Advances in Sustainable Extraction of Arsenic and Cadmium from Sewage Sludge: Use of Hydrophobic Deep Eutectic Solvent Modified with Magnetic Nanoparticles

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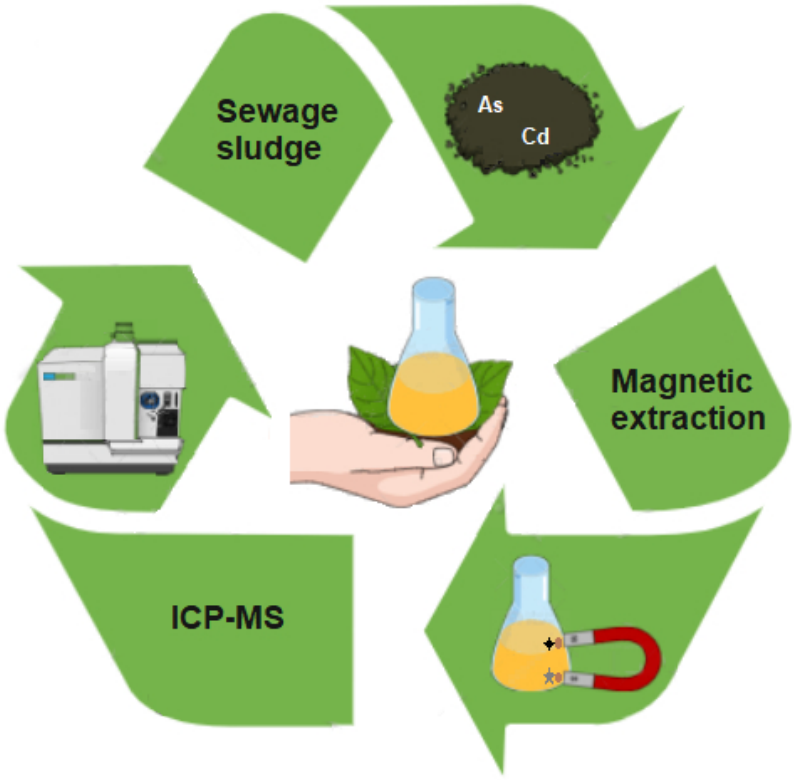

abstract graphic

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Advances in Sustainable Extraction of Arsenic and Cadmium from Sewage Sludge: Use of Hydrophobic Deep Eutectic Solvent Modified with Magnetic Nanoparticles

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Abstract

A novel magnetic hydrophobic deep eutectic solvent (MHDES) was synthesized, based on DL-menthol, acetic acid, and pyruvic acid, for subsequent use in the magnetic extraction of inorganic contaminants in sewage sludge samples. Firstly, α-Fe_2O_3 nanoparticles were synthesized using the co-precipitation method and were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) techniques. These nanoparticles were then incorporated into the HDES and this modified material was used as a magnetic extracting agent. The stability of the α-Fe_2O_3 nanoparticles in HDES medium was confirmed by zeta potential measurements. The developed MHDES was tested in the extraction of arsenic (As) and cadmium (Cd) from certified samples of sewage sludge, obtaining average recovery values of 106% and 93.2% for As and Cd, respectively. The limit of detection (LOD) and limit of quantification (LOQ) values for As were 0.160 and 0.530 μg L^{-1}, respectively, while the corresponding values for Cd were 0.280 and 0.940 μg L^{-1}, respectively. The elemental compositions of real sewage sludge samples were evaluated by X-ray photoelectron spectroscopy (XPS). The MHDES was used to extract two samples of real sewage sludge, obtaining values of 4.89 ± 0.2 μg g^{-1} (sample A) and 3.80 ± 0.1 μg g^{-1} (sample B) for arsenic, and 2.11 ± 0.07 μg g^{-1} (sample A) and 2.10 ± 0.07 μg g^{-1} (sample B) for cadmium. The extraction process was evaluated using AGREE software, obtaining a score of 0.73 (out of a total of 1.0). The proposed method using vortex and MHDES provided effective extraction of As and Cd from sewage sludge, with high potential for application to other matrices.

Keywords: Magnetic hydrophobic deep eutectic solvent (MHDES), ICP-MS, sample preparation, green metrics.

1. Introduction

In recent years, there has been a significant increase in population density, with concomitant increases in the generation of wastewater and solid waste, including sewage sludge [1]. Sewage sludge, a byproduct of wastewater treatment processes, contains pathogens, a high load of organic matter, nitrogen, phosphorus, and other inorganic contaminants, and has a high moisture content [2, 3]. The final chemical composition of sewage sludge depends on the composition of the influent and on the processes used in the treatment plant [4].

Several contaminants present in wastewater accumulate in sewage sludge (around 80-90% of total contaminants), due to inefficiency of the treatments used in the plants, or the inability to treat all the wastewater produced by human activities [5]. The problem is exacerbated by the fact that agriculture may use sewage sludge as a source of nutrients including nitrogen to increase soil fertility, leading to the contamination of surface waters and groundwater [5]. The presence of contaminants affects food quality, with concerns due to the potential for their accumulation at high concentrations in the edible parts of vegetables, fruits and grains, where they can lead to reductions of nutrients and vitamins. Contaminants can affect plant growth, reduce seed germination rates, and may make foods unsuitable for human consumption [6].

Some inorganic contaminants, such as cadmium (Cd), arsenic (As), zinc (Zn), and lead (Pb), are routinely found in sewage sludge [5, 7, 8] and can have impacts on human health. It is known, for example, that As and Cd can cause disruption of the body's metabolic activities in different ways [9]. Arsenic is recognized for its carcinogenic effect, potentially causing lung, kidney, and liver cancers [9, 10]. Arsenic predominantly exists in sludge as As(III) and As(IV) species, with the former being the most toxic. Cadmium is another inorganic contaminant often found in sewage sludge [11]. Cd is recognized as a toxic, highly bioaccumulating, and carcinogenic element [11, 12]. The presence of both As and Cd is linked to the fact that they coexist in certain media, such as mine drainage, pesticides, and mining and smelting wastes and emissions [12]. Therefore, methods for the extraction and removal of these contaminants are essential in sewage and water treatment plants.

One suitable method that has been widely discussed for this purpose is the use of adsorbents. Adsorption is a physicochemical process in which atoms, molecules, or ions interact with a solid surface, enabling extraction of the species of interest. In addition to

being efficient and inexpensive, adsorption is also an environmentally friendly method [13, 14]. Recent work has investigated the use of new adsorbents for the removal and/or extraction of As and Cd, such as materials modified with iron or manganese [15]. Magnetic adsorbents, including those containing oxides and hydroxides of aluminum, manganese, and iron, can be highlighted for their good adsorption properties, in addition to being considered "green" [15].

Magnetic iron oxide nanoparticles have been shown to be versatile in applications for the extraction of species of interest, including in the area of biomedicine. There have been various approaches for the synthesis of hydrophilic magnetic nanoparticles, although the production of highly water-dispersible magnetic nanoparticles in sufficiently large quantities and with adequate process control remains a significant difficulty [16].

Iron oxide, a low-cost material, is easy to prepare and has useful magnetic properties. The forms hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), and magnetite (Fe_3O_4) are suitable for use as adsorbents in the extraction of inorganic contaminants [15, 17]. Magnetite is a natural magnetic mineral that transforms into maghemite when oxidized by air at room temperature. Maghemite, which is present in soils, transforms into hematite at temperatures above 300 °C. Hematite is the most thermodynamically stable form of iron oxide and is the most common in natural systems [15, 17]. Due to the high abundance of hematite, together with its low toxicity, low cost, high thermal stability, and adjustable optical and magnetic properties, α-Fe_2O_3 nanoparticles have received considerable attention in studies of catalytic reactions, gas sensors, environmental applications, and magnetic storage devices [18]. Iron oxide particles can be synthesized by different routes, including microemulsion, ultrasonic, sol-gel, hydrothermal, and co-precipitation methods [19]. Iron oxide nanoparticles, which have sizes in the range 1-100 nm, present high surface areas, high numbers of active sites, and excellent magnetic character, making them suitable for use in the extraction of various analytes [15, 20].

Several studies have investigated the use of modified deep eutectic solvents (DES) to achieve high efficiency in the extraction of inorganic contaminants [21, 22, 23]. DES are prepared using binary or ternary combinations of hydrogen bond donor (HBD) species and hydrogen bond acceptor (HBA) species, with their main characteristic being a low melting point, compared to the individual constituents [24, 25, 26]. This decrease in the melting point in relation to the individual constituents occurs due to delocalization of the hydrogen bonding charge between the HBD moiety and halide ion [26, 27]. These solvents are easy to prepare, inexpensive, and present high extraction efficiencies. They

have been used for a multitude of uses, such as the extraction of analytes in complex matrices, dissolution of solid samples, modifications of nanoparticles, and mobile phases in chromatographic methods [28].

Among several possible ways to modify DES, magnetic modification can be used to expand their applications in magnetic catalysis, magnetic recovery of contaminants, and magnetic separation of compounds. The use of magnetic DES (MDES) directly competes with conventional methods such as solid phase extraction (SPE) and magnetic solid phase extraction (MSPE). However, compared to these conventional methods, the use of MDES can provide higher sensitivity, avoid interferences, and reduce the time and effort required [29-31].

The innovative combination of DES with magnetic nanoparticles can facilitate and accelerate separation procedures, resulting in significantly shorter total extraction times. This advancement paves the way for notable improvements in chemical, environmental, and industrial applications, since processes can become more efficient, sustainable, and economically viable. A very promising class of DES to be modified are hydrophobic deep eutectic solvents (HDES). These are formed by mixing a long-chain hydrogen bond donor compound, such as octanoic acid, decanoic acid, or dodecanoic acid, with a shorter chain acceptor compound, such as menthol, showing low solubility in water [32].

The aim of the present work was to modify a ternary HDES (based on DL-menthol, acetic acid, and pyruvic acid) with magnetic α-Fe_2O_3 nanoparticles, for use in the extraction of As and Cd from sewage sludge samples.

2. Experimental procedures

2.1. Materials and reagents

Before use, all materials were previously decontaminated in an acid bath (10% v/v HNO_3) for 48 h, followed by washing with ultrapure water from a Milli-Q system (Millipore).

The reagents acetic acid (≥99%), pyruvic acid (98%), DL-menthol (≥95%), $FeSO_4.7H_2O$ (≥99%), $FeCl_3.6H_2O$ (≥99%), and NH_4OH were purchased from Sigma-Aldrich (St. Louis, MO, USA). A cadmium standard (1000 ± 2 mg L^{-1}) and an arsenic standard (1000 ± 2 mg L^{-1}), both for ICP, were purchased from Fluka Analytical (St.

Louis, MO, USA). A sewage sludge certified reference material (CRM) was purchased from SCP Science.

2.2. Preparation and characterization of the HDES

An HDES composed of acetic acid, pyruvic acid, and DL-menthol (1:1:1 molar ratio) was prepared by stirring and heating at 60 °C for 15 min. The HDES was characterized using density, viscosity, FTIR, DSC, and TG/DTA analyses, as described in our previous work [33].

2.3. Synthesis and characterization of the α-Fe_2O_3

Synthesis of the α-Fe_2O_3 nanoparticles used solutions of the salts $FeSO_4.7H_2O$ and $FeCl_3.6H_2O$, in a ratio of $2Fe^{3+}$: $1Fe^{2+}$. After mixing the two solutions, they were slowly homogenized for 1 h, using a magnetic stirrer (AccuPlate Hotplate Stirrer, Model PC-420D, Labnet, Edison, Mexico). During the mixture homogenization process, it was necessary to adjust the pH using NH_4OH (1 M), since precipitation of iron oxide occurs in a basic medium (pH 9-12) [34].

The beaker containing the mixture was then placed in an oven at 120 °C, to evaporate the supernatant, followed by heat treatment at 300 °C for 10 h. The resulting nanoparticles were characterized by X-ray diffraction, using a Siemens D5000 diffractometer fitted with an Ni filter and operating using Cu Kα radiation, with scanning in the 2θ range from 10 to 70° (step size of 0.01° and step time of 2 s). Transmission electron microscopy (TEM) (Model CM200, Philips) and scanning electron microscopy (SEM) coupled to energy-dispersive X-ray spectroscopy (EDS) (Model JSM-IT500HR, JEOL) analyses were performed with the carbon-coated samples. The sizes of the α-Fe_2O_3 nanoparticles were evaluated using the TEM micrographs and IJ 1.46 processing software.

Imaging techniques such as TEM and SEM are valuable tools for characterizing Fe_2O_3 nanoparticles, understanding their properties, revealing the arrangement of atoms in amorphous Fe_2O_3, and evaluating particle morphology, size, and crystal structure. The use of TEM can resolve details down to the atomic level, showing crystal lattices, dislocations, and defects in Fe_2O_3 nanoparticles. TEM provides detailed information on internal structures, including grain boundaries and interfaces [35], while SEM assists in identifying defects, grain boundaries, and structural imperfections, providing information

about the size and shape of the Fe_2O_3 nanoparticles. High-resolution SEM images of the sample surface reveal details such as topography, cracks, and pores. The coupling of EDS with SEM enables determination of the elemental composition [35].

2.4 Study of the stability of the α-Fe_2O_3 nanoparticles in the HDES

The stability of the α-Fe_2O_3 nanoparticles dispersed in the HDES medium was investigated by measuring the zeta potential (ζ). For this, 15.0 mg of α-Fe_2O_3 NPs were dispersed in 4.0 mL of HDES, followed by analysis.

Measurements of zeta potential generally give a good indication of the degree of electrostatic repulsion among the nanoparticles, since the zeta potential is related to the surface charge on nanoparticles. The zeta potential of the α-Fe_2O_3 NPs was determined using a Zetasizer Nano ZS system (Malvern Instruments) and Zetasizer software.

2.5 ICP-MS analysis

Analyses of arsenic and cadmium were performed by ICP-MS, employing a NexION 300X instrument (PerkinElmer, Shelton, USA). The equipment was fitted with a conventional nebulizer, with the torch and gas flow adjusted according to the manufacturer's instructions. The analyses used kinetic energy discrimination (KED) mode, with He gas supplied at flow rates of 2.0 and 3.0 mL min^{-1} for As and Cd, respectively. The As and Cd standard solutions used in the analyses were prepared from 1000 mg L^{-1} stock solutions. For the analysis of sewage sludge, a calibration curve was prepared in the range from 0.500 to 50.0 μg L^{-1}, using a matrix-matched medium containing 1.0% HDES (acetic acid and menthol at a 1:1 molar ratio). Table 1 summarizes the operating conditions for analysis of the samples by ICP-MS.

Table 1. ICP-MS operating conditions.

Parameter	**Operating condition**
Plasma gas flow rate (L min^{-1})	18
Radiofrequency power (kW)	1.6
Nebulizer gas flow rate (L min^{-1})	1.0
Sample uptake rate (L min^{-1})	0.70
Auxiliary gas flow rate (L min^{-1})	1.2
KED mode	
Gas channel	He
He flow rate (mL min^{-1})	2.0 and 3.0
Calibration range (µg L^{-1})	0.500 - 50.0
Spray chamber	Cyclonic
Nebulizer	Concentric
Monitored isotope	$^{111}Cd^{+}$
	^{75}As
Number of replicates	3

2.6 Quality parameters of the method for determination of arsenic and cadmium in the samples

The linearity of the method was evaluated using ANOVA (95% confidence level), based on analytical curves obtained in triplicate, on the same day, in the concentration range 0.500 - 50.0 µg L^{-1}. The detection and quantification limits were calculated using the formulas "*3 x s/a"* and "*10 x s/a"*, respectively, where "*s*" is the standard deviation of ten analytical blanks and "*a*" is the slope of the analytical curve [36].

The accuracy and precision of the method were evaluated using the percentage recovery (recovery %) and relative standard deviation (RSD %), respectively, obtained for analysis of the sewage sludge CRM.

2.7 Sample collection and extraction

The sewage sludge samples analyzed were collected during the southern hemisphere winter of 2023, at two different sewage treatment plants in São Paulo State

(Brazil). The bottles used for the collection were previously decontaminated for 24 h in a 10 % HNO_3 bath. Immediately after collection, all samples were dried in an oven at 60 °C for 72 h, and the possible water content remaining after drying did not affect the determinations nor the results [37]. After drying, the materials were ground and passed through a 63 µm mesh sieve.

The optimized analytical conditions were based on previously published work [33], with adaptations. Around 4.0 mL of HDES were transferred to a Falcon tube, followed by addition of approximately 15.0 mg of NPs and homogenization using a vortex (Model VXMNDG, 50/60 Hz, 135 W, Ohaus) for 30 s at 3000 rpm. A mass of 150 mg of sample was added and the mixture was vortexed again for 30 s. A neodymium magnet was used to separate the nanoparticles from the HDES and the collected solvent was diluted 100-fold in aqueous 1% HDES solution, for analysis by ICP-MS. A 5.0 mL volume of ultrapure water was added to the NPs, with vortex stirring for 1 min to desorb the analytes. This solution was then also diluted in a 1% HDES mixture, followed by ICP-MS analysis. The calculation of the final concentration extracted by the method considered the part of the HDES analyzed at the beginning of the extraction process and the part that was adsorbed by the nanoparticles. A schematic illustration of the extraction procedure is provided in Figure 1.

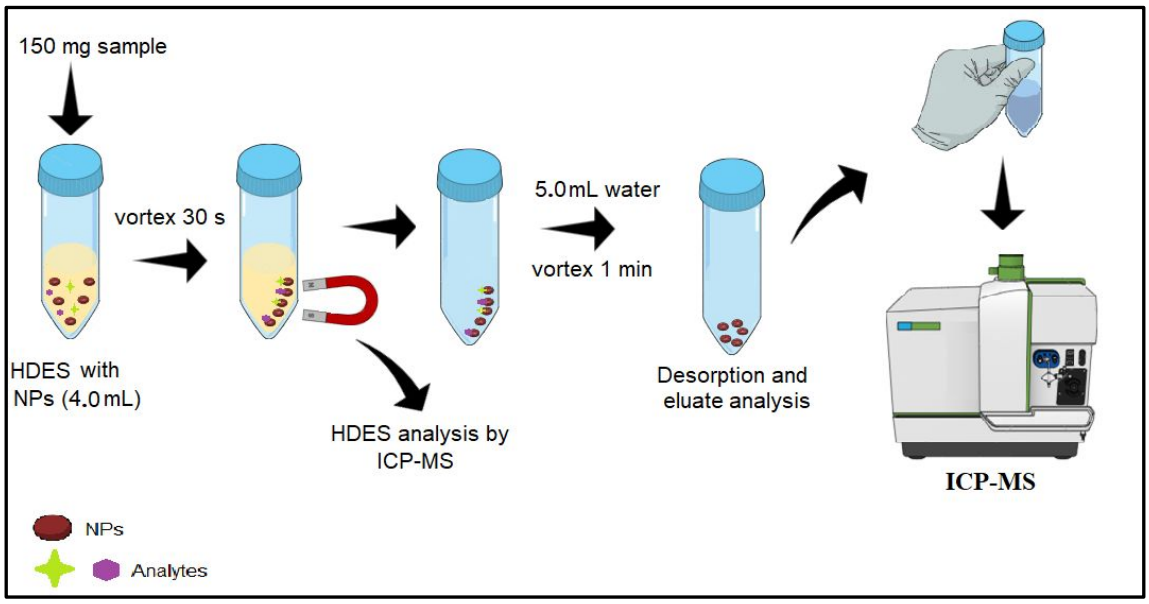

Figure 1. Schematic illustration of the process for extraction of As and Cd from the samples.

2.8 Chemical composition assessment of the sewage sludge samples

The chemical compositions of the sewage sludge samples were evaluated using X-ray photoelectron spectroscopy (XPS) analyses of the previously dried and sieved samples, employing a UNI-SPECS UHV spectrometer, at pressure lower than 5 x 10^{-7} Pa. The Mg Kα line was used (hν = 1254.6 eV) as an ionization source and the pass energy of the analyzer was set to 10 eV. The inelastic noise of the high-resolution C 1s, O 1s, As 3d, and Cd 3d spectra was subtracted using the Shirley method. The composition was determined from the relative proportions of the peak areas, corrected by Scofield atomic sensitivity factors, with an accuracy of ±5%. The width at half height varied between 1.3 and 2.0 eV, and the peak positions were determined with an accuracy of ±0.1 eV.

3. Results and Discussion

3.1 Characterization of the HDES

The HDES prepared from acetic acid, pyruvic acid, and DL-menthol was formed by combining hydrophobic components, as described in detail in our previous work [33]. Acetic acid is a simple carboxylic acid, pyruvic acid is an α-keto acid derived from pyruvate, and DL-menthol is a cyclic terpene alcohol derived from mint oil. The characteristics of hydrophobic DES, such as density, viscosity, conductivity, and surface tension, depend on their component ratios and temperature.

3.2 Characterization of the α-Fe_2O_3

Figure 2A shows the X-ray diffractogram of a hematite standard, according to the Crystallographica Search-Match database (ICDD card #1011240: Fe_2O_3). The crystallographic data for α-Fe_2O_3, extracted from ICDD card #1011240, showed hexagonal close packing, space group (-P 3* 2n), and a = b = c = 5.43 Å [38]. Figure 2B shows the diffractogram for the α-Fe_2O_3 synthesized in this work, highlighting the main diffraction peaks (2θ) of α-Fe_2O_3 at 24.3°, 33.2°, 35.6°, 41.1°, 49.6°, 54.1°, 57.6°, 62.5°, and 63.9°, corresponding to the planes (0 1 2), (1 0 4), (1 1 0), (1 1 3), (0 2 4), (1 1 6), (1 1 2), (2 1 4), and (3 0 0), respectively [18, 39].

It is known that the α-Fe_2O_3 polymorph phase is the most thermodynamically stable form of iron oxide [15]. Hematite is a ferrimagnetic oxide at room temperature and its magnetic properties have been explored for many years [15, 17, 19, 40]. Figure 2C shows the phenomenon of attraction between the α-Fe_2O_3 synthesized in this work and a commercial neodymium magnet.

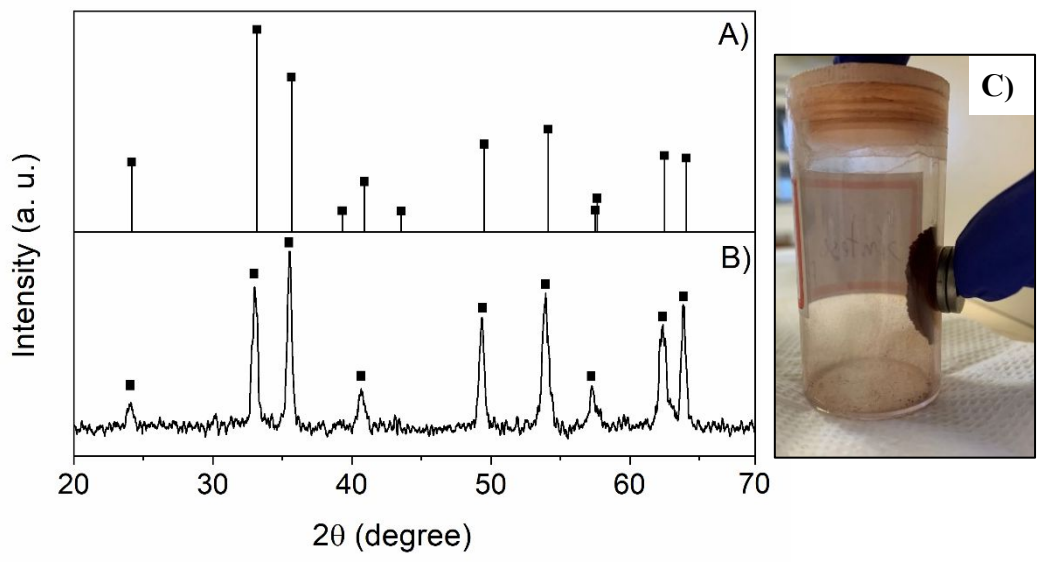

Figure 2. X-ray diffractograms of A) an α-Fe_2O_3 standard (ICDD card #1011240) and B) the synthesized α-Fe_2O_3 nanoparticles. C) Photograph of α-Fe_2O_3 nanoparticles attracted to a neodymium magnet.

Figure 3A shows a TEM image of the α-Fe_2O_3 nanoparticles, revealing their spherical morphology and dimensions smaller than 200 nm. Figure 3B shows the size distribution histogram for the nanoparticles, with sizes in the range 10-50 nm and an average of around 25.0 ± 4.90 nm.

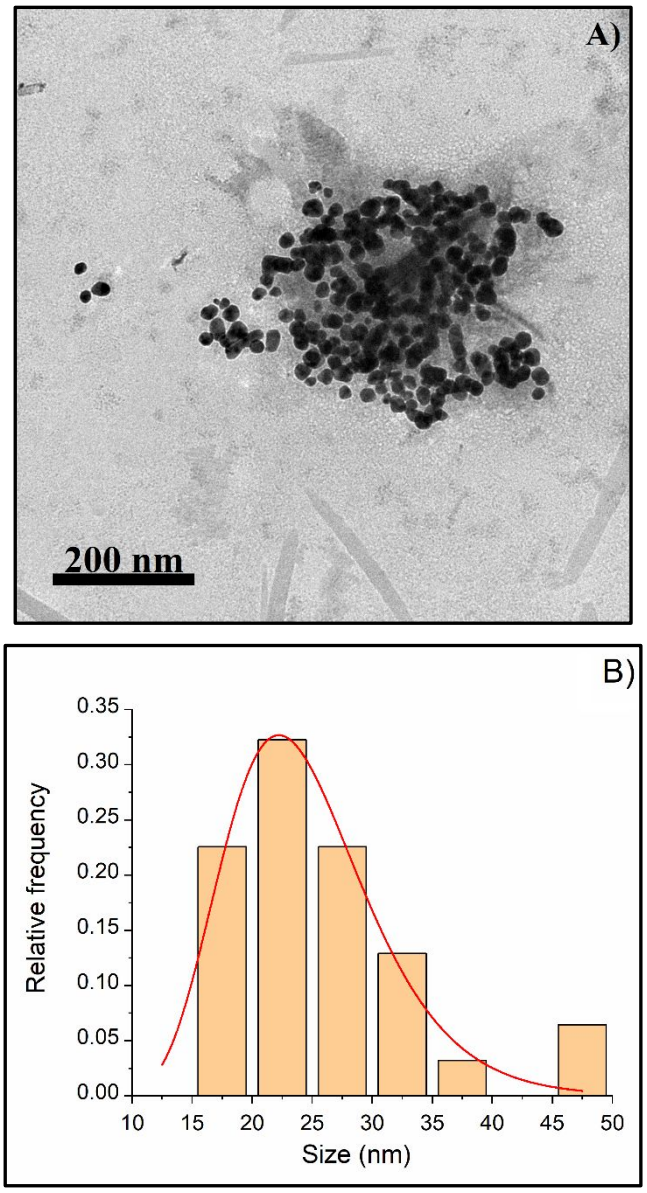

Figure 3. A) TEM image of the α-Fe_2O_3 nanoparticles. B) Size distribution histogram for the nanoparticles shown in the TEM image.

SEM-EDS elemental mapping was performed to confirm that the α-Fe_2O_3 NPs were able to adsorb the target analytes (As and Cd). For this analysis, the HDES was firstly mixed with the nanoparticles and the CRM, with vortex stirring for 1 min. After this time, the HDES was removed and the α-Fe_2O_3 NPs were allowed to dry completely in a vacuum oven, prior to the analysis. The SEM-EDS mapping of the α-Fe_2O_3 nanoparticles (Figure 4) showed that As and Cd were adsorbed on the nanoparticles, confirming the ability of the NPs to remove these inorganic contaminants.

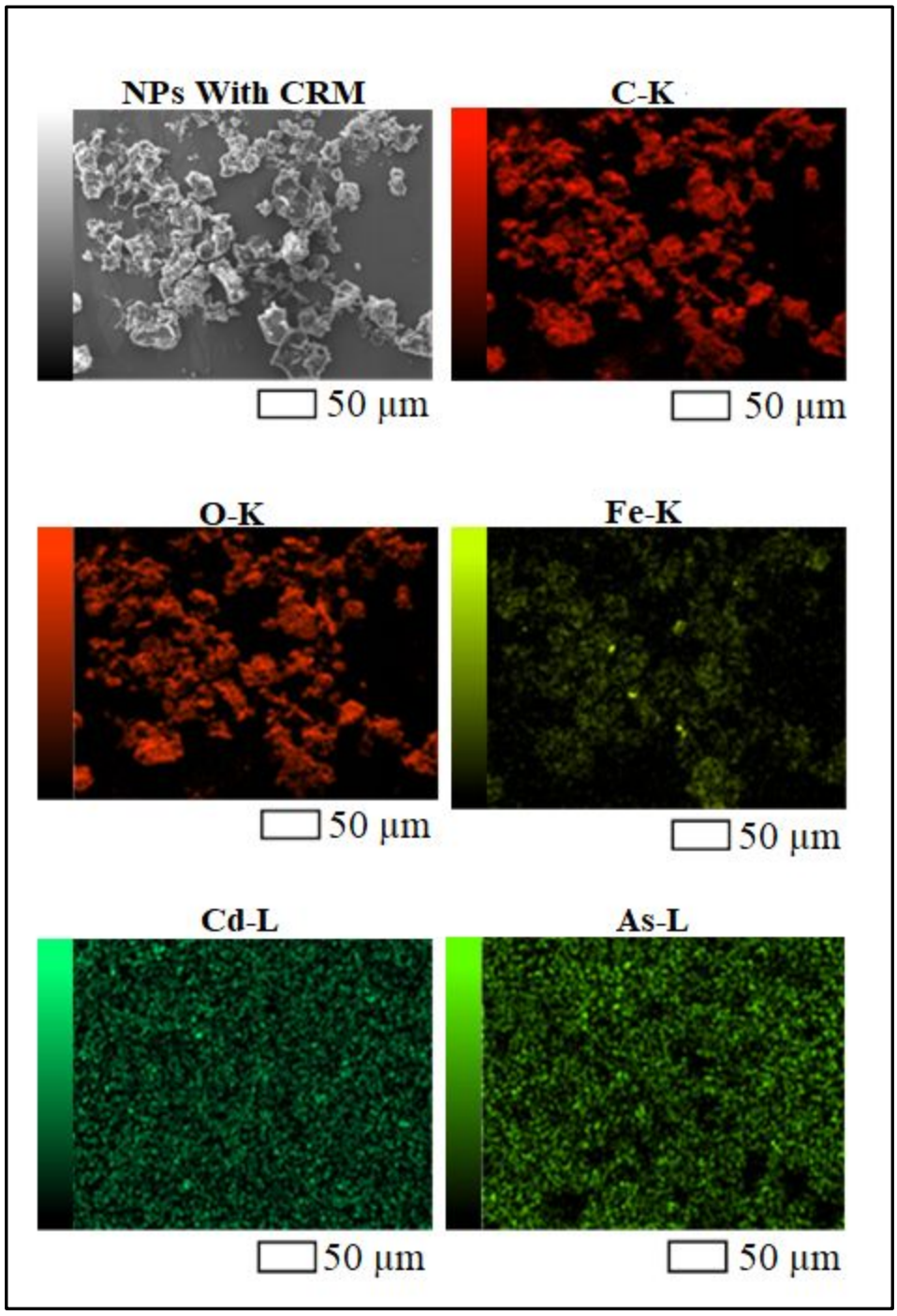

Figure 4. SEM-EDS elemental mapping of the α-Fe_2O_3 NPs mixed with the CRM.

3.3 Chemical composition of sewage sludge samples

XPS analysis was used to determine the surface layer (<5 nm) chemical composition of sewage sludge samples. Figure 5 shows the XPS scan spectra, indicating the locations of the peaks for all the elements detected with accuracy values > ±10%. The peak positions and atomic compositions are provided in Table 2. It should be noted that

the presence of Cd and As corroborated the ICP-MS data. As expected, C 1s and O 1s peaks were observed, in addition to peaks corresponding to Fe 2p, Ca 2p, Si 2p, As 3d, Cd 3d, Al 2p, N 1s, and P 2p, as well as others of lower intensity [41, 42, 43].

It is known that carbon atoms derive from the organic materials present in sewage sludge, N and Fe mainly originate from intrinsic organic and inorganic compounds, such as proteins and iron salts, and Si derives from residual SiO_2 [41]. The aluminum and iron contents in sewage sludge samples are highly influenced by the method used to eliminate phosphorus from effluents [44]. The phosphorus present in sewage sludge is a result of the wastewater treatment process that leads to dissolved phosphorus being transferred to the sludge, in the attempt to eliminate this element from the water and protect water resources from eutrophication [3,44].

Contaminants present in samples of sewage sludge from treatment plants include Cd, Hg, Pb, Cr, As, Ni, Zn, Cu, B, pathogens, and organic compounds such as polyaromatic hydrocarbons, absorbable organic halogens, di-ethylhexylphthalate, and linear alkylbenzenesulfonates, among others [3,45].

Table 2. Surface atomic composition of sewage sludge samples determined from the XPS measurements.

Element	Peak position (eV)		% at	
	Sample A	Sample B	Sample A	Sample B
C 1s	285.0	284.5	64.64	67.57
N 1s	400.0	399.5	1.861	2.455
O 1s	532.0	532.0	22.75	22.21
Al 2p	74.50	74.00	3.715	1.843
Si 2p	102.5	102.0	6.155	4.867
P 2p	43.50	41.50	0.108	0.137
Ca 2p	347.5	347.5	0.492	0.622
Fe 2p	711.5	711.0	0.197	0.158
As 3d	146.0	145.0	0.075	0.132
Cd 3d	405.0	411.0	0.003	0.001

% at: atomic concentration

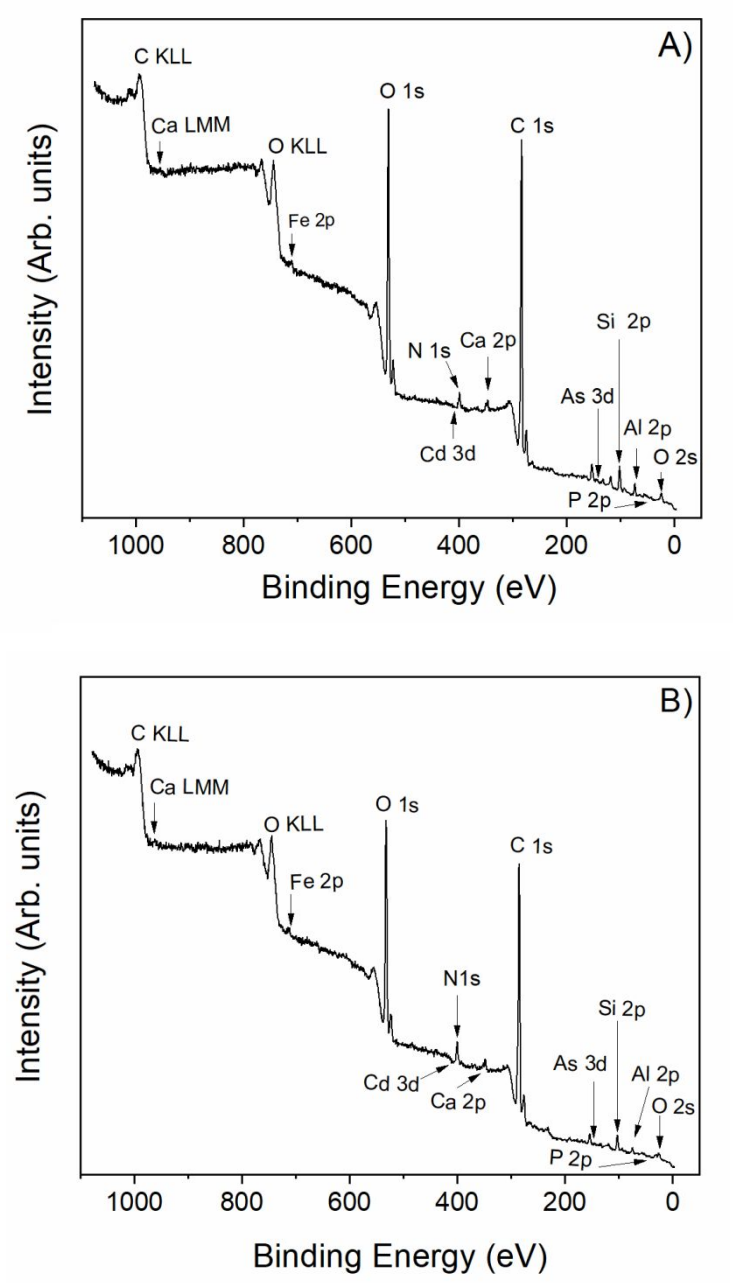

Figure 5. XPS scan spectra of sewage sludge samples: A) sample A; B) sample B.

In the case of samples as complex as sewage sludge, which contains a wide variety of chemical species, additional care must be taken in relation to chemical similarities that may interfere with sample extractions and consequently compromise the analyses. For example, there are similarities between the chemistries of As and P, which form arsenate and phosphate in soils, with direct effects on the specific adsorption of these elements [46]. In soils rich in iron oxides, arsenic can be removed and replaced by phosphate, because the presence of iron ions influences the mobility of arsenate [46,47]. Another

close similarity is between the chemistries of cadmium and zinc (both with +2 oxidation state), which can result in these two elements competing for adsorption sites on soil particles and sewage sludge. In soil, for example, a high concentration of Zn can favor Cd desorption, consequently increasing the Cd concentration in the soil solution [48].

3.4 Stability of the α-Fe_2O_3 nanoparticles in the HDES

Determination of the zeta potentials (ζ) of the synthesized α-Fe_2O_3 NPs in the HDES was crucial for determining their surface charge in the colloidal phase and evaluating their stability. The ζ value was - 33.5 ± 1.8 mV, indicating that the α-Fe_2O_3 NPs had a negative surface charge. The high ζ value showed that the particles were stable in suspension, due to good electrostatic repulsion between them [49], indicating their potential suitability in the sustainable extraction of sewage sludge samples.

3.5 Quality parameters of the proposed methods after desorption

The extraction parameters were optimized according to an experimental design in our earlier work [33], where evaluation was made of the use of smaller and larger masses of sewage sludge, different volumes of extractant solvent, and different extraction times, considering how these parameters mutually influenced the extraction process. Based on analysis of the data, the parameters were defined and were used in this work. The results obtained previously [33] enabled understanding of practical aspects of the extractions, indicating that small variations in the mass concentrations (or mass percentages) of As and Cd would not compromise the optimized extraction process.

The method linearity was evaluated using the triplicates of the calibration curves, in the concentration range 0.500-50.0 μg L^{-1}. The equations describing the curves were y = 37.7[As] – 11.3 (Eq. 1) (R^2 = 0.998) and y = 8.80[Cd] – 1.90 (Eq. 2) (R^2 = 0.999), for As and Cd, respectively. Application of ANOVA showed no lack of fit for the two analytes ($F_{cal\ As}$ (5.88 x 10^{-8}) < $F_{tab\ As\ 95\%}$ (1.00 x 10^4); $F_{cal\ Cd}$ (5.32 x 10^{-6}) < $F_{tab\ Cd\ 95\%}$ (413)).

The precision of the method (% RSD) was determined by the repeatability of CRM analyses in triplicate (n = 3), obtaining values of 1.60% (As) and 3.40% (Cd). The accuracy (% recovery) was determined by analysis of the CRM (n = 3), obtaining values

of 106% for As and 93.2% for Cd. The LOD and LOQ values were, respectively, 0.160 and 0.530 μg L^{-1} for As, and 0.280 and 0.940 μg L^{-1} for Cd.

Arsenic and cadmium were determined in the sewage sludge and CRM samples using external calibration. About 10% of all the As and Cd was found in the HDES solvent collected at the beginning of the extraction process, while the rest was adsorbed on the NPs and was determined after desorption. The details of the concentrations obtained for sewage sludges A and B are shown in Table 3.

It can be seen from Table 3 that higher As recovery (106% for the total As) was obtained employing the environmentally benign MHDES technique, compared to the other As analysis methods [50,51]. High recovery of Cd (93.2%) was also obtained, in comparison with the other two reported methods [52, 53], indicating that a green extraction method using MHDES had been successfully developed.

Evaluation of the reusability of the nanoparticles indicated that reuse was not viable, because the extraction capacity decreased by more than 30% after the first cycle. Other work has also reported the inability to successfully reuse a magnetic sorbent [21].

Table 3. Details of the concentrations of As and Cd in the samples analyzed by ICP-MS. The values are shown as average (μg g^{-1}) ± standard deviation (n = 3).

Analyte	Samples					
	Sewage sludge A		Sewage sludge B		CRM	
	HDES*	NPs**	HDES*	NPs**	HDES*	NPs**
As	0.490 ±0.004	4.40 ± 0.2	0.400 ± 0.002	3.40 ± 0.1	0.490 ± 0.004	4.40 ± 0.2
Cd	0.210 ±0.002	1.90 ± 0.07	0.200 ± 0.001	1.90 ± 0.06	0.180 ± 0.003	1.60 ± 0.03

* HDES analyzed at the beginning of extraction; ** Eluate analysis after desorption of NPs.

Magnetic materials, including nanoparticles, are considered excellent adsorbents, since they are not miscible in many samples, so they can be easily separated by attraction using a magnet, eliminating the need for time-consuming centrifugation steps [54]. Fe_2O_3 nanoparticles can effectively adsorb both cations and anions, according to mechanisms

that may be physical or chemical, so modification of the HDES with magnetic nanoparticles provided an environment conducive to the extraction of As and Cd [15].

In the present work, the adsorption and desorption of inorganic contaminants was accelerated by vortex stirring, which increased the rate of migration of the analytes to the NPs in the HDES, and vice versa. Longer vortexing times (1-3 min) were tested, but it was found that the same efficiency values were obtained in all the tests. Similar findings were reported by Dilmaghani et al. [54], who tested times of 1-3 min in the extraction of polycyclic aromatic hydrocarbons using a magnetic DES [54].

Previous studies have used MHDES for the removal of Cr(VI), pesticides, nickel, and copper in foods, and fungicides in foods [55-57], but there have been no reports of the use of a ternary MDES for the extraction of As and Cd present in sewage sludge samples.

The extraction of As and Cd from sewage sludge and other media has generally employed HNO_3, followed by analysis using ICP-OES or ICP-MS [52, 58]. Table 4 provides a comparison of the main acid solutions used for the extraction of As and Cd from sewage sludge samples. It should be highlighted that the present work proposes an environmentally friendly technique using MHDES for the extraction of these elements from environmental matrices. The traditional methods using acid solutions and microwave irradiation have the drawbacks of high toxicity and long sample preparation times, which can lead to health risks and compromise analytical frequency.

Table 4. Main solutions used for extraction of As and Cd from environmental matrices.

Analyte	Solution used	Sample	Recovery (%)	Instrumental apparatus	Ref.
As	Aqua regia + H_2O_2	Sewage sludge	84.0	ICP-OES	50
	$HCl + HNO_3 + HClO_4$	Sewage sludge	98.6	ICP-OES	51
	MHDES	Sewage sludge	106	ICP-MS	This work
Cd	Aqua regia (HCl + HNO_3)	Municipal sewage sludge	83.0	ICP-OES	53
	HNO_3	Sewage sludge	>95.0	ICP-OES	52
	MHDES	Sewage sludge	93.2	ICP-MS	This work

The energy consumed during an extraction process varies depending on the specific method used and the type of material being extracted. Optimizing energy consumption during extraction contributes to both cost-effectiveness and environmental responsibility [59], with a focus on green extraction techniques, rather than traditional methods, which can minimize both energy use and adverse environmental impacts [60, 61]. Balancing energy efficiency with extraction yield is essential for sustainable practices.

In this study, calculation of the energy consumption in the sample extraction process resulted in a value of 0.000843 kWh mL^{-1} for each extraction. Evaluation of the greenness of the arsenic and cadmium extraction procedures was performed using the open-source AGREE software, which produces a graph with values varying from 0 to 1, corresponding to the lowest and highest greenness, respectively, based on the 12 principles of green analytical chemistry (GAC) [62]. A graphical image is generated by the software, with colors ranging from red to green, where red indicates weak points and green indicates strong points (Figure 6). The items evaluated by AGREE are as follows:

1) sample treatment; 2) sample amount; 3) device positioning; 4) sample preparation stages; 5) automation and miniaturization; 6) derivatization; 7) wastes; 8) analysis throughput; 9) energy consumption; 10) source of reagents; 11) toxicity; 12) operator safety. In the present work, a score of 0.73 was obtained (without considering the energy consumption of analyses by ICP-MS), indicating that the developed extraction method was in accordance with the 12 principles of GAC, so it could be considered a green method.

Figure 6. Use of AGREE to evaluate the greenness of the extraction method.

Conclusions

This study presents an environmentally friendly new technique using MHDES to replace traditional methods based on acid solutions and microwave irradiation, since the latter have drawbacks related to toxic chemicals and time-consuming procedures. The sample preparation time was short, with vortex stirring for only 90 s, enabling high analytical frequency. The MHDES proved to be a good substitute for the HNO_3 solutions conventionally used in the extraction of these analytes.

A solvent based on DL-menthol, acetic acid, and pyruvic acid was modified with magnetic nanoparticles, for subsequent use in the extraction of arsenic and cadmium from sewage sludge samples. The combination of a HDES and magnetic nanoparticles facilitated and accelerated collection of the analytes, reducing the total extraction time. The magnetic nanoparticles were synthesized by the co-precipitation method and were characterized by TEM, SEM, XRD, and EDS analyses. The Crystallographica Search-

Match database provided information about the X-ray diffraction pattern of hematite, enabling comparison with the synthesized Fe_2O_3.

TEM micrographs showed that the α-Fe_2O_3 nanoparticles were spherical, with average size of around 25.0 ± 4.90 nm. SEM-EDS analysis confirmed that the NPs could bind to As and Cd, demonstrating that they were suitable for the extraction of inorganic contaminants.

Determination of the zeta potential of the synthesized α-Fe_2O_3 NPs in HDES, indicating their surface charge in the colloidal phase, confirmed the stability of the particles.

The elemental compositions of real sewage sludge samples, determined by XPS, showed the presence of the elements As and Cd, in addition to C, O, Si, Al, N, Ca, P, and Fe.

The developed method was used to extract As and Cd from real sewage sludge samples, obtaining values for As of 4.89 ± 0.2 μg g^{-1} (sample A) and 3.80 ± 0.1 μg g^{-1} (sample B), while the values for Cd were 2.11 ± 0.07 μg g^{-1} (sample A) and 2.10 ± 0.07 μg g^{-1} (sample B). The method presented satisfactory linearity and accuracy for the determination of As and Cd in the sewage sludge samples. Precisions of 1.60% for As and 3.40% for Cd were obtained for repeated analyses of the CRM. The accuracies of the method were 106% for As and 93.2% for Cd. The LOD and LOQ values were, respectively, 0.160 and 0.530 μg L^{-1} for As, and 0.280 and 0.940 μg L^{-1} for Cd.

Finally, the AGREE software was employed to evaluate the green nature of the extraction process, obtaining a score of 0.73 (out of a total of 1.0), demonstrating that the extraction process could be considered environmentally friendly. To improve energy and material usage, further research on the behavior, applications, and optimization of MHDES is recommended.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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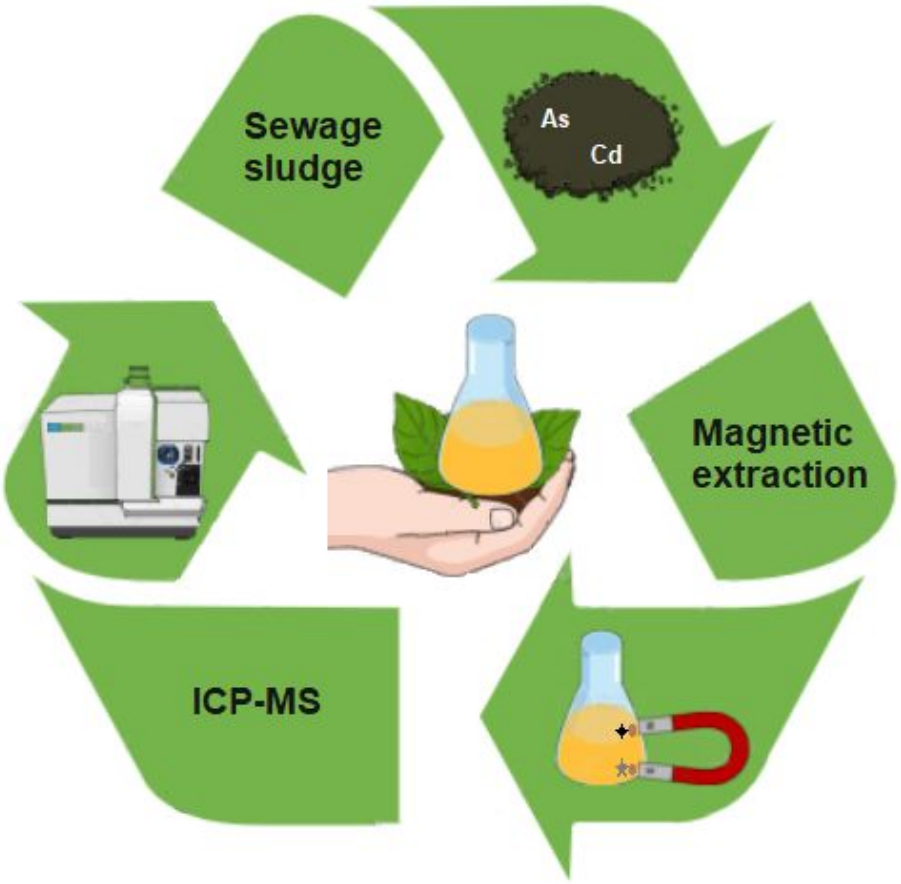
TOC/Graphical abstract



A sustainable method utilizing hydrophobic deep eutectic solvents modified with magnetic nanoparticles was employed for the magnetic extraction of arsenic and cadmium in sewage sludge samples.

Synopsis

Inorganic contaminants in sewage sludge cause long-term environmental damage; therefore, development of sustainable extraction methods is crucial for their removal.