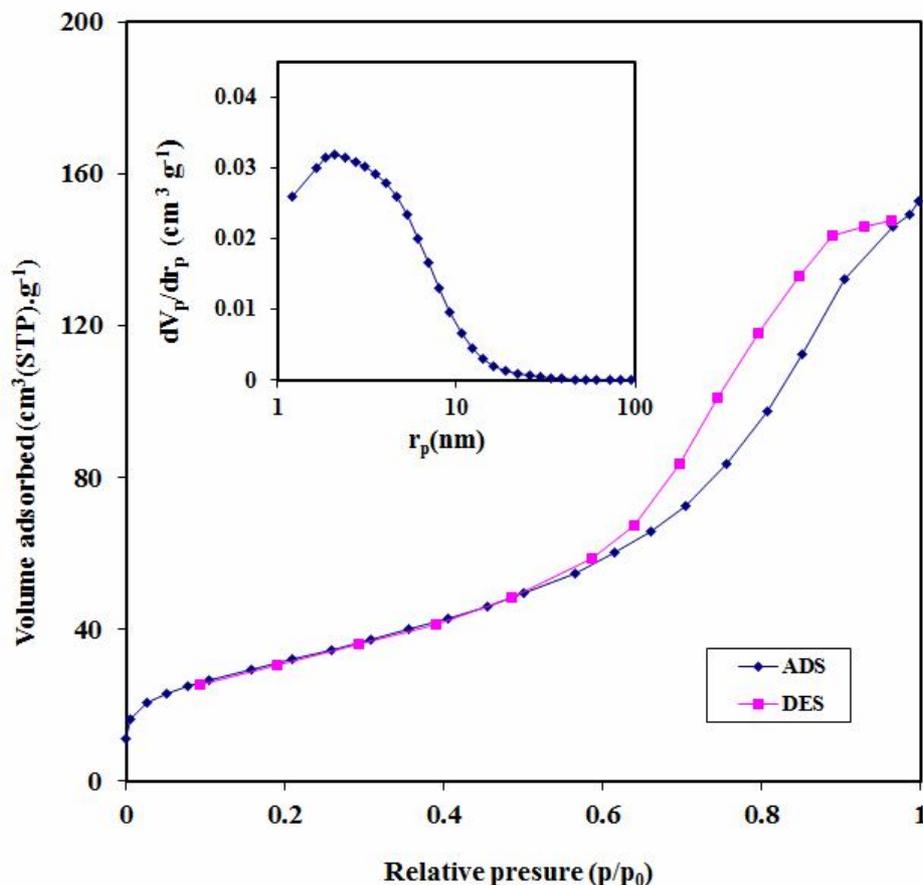
Fig. 6. N$_2$ adsorption-desorption isotherm of the ZnO@Ag$_2$O@Fe$_3$O$_4$ nanocomposite. Inset is the plot of BJH pore size distribution.

performed by varying the amounts of the sorbent from 50 to 400 mg. According to the obtained results, shown in Fig. 9, the quantitative recoveries of the working analyte were obtained with 200 mg of the nano-sorbent. Therefore, 200 mg of the nano-sorbent was employed for the next experiments.

Optimization of Elution Variables

To choose the best eluent for elution of the retained Cd(II) ions from the magnetic ZnO@Ag$_2$O NC, various reagent solutions such as HNO$_3$, HCl, H$_2$SO$_4$, sodium citrate, acetic acid and EDTA were tested. According to the obtained results, shown in Fig. 10, acetic acid provides the best recovery. Hence, acetic acid was selected as the best eluent. The concentration and volume of the acetic acid

solution was also investigated. For this purpose, various concentrations (0.5-3 M) of acetic acid were tested for the elution of the adsorbed analytes from the sorbent. As can be seen from Figs. 11, 1.5 M acetic acid was sufficient for elution of the Cd(II) ions from the sorbent. In addition, the recovery of the analyte increased by increasing the volume of the eluent up to 2 ml and then remained constant (Fig. 12). So, 2 ml of the eluent was considered as the optimum value.

Effect of Adsorption/desorption Time

Due to the magnetic property of the ZnO@Ag$_2$O@Fe$_3$O$_4$ nanocomposite, the nano-sorbent could be rapidly separated from the reaction system using a magnet. However, to obtain satisfactory recovery values
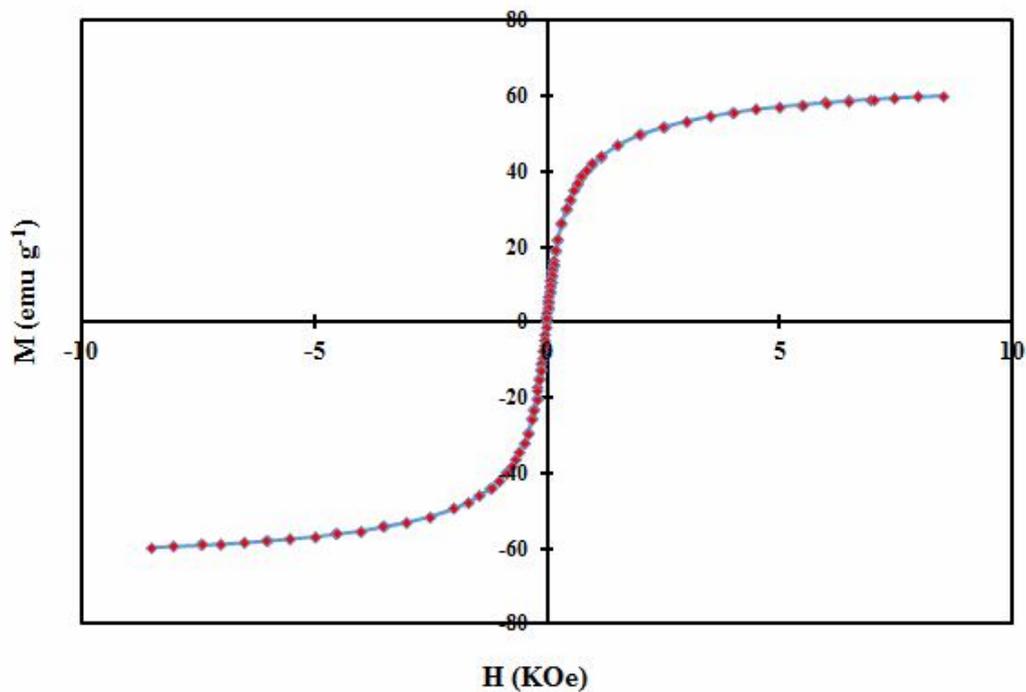
Fig. 7: Hysteresis loop of the ZnO@Ag$_2$O@Fe$_3$O$_4$ nanocomposite.
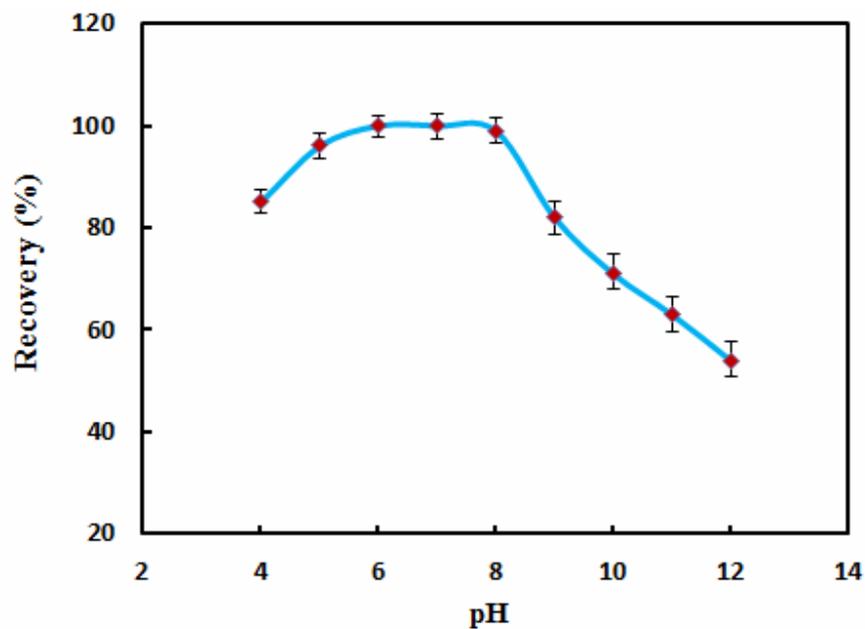
Fig. 8. Effect of pH on adsorption of Cd(II) ions by ZnO@Ag$_2$O@Fe$_3$O$_4$ NC. Utilized conditions: sample volume: 100 ml, Cd(II) ions concentration: 4 ng ml^{-1}, amount of the nanosorbent: 200 mg, extraction time: 20 min, and desorption time: 20 min.
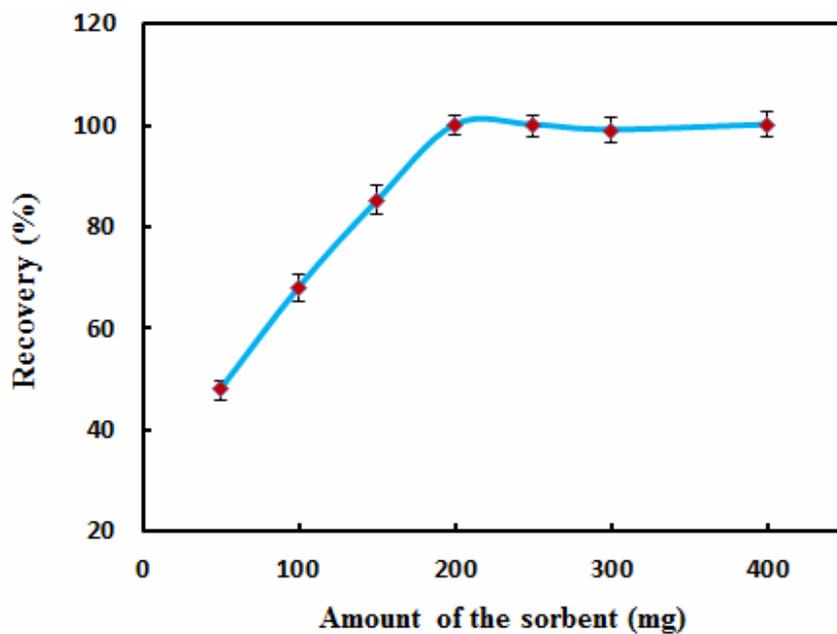
Fig. 9: Effect of the SPE agent amount on adsorption of Cd(II) ions by ZnO@Ag$_2$O@Fe$_3$O$_4$ NC. Utilized conditions: pH: 7, sample volume: 100 mL, Cd(II) ions concentration: 4 ng mL^{-1}, amount of the nanosorbent: 200 mg, extraction time: 20 min, anddesorption time: 20 min.
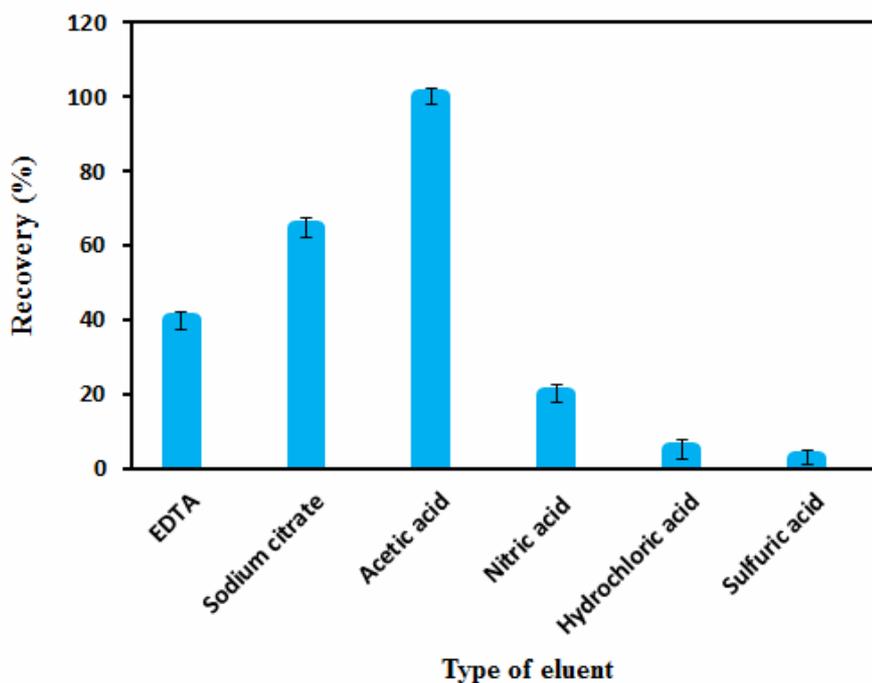
Fig. 10. Effect of the type of elution agent on recovery of Cd(II) ions by the ZnO@Ag$_2$O@Fe$_3$O$_4$ NC. Utilized conditions: pH: 7, sample volume: 100 ml, Cd(II) ions concentration: 4 ng ml^{-1}, amount of the nanosorbent: 200 mg, extraction time: 20 min, and desorption time: 20 min.
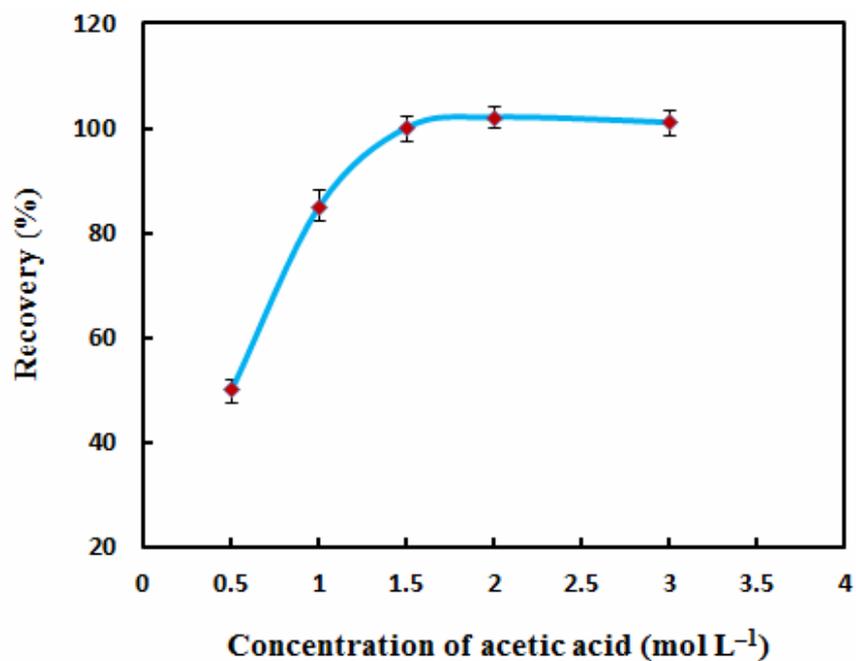
Fig. 11: Effect of the eluent concentration on recovery of Cd(II) ions by the ZnO@Ag$_2$O@Fe$_3$O$_4$ NC. Utilized conditions: pH: 7, sample volume: 100 mL, Cd(II) ions concentration: 4 ng mL^{-1}, amount of the nanosorbent: 200 mg, extraction time: 20 min, desorption time: 20 min, and eluent volume: 2 mL.
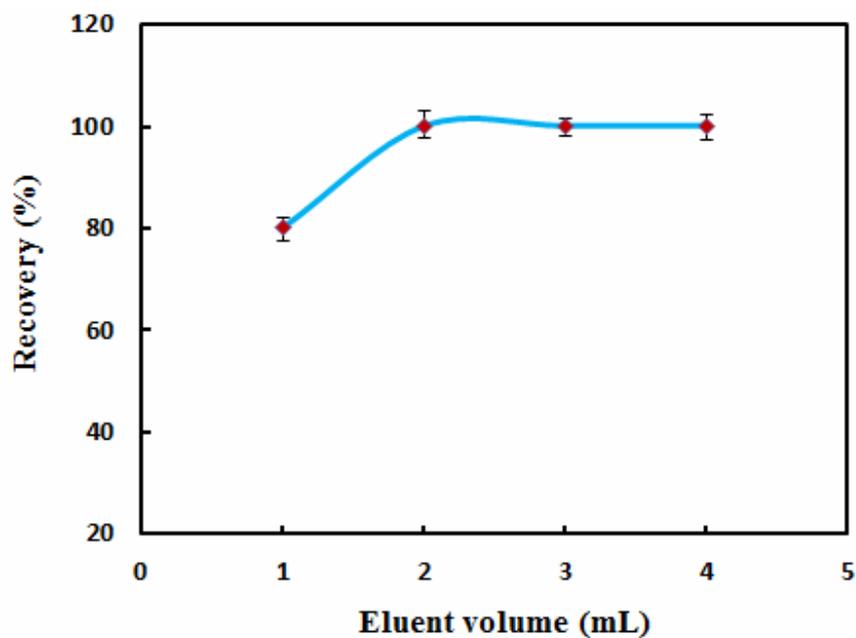
Fig. 12. Effect of the eluent volume on recovery of Cd(II) ions by the ZnO@Ag$_2$O@Fe$_3$O$_4$ NC. Utilized conditions: pH: 7, sample volume: 100 ml, Cd(II) ions concentration: 4 ng ml^{-1}, amount of the nanosorbent: 200 mg, extraction time: 20 min, desorption time: 20 min, and eluent concentration: 1.5 M.
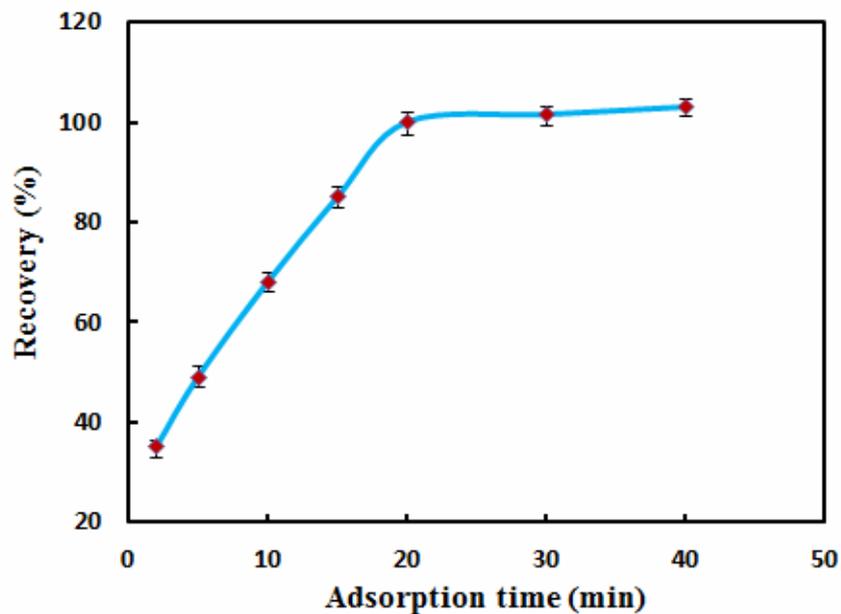
Fig. 13. Effect of the adsorption time on recovery of Cd(II) ions by the ZnO@Ag$_2$O@Fe$_3$O$_4$ NC. Utilized conditions: pH: 7, sample volume: 100 ml, Cd(II) ions concentration: 4 ng ml^{-1}, amount of the nanosorbent: 200 mg, desorption time: 20 min, and elution condition: 2 ml of 1.5 M acetic acid solution.
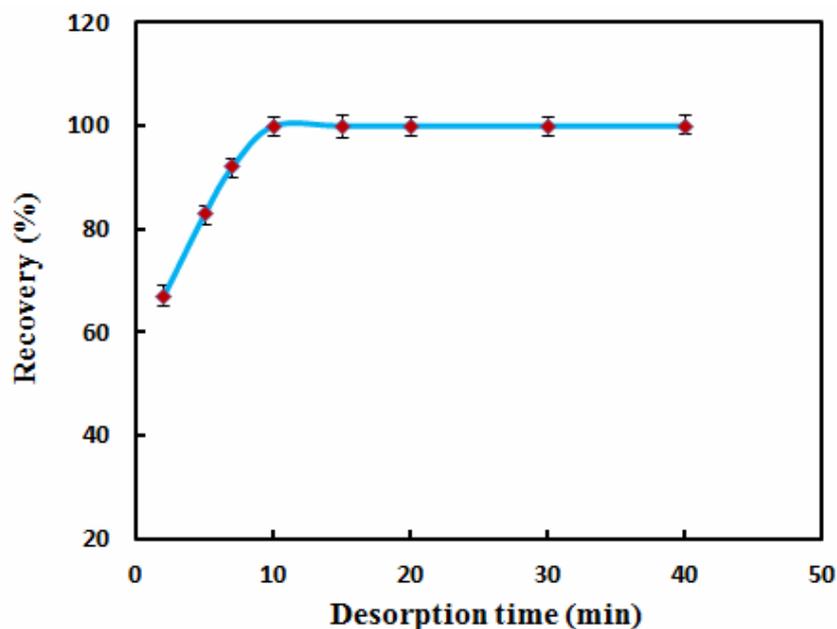
Fig. 14. Effect of the desorption time on recovery of Cd(II) ions by the ZnO@Ag$_2$O@Fe$_3$O$_4$ NC. Utilized conditions: pH: 7, sample volume: 100 ml, Cd(II) ions concentration: 4 ng ml^{-1}, amount of the nanosorbent: 200 mg, extraction time: 20 min, and elution condition: 2 ml of 1.5 M acetic acid solution.

during the extraction of the analyte, the effect of adsorption and desorption times on the recovery values were studied as analysis time. For this purpose, both adsorption and desorption times were individually varied in the range of 1-40 min. The results shown in Figs. 13 and 14 indicated that 20 and 10 min are sufficient for adsorption and desorption stages, respectively.

Sample Volume and Pre-concentration Factor

The possibility of enriching low concentrations of Cd(II) ions from large volumes of samples was investigated by studying the effect of sample volume on the recovery values. For this purpose, the volume of sample solutions containing 1.6 μg of Cd(II) ion were altered from 10 to 500 ml. As shown in Fig. 15, the quantitative recovery of Cd(II) ions on the $ZnO@Ag_2O@Fe_3O_4$ nanocomposite can be obtained for sample volumes up to 400 ml. Accordingly, by analyzing 2 ml of the final solution obtained after the pre-concentration of 400 ml of Cd(II) sample solution using the synthesized SPE reagent, a pre-concentration factor of 200 was provided for Cd(II) ion.

Adsorption Isotherm and Adsorption Capacity

In order to obtain isotherm of adsorption and determine the adsorption capacity, 400 ml of sample solution containing Cd(II) ion concentration in the range of 1-100 mg l^{-1} were adjusted to pH 7 and procedure was proceed by using 200 mg of the $ZnO@Ag_2O@Fe_3O_4$ nanocomposite. After shaking for 20 min with mechanical stirrer at ambient temperature, the nano-sorbent was gathered by a magnet and the adsorbed analyte on the nano-sorbent was then stripped with 2 ml of acetic acid (1.5 M). Finally, the Cd concentration in the solution was determined by FAAS. As shown in Fig. 16, the profile of the adsorption isotherm for Cd(II) ion was constructed by plotting the milligrams of Cd(II) ion adsorbed per gram of $ZnO@Ag_2O@Fe_3O_4$ nanocomposite (Q_e, mg g^{-1}) versus the initial concentration of Cd(II) ion (C_0, mg l^{-1}). The Q_e, (mg g^{-1}) of the nano-sorbent for Cd(II) ion was calculated using the following equation:

$$Q_e = \frac{V(C_0 - C_e)}{W} \qquad (1)$$

where C_0 (μg ml^{-1}) and C_e (μg ml^{-1}) are the initial and

equilibrium concentration of Cd in aqueous solution, respectively, V (L) is the sample volume, and W (g) is mass of the $ZnO@Ag_2O@Fe_3O_4$ nanocomposite. The adsorption capacity of the $ZnO@Ag_2O@Fe_3O_4$ nanocomposite toward Cd(II) ion was found to be 48 mg g^{-1}, as indicted in Fig. 16.

Reusability of the Nano-sorbent

The stability of the $ZnO@Ag_2O@Fe_3O_4$ nanocomposite was investigated by repeating the adsorption-desorption cycle experiments. After each cycle, the SPE agent was recycled by magnetic separation, followed by washing with deionized water. After 100 times adsorption-desorption cycle, a good recoverability was obtained with the standard error <5%. These results confirm that the magnetic removable nanocomposite is not destroyed or poisoned during the adsorption-desorption cycles. Furthermore, after magnetic separation, the sample solution was analyzed for Zn, Ag and Fe using FAAS. There was no detectable value of these metals after each recycle, which was coincident with the results for stability studies. Consequently, the prepared magnetic SPE agent was found to be suitable for reuse without significant decrease in its adsorption capacity for Cd(II) ions until 100 cycles.

Adsorption/desorption Mechanism

In the case of metal oxide-based adsorbents containing -OH functional groups, the pH value has an important role in the analyte adsorption by these adsorbents. It is due to the protonation and deprotonation of the -OH groups in nanostructure surface and the metal species in acidic/basic media. As mentioned in the previous sections, pH_{pzc} of the as-prepared $ZnO@Ag_2O@Fe_3O_4$ nanocomposite and optimum pH value of the sample solution were found to be 6 and 7, respectively. Accordingly, a negative charge can be induced on the surface of the nano-sorbent owing to deprotonation of the -OH groups at pH 7, leading to a quantitative retention and/or pre-concentration of Cd(II) ions on the nano-sorbent surface. In contrary, retained Cd(II) ions could be eluted from the nano-sorbent by acidic or other solutions with pH < pH_{pzc} of the nano-sorbent due to protonation of the functional groups. According to the obtained results, among the investigated reagents, acetic acid has a best performance, not only due to its acidic property, but also its potential to form a stable complex
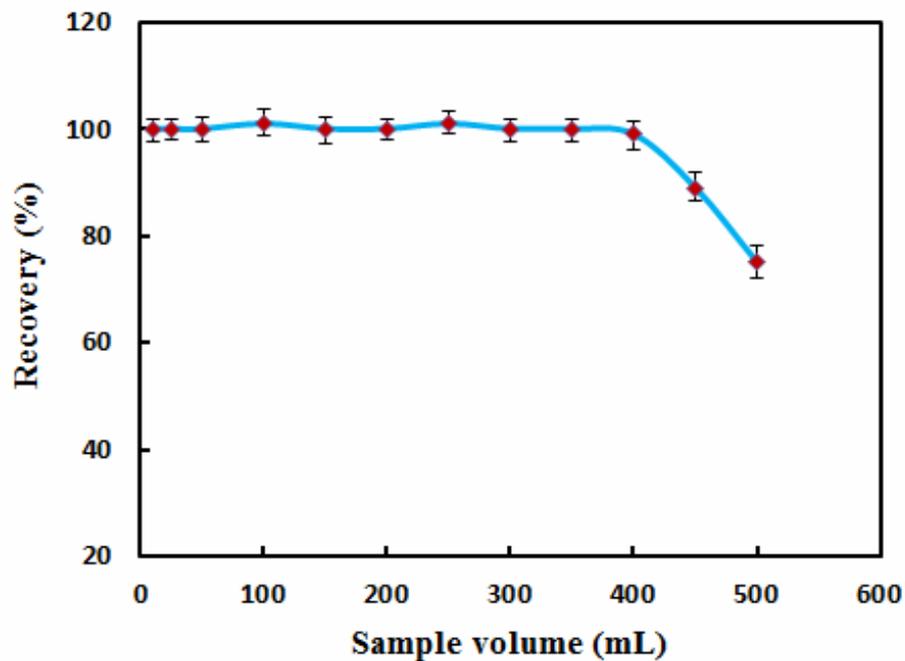
Fig. 15. Effect of the sample volume on recovery of Cd(II) ions by the ZnO@Ag$_2$O@Fe$_3$O$_4$ NC. Utilized conditions: pH: 7, Cd(II) ions concentration: 4 ng ml^{-1}, amount of the nanosorbent: 200 mg, extraction time: 20 min, desorption time: 10 min, and elution condition: 2 ml of 1.5 M acetic acid solution.
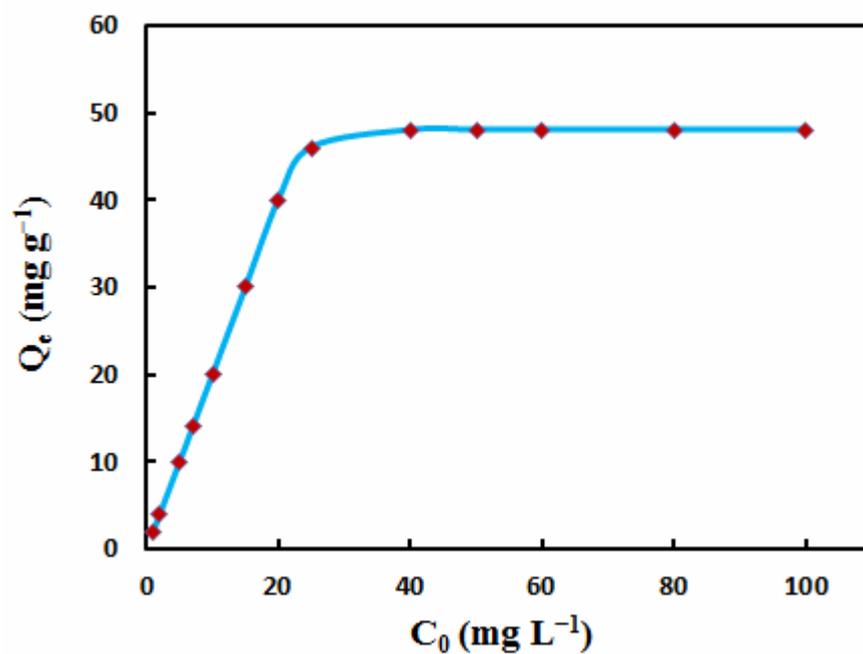
Fig. 16. The profile of the adsorption isotherm for Cd(II) ion by the ZnO@Ag$_2$O@Fe$_3$O$_4$ NC.

Table 1. Tolerance Limits of Interfering Ions in the Retention of Cd(II) Ions. Utilized Conditions: pH: 7, Cd(II) Ions Concentration: 4 ng ml^{-1}, Amount of the Nanosorbent: 200 mg, Extraction Time: 20 min, Desorption Time: 10 min, Elution Condition: 2 ml of 1.5 M Acetic Acid Solution

Ions	Tolerance limit
SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, F^-, Na^+, K^+, Mn^{2+}, Mg^{2+}, NO_3^-, CH_3COO^-	1000>
Ca^{2+}, Cl^-, As^{3+}	800
Ni^{2+}, Cr^{3+}	500
Co^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}	200
Fe^{3+}	10

Table 2. Comparison of the Presented Method with other Pre-concentration Methods for Cd(II) Ions Reported in the Literature

Method	Sorbent	Linear range (ng ml^{-1})	LOD (ng ml^{-1})	RSD (%)	Ref.
MSPE-FAAS[a]	Fe_3O_4@SiO_2@polypyrrole magnetic nanocomposite	1-100	0.3	6.9	[29]
CAF[b]-SPE-FAAS	ZrO_2/B_2O_3 nanohybrid	10.3-3000	3.1	-	[30]
SPE-FAAS	Nano B_2O_3/TiO_2 composite	216-3000	72	<10%	[31]
MSPE-FAAS	Diphenyl carbazone/SDS @ Fe_3O_4	10-500	3.71	0.503	[32]
SPE-FAAS	MWNTs[c]	5-120	0.43	<3.5	[33]
SPE-FAAS	Cibacron Blue (F_3-GA)-poly (HEMA)[d]	1.25-20	-	3.7	[34]
SPE-FAAS	AXAD-2-DHP[e]	28-2000	4.71	<2.6	[35]
MSPE-FAAS	ZnO@Ag_2O@Fe_3O_4 nanocomposite	0.1-10	0.03	1.8	This work

[a]Magnetic solid phase extraction-Flame Atomic Absorption Spectrometry. [b]Chelating agent free. [c]Multiwalled carbon nanotubes. [d]Poly (hydroxyethylmethacrylate). [e]2,3-Dihydroxypyridine Loaded Amberlite XAD-2.

with Cd(II) ions, leading to a completely elution of the retained ions from the SPE agent surface.

Study of Interferences

In order to determine the selectivity of the SPE method for extraction/pre-concentration of Cd(II) ion, the effect of several potentially interfering substances present in real samples on the recovery of Cd(II) ion was investigated. For this purpose, tolerance limits of some interfering ions in retention of 4 ng ml^{-1} of Cd(II) ion were studied. As shown in Table 1, with the exception of Fe(III), all other tested ions did not interfere with determination of 4 ng ml^{-1} Cd(II)

Table 3. Determination of Cadmium in Real Samples (Result of Recoveries of Spiked Samples with Different Amounts of Cd(II)). Utilized Conditions: Sample Volume: 400 ml, pH: 7, Amount of the Nanosorbent: 200 mg, Extraction Time: 20 min, Desorption Time: 10 min, Elution Condition: 2 ml of 1.5 M Acetic Acid Solution

Samples	Added (ng ml⁻¹)	Found[a] (ng ml⁻¹)	Recovery (%)
Tab water[b]	-	Not detected	-
	1.0	0.99 ± 0.02	99.0
	3.0	2.94 ± 0.07	98.0
River water[c]	-	1.85 ± 0.11	
	1.0	2.87 ± 0.03	102.0
	3.0	4.89 ± 0.08	101.3
Underground water[d]	-	1.59 ± 0.07	
	1.0	2.57 ± 0.03	98.0
	3.0	4.65 ± 0.04	102.0
Treated affluent[e]	-	0.83 ± 0.05	
	1.0	1.85 ± 0.03	102.0
	3.0	3.84 ± 0.02	100.3

[a]Mean of three experiments ± standard deviation. [b]From drinking water system of Azarshahr, Iran. [c,d]Obtained from local source, Azarshahr, Iran. [e]Obtained from Miandoab wastewater treatment plant, Miandoab, Iran.

ion. Fluoride ion solution (0.25 mg l⁻¹) was used for the elimination of Fe(III) ion interference [28]. Fe(III) ion can form stable water-soluble complex with F⁻ that it did not interfere with the Cd(II) ion extraction. The satisfactory results demonstrate that the ZnO@Ag₂O@Fe₃O₄ nanocomposite was well appropriated for the Cd(II) ion pre-concentration, and it was not significantly affected by the addition of the other ions.

Analytical Figures of Merit

The analytical figures of merit of the presented method for determination of Cd(II) ions were obtained by processing standard solutions of the analytes. Under the optimized conditions, with the use of 400 ml sample solution, the calibration curve exhibits the linearity range of 0.1-10 ng ml⁻¹ of Cd (R^2 = 0.9918) with the limit of

detection (LOD) of 0.03 ng ml⁻¹. The precision of the presented method was assessed by repeating the cadmium analysis during the course of experiment on the same day and on different days under the optimized conditions. The RSD% (Cd(II) ion concentration; 4 ng ml⁻¹, n = 6) for inter-day and intra-day analyses were found to be 2.6 and 1.8%, respectively. Similarly, to calculate intra-day and inter-day precisions in real samples, tap water samples containing different levels (0.5, 1.0, 3.0, and 8.0 ng ml⁻¹) of Cd(II) ions were extracted and analyzed under the optimum conditions. The relative standard deviation for detection of Cd(II) ions by the presented MSPE-FAAS method was found to be <4%. Other sorbents applied for the extraction/pre-concentration of Cd(II) ion are compared with the present SPE reagent in Table 2. The presented method has a good LOD, good enrichment factor with a sample volume of 400

ml and good adsorption capacity. As verified, compared with other reported sorbents, the presented SPE method using the synthesized ZnO@Ag$_2$O@Fe$_3$O$_4$ nanocomposite is one of the most effective methods for the determination of trace amounts of Cd(II) ion.

Validation of the Method and Real Sample Analysis

To validate the accuracy of the presented method, the standard reference material NIST SRM 1643e was analyzed. The certified value of Cd in SRM 1643e is 6.568 ± 0.073 μg l^{-1}. The corresponding value was 6.559 ± 0.076 μg l^{-1}, and no significant difference was found between the certified and obtained values by this method at 95% confidence level. In order to evaluate the applicability and reliability of the synthesized sorbent, it was applied to the pre-concentration and subsequence determination of Cd in various water samples including tab water, river water, underground water and treated effluent. To validate the accuracy of the developed method, the samples were spiked with different amounts of Cd(II) ion before any pretreatment and the Cd content of the samples and their relative recoveries were calculated. According to the results, shown in Table 3, the relative recoveries were between 98.0 and 102.0 % confirming the accuracy of the developed method.

CONCLUSIONS

In this research, a ZnO@Ag$_2$O@Fe$_3$O$_4$ nanocomposite was synthesized using a simple chemical precipitation method. The synthesized material, used as a magnetic solid-phase extraction agent, showed a promising application for highly selective separation and determination of cadmium in several water samples by FAAS. To obtain quantitative recovery of the analyte, there was no need for modifying the nano-sorbent with any chelating agent before the pre-concentration procedure. Moreover, the synthesized SPE agent was used without need to pack in the cartridge and had a renewable use. Based on the results, the recovery values of the Cd(II) ion after 100 times of adsorption/desorption cycle were still quantitative. The presented method possesses some advantages such as simplicity, low detection limit, good precision, good

accuracy and high sorption capacity. This is the first study on application of the synthesized ZnO@Ag$_2$O@Fe$_3$O$_4$ nanocomposite as an adsorbent via a MSPE–FAAS method for trace analysis of cadmium in water samples and this technique can be considered as an alternative for GF-AAS.

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