

Article

Enhancing Trace Metal Extraction from Wastewater: Magnetic Activated Carbon as a High-Performance Sorbent for Inductively Coupled Plasma Optical Emission Spectrometry Analysis

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Abstract: A new fast, sensitive, and environmentally friendly analytical method has been developed for the simultaneous determination of Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn in wastewater samples using inductively coupled plasma optical emission spectroscopy (ICP OES). A preconcentration step using a magnetic dispersive solid-phase extraction (MDSPE) technique with a new magnetic sorbent was performed. The new sorbent material was a carbon containing magnetic cobalt and nitrogen groups. This material was synthesized using controlled pyrolysis of a zeolitic imidazolate framework (i.e., ZIF-67). In order to optimize the experimental parameters that affect the MDSPE procedure, a multivariate optimization strategy, using Plackett–Burman and circumscribed central composite designs (CCD), was used. The method has been evaluated employing optimized experimental conditions (i.e., sample weight, 10 g; sample pH, 7.6; amount of sorbent, 10 mg; dispersive agent, vortex; complexing agent concentration, 0.5%; ionic concentration, 0%; eluent, HCl; eluent concentration, 0.5 M; eluent volume, 300 µL; elution time, 3 min and extraction time, 3 min) using external calibration. Limits of detection (LODs) in a range from 0.073 to 1.3 µg L⁻¹ were obtained, and the repeatability was evaluated at two different levels, resulting in relative standard deviations below 8% for both levels ($n = 5$). An increase in the sensitivity was observed due to the high enrichment factors (i.e., 3.2 to 13) obtained compared with direct ICP OES analysis. The method was also validated through carrying out recovery studies that employed a real wastewater sample and through the analysis of a certified reference material (ERM[®]-CA713). The recovery values obtained with the real wastewater were between 94 and 108% and between 90 and 109% for the analysis of ERM[®]-CA713, showing negligible matrix effects.

Keywords: magnetic dispersive solid-phase extraction (MDSPE); magnetic activated carbon; trace metal analysis; multivariate optimization; wastewater samples; inductively coupled plasma optical emission spectrometry (ICP OES)



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1. Introduction

An important effect of industrial processes and human activities is the pollution of several ecosystems [1–3]. In this regard, heavy metals pollution has risen in recent years and has become an ongoing issue for environmental organizations, being one of the most serious ecological concerns at present [4,5]. These pollutants may enter the human body through air, water, food, or absorption through the skin [6]. It is well known that exposure to certain heavy metals has been linked to a number of disorders that are harmful to human

health since, some of them are not metabolized and can accumulate in soft tissues [7,8]. According to the World Health Organization (WHO), long-term exposure to environmental pollution, such as air, soil, and water pollution, causes around 25% of the illnesses that humans face today [9]. Therefore, the determination of these toxic metal ions in water and aquatic ecosystems is of great importance, as these contaminants are detrimental to the environment and have serious impacts on human health [10].

Various analytical techniques such as inductively coupled plasma optical emission spectrometry (ICP OES) [11–13], inductively coupled plasma mass spectrometry (ICP-MS) [14–16], electrothermal atomic absorption spectrometry (ETAAS) [17–19], flame atomic absorption spectrometry (FAAS) [20–22], and atomic fluorescence spectrometry (AFS) [23,24] have been applied for the determination of trace amounts of heavy metal ions in water and biological samples. Because of its superior sensitivity, broad dynamic linear range, reduced detection limits, excellent accuracy, and simultaneous multi-elemental analysis capacity, ICP OES is one of the most popular analytical techniques for elemental analysis [11,25]. Despite these benefits, trace metals concentration in real samples is extremely low and the complexity of matrices in real samples may substantially interfere with the determination of analytes [26,27]. Therefore, to solve such problems, it is necessary to develop simple, selective, reliable, efficient, and eco-friendly sample pretreatment methods for the extraction of trace amounts of heavy metals in environmental and biological samples before ICP OES determination [28]. Under these conditions, a separation and enrichment step such as liquid–liquid extraction (LLE) [29–31], coprecipitation [32–34], filtration [35], ion exchange [36–38], cloud point extraction (CPE) [39,40], or solid-phase extraction (SPE) [41–44] have been used prior to its determination.

Among the above-mentioned separation and preconcentration techniques, solid-phase extraction (SPE) is one of the most widely used sample pretreatment techniques [45]. SPE has some advantages over other sample pretreatment techniques due to its simplicity, reduced extraction time, greater enrichment factors, cheaper cost, and the reduction in the consumption of organic solvents [46,47]. The fundamental concept of SPE is the transfer of analytes from the liquid phase to the solid phase's adsorption sites where they remain during the extraction process [48]. Then, both phases are separated by centrifugation or simply recovered by flotation [49,50]. After adsorption, the analytes retained in the solid sorbent can be eluted [51], thermally desorbed [52], or directly determined using a suitable analytical technique [53]. SPE has been extensively employed for the preconcentration of metals in polluted waters [54].

Despite all these advantages, there is growing interest in developing ecological analytical methods based on the Green Analytical Chemistry principles [55]. The Green Analytical Chemistry principles and the processes which are adhered to them aim to replace harmful chemicals, reduce waste in laboratories, and, as a result, miniaturize traditional analytical procedures. Furthermore, in recent years, interest in the sample preparation step has increased in relation to the principles of Green Analytical Chemistry. For that reason, the continuous search for innovative sample preparation methods has led to the creation of new procedures such as solid-phase microextraction (SPME) [56] and dispersive solid-phase extraction (DSPE) [57]. In DSPE, the solid sorbent is dispersed in the solution. This strategy encourages quick interaction of the analytes with the sorbent, minimizing the consumption of sorbent and leading to a faster extraction process in comparison with traditional SPE [58]. New advances in sample preparation that employ DSPE try to reduce the consumption of sorbents by using smaller amounts (i.e., microgram); this tendency has led to the development of dispersive micro-solid-phase extraction (D μ SPE) [59].

Magnetic materials have recently been reported to be used as sorbents in several papers [6,60,61]. Magnetic dispersive solid-phase extraction (MDSPE) is gaining popularity because it decreases sample preparation time and allows for easier sorbent manipulation [62,63]. In MDSPE, the magnetic sorbent material is dispersed into the liquid phase; after the extraction, it is simply removed from the sample solution using a magnet [64], avoiding time-consuming filtration or centrifugation steps to carry out the phase separation [61,65,66].

The sorbents decorated with magnetic solids simultaneously combine the exceptional sorbent capability and the easy sorbent handling, reducing analysis time, sorbent amounts, and the consumption of solvents [67,68]. Finally, analytes can be desorbed employing an eluent solvent or heating for further analysis [69].

One of the most important MDSPE-related research areas at present is the quest for novel magnetic sorbent materials with high selectivity and strong adsorption capacity that are chemically and thermally stable, inexpensive, and environmentally benign [14,70].

Different magnetic sorbents have been used in magnetic dispersive solid-phase extraction, such as inorganic oxides, porous polymers, molecularly imprinted polymers (MIP), biosorbents, or carbon nanomaterials [71,72]. In addition, magnetic composites based on zeolitic materials have been described for the extraction and preconcentration of organic compounds and metals from different samples, including water, environment, food, and biological samples [6,73–75].

The aim of this work is to develop a new analytical method for the determination of trace metals (i.e., Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) in wastewater samples through MDSPE using a new magnetic material developed specifically for this application. This material is carbon, containing magnetic cobalt and nitrogen groups. These groups can serve as anchoring centers for the metals and have been prepared using controlled pyrolysis of a zeolitic imidazolate framework (ZIF). These materials are composed of tetrahedrally coordinated transition metal ions (e.g., Fe, Co, Cu, Zn) that are connected by imidazolate linkers; this is further carbonized in order to obtain Co-doped magnetic carbon. More information about the employed material can be found in the bibliography [76]. To the best of our knowledge, the new magnetic material has not been employed for the determination of trace metals before.

2. Materials and Methods

2.1. Instrumentation

All the measurements were carried out using an Agilent 720 inductively coupled plasma optical emission spectrometer (Agilent Technologies, Melbourne, Australia). The operating conditions employed using the ICP OES are shown in Table S1. The instrumental parameters were optimized, accomplishing the maximum signal intensity for the set of emission lines evaluated. In addition, the sample uptake rate (i.e., 100 $\mu\text{L min}^{-1}$) was the minimum liquid flow required in order to measure all emission lines analyzed. A pH meter Basic 20 (Crison Instrument, Barcelona, Spain) provided with a combined glass electrode was used for the pH measurements. In order to disperse the extractant into the sample, a Vortex Reax Top (Heidolph Instruments, Schwabach, Germany) was used. A neodymium magnet (1.32–1.37 T) was used to bring about the phase separation (Supermagnete, Gottmadingen, Germany). NemrodW statistical software (NemrodW[®] v.2007/2010, LPRAI, Marseille, France) and Statgraphics[®] Centurion (Statpoint Technologies, Warrenton, VA, USA) were employed to construct the experimental designs and evaluate the optimization results and the desirability function. NemrodW was used to evaluate the screening and the central circumscribed design of the developed method and Statgraphics[®] Centurion was employed to construct the desirability function to obtain a common experimental condition for all the analytes evaluated.

Characterization of the porosity of the samples was performed using N_2 adsorption–desorption isotherms as well as CO_2 adsorption isotherms [77]. Before measurement, samples were outgassed at 150 °C during 4 h (Autosorb degasser, Quantachrome, Boynton Beach, FL, USA). The nitrogen adsorption–desorption isotherms were measured at -196 °C (Autosorb-6, Quantachrome). The Brunauer–Emmett–Teller (BET) equation was utilized for the estimation of the surface area, which was determined from the N_2 adsorption branch. The number of points used to apply the BET equation was higher than five, and the BET constant was always positive. The Dubinin–Radushkevich method was utilized to obtain the micropore volume (V_{micro}) and determine whether any diffusional restrictions in the adsorption took place. Pore volume has been obtained at $P/P_0 = 0.95$. All data

treatment related to sorbent characterization was carried out using the software Quadrawin (Quantachrome). The same device was used for the CO₂ adsorption isotherms at 0 °C. No diffusional restrictions were observed. Powder X-ray diffraction was utilized for the identification of crystallographic phases using a D8-Advanced diffractometer with a Goebel mirror and a Kristalloflex K 760-80F X-ray generation system, fitted with a Cu cathode and a Ni filter (Bruker, Billerica, MA, USA). Spectra were registered between 5° and 80° with an angular step of 0.05° and a three second step time. X-ray photoelectron spectroscopy (XPS) analysis was carried out in a VG-Microtech Multilab device with a MgKalpha (Hv:1253.6 eV) radiation source, pass energy of 50 eV, and background pressure of 5·10⁻⁷ Pa (VG-Microtech, Uckfield, UK). The spectra were carefully deconvoluted and the peak areas estimated through integration of each peak, prior subtraction of a Shirley background, and fitting the experimental peaks to a 30/70 proportion of a combination of Lorentzian/Gaussian lines. Field emission scanning electron microscopy (FESEM model Merlin VP Compact, Zeiss, Jena, Germany) with energy-dispersive X-ray spectroscopy (EDS, model Quantax 400, Bruker) in both backscattered electron (BSE) and secondary electron (SE) modes were employed to study the morphology of the samples. Raman spectroscopy characterization was carried out in an NRS-5100 device from Jasco (Tokyo, Japan) using a 633 nm He laser. Magnetic susceptibility measurements were carried out at 300 K in a magnetic field ranging from -30 to 30 kOe using a MPMS XL (SQUID) magnetometer from Quantum Design (San Diego, CA, USA). Finally, the zeta potential was measured using a Colloid Metrix Stabino II instrument (Meerbusch, Germany).

2.2. Samples and Reagents

Standard reference solutions of Hg and Be used for ICP OES calibration and for addition and recovery experiments were purchased from High Purity Standard (Charleston, SC, USA) with a concentration of 1000 mg L⁻¹. Standard reference solutions of Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were obtained from Merck IV solution of 1000 mg L⁻¹ (Merck, Darmstadt, Germany). Working solutions of analytes were prepared using appropriate dilution of the commercial standard reference solutions. To prepare the buffer solutions during the optimization and measurement process, H₃PO₄ 85% purity (Scharlau, Barcelona, Spain) and KH₂PO₄ and K₂HPO₄ pro-analysis (Merck) were employed. Sodium diethyldithiocarbamate (DDTC, 99%, Merck) was used as a complexing agent. HCl 30% purity (Merck) and HNO₃ 65% purity (Scharlau) were employed as eluent phases during the measurement and optimization process. During the optimization process, NaCl pro-analysis (Scharlau) was used to adjust the ionic strength of the samples. All the experiments were prepared using ultrapure water with resistivity higher than 18.0 MΩ cm obtained using a PURELAB flex 3 purification system (Elga LabWater, High Wycombe, UK). Reagents employed during the synthesis of ZIF-67 were provided by Merck in analytical grade and were used without further purification.

The standard reference material employed in this work was ERM[®]-CA713 wastewater (Joint Research Center, European Commission, Geel, Belgium). A real water sample used was obtained from a wastewater treatment plant (Aguas Municipalizadas de Alicante E.M., Spain). Sample was collected in amber glass containers and then stored in the dark at 4 °C. To perform the analysis, the sample supernatant was collected and measured (i.e., dissolved metals) after decantation during 24 h without any sample digestion or filtration step.

2.3. Synthesis of the Magnetic Sorbent

The synthetic procedure followed the classical ZIF-67 synthesis [78,79], in which 144 mmol of 2-Methylimidazole were dissolved in 50 mL of deionized water. This solution was blended with a 25 mL deionized water solution in which 12 mmol of cobalt acetate were previously dissolved. The mixture was stirred vigorously for 5 min and kept at room temperature for 72 h. ZIF-67 was recovered by centrifugation at 12,000 rpm and washed three times with methanol. Then, the powder was dried at 60 °C for 24 h in a conventional oven. Lastly, the ZIF was put in a tubular furnace under a 100 mL min⁻¹ N₂ dynamic atmosphere, heated up at 5 °C min⁻¹, and carbonized at 900 °C for 2 h. The carbon material was then washed with HCl following the procedure of Villagordo-Hernández et al. [76] (i.e., ZIF67C_900_1 meaning activated carbon obtained by carbonization at 900 °C and washed once with HCl). Previously, a screening study of different magnetic carbons was conducted, finding that this material was the most suitable for this specific application.

2.4. MDSPE Procedure

For the magnetic microextraction process, the first step was to adjust the pH of the sample or standards at 7.6 using the necessary amount of KH₂PO₄ and K₂HPO₄. Subsequently, DDTC was added as a complexing agent until its concentration was 0.5%. Once the sample (or standard) was prepared, it was transferred (i.e., 10 g) to a glass centrifugation tube and 10 mg of the magnetic solid extractant (ZIF67C_900_1) was introduced in the tube that contains the sample or standard. Then, the mixture was shaken using the vortex for 3 min to extract the analytes. After shaking, the supernatant (i.e., sample) was removed and the sorbent was washed 3 times with 1 mL of ultrapure water and the wash water was removed. Afterwards, 300 µL of HCl 0.5 M was added to the sorbent in order to elute the analytes. The elution was carried out using the vortex for 3 min. Finally, the eluate was removed from the solution containing the sorbent and measured directly with the ICP OES. During the extraction, washing, and elution process, the neodymium magnet was used to ease the separation step between the solid and liquid phases. The entire MDSPE process is shown in Figure 1.

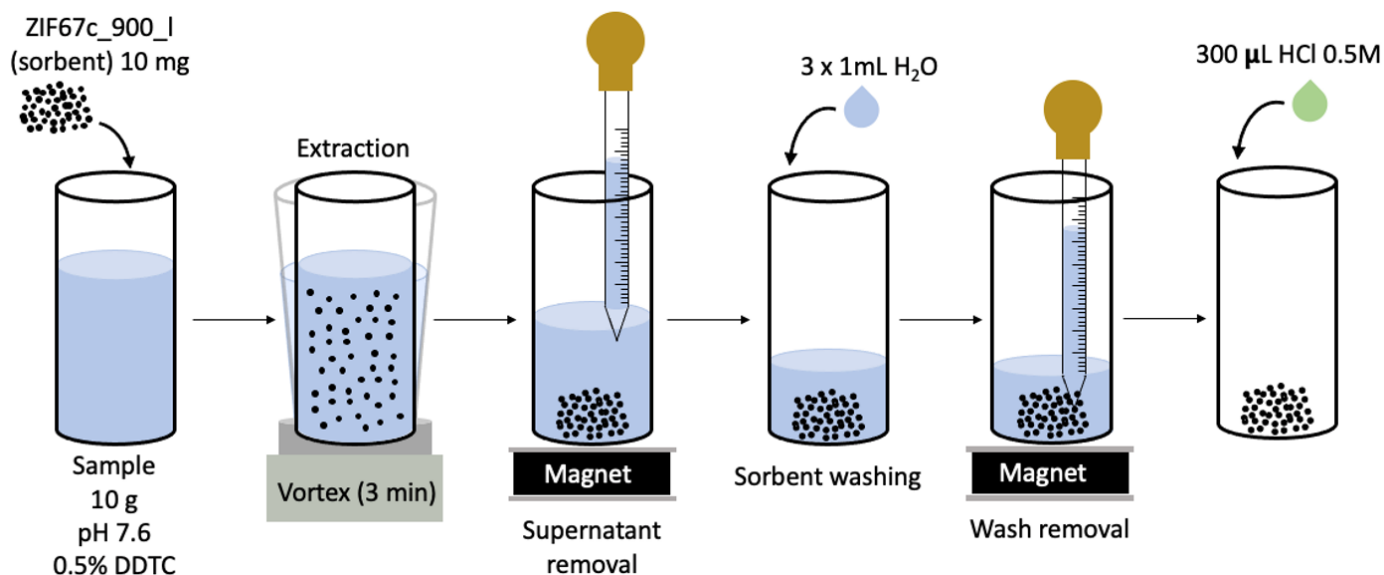


Figure 1. Cont.

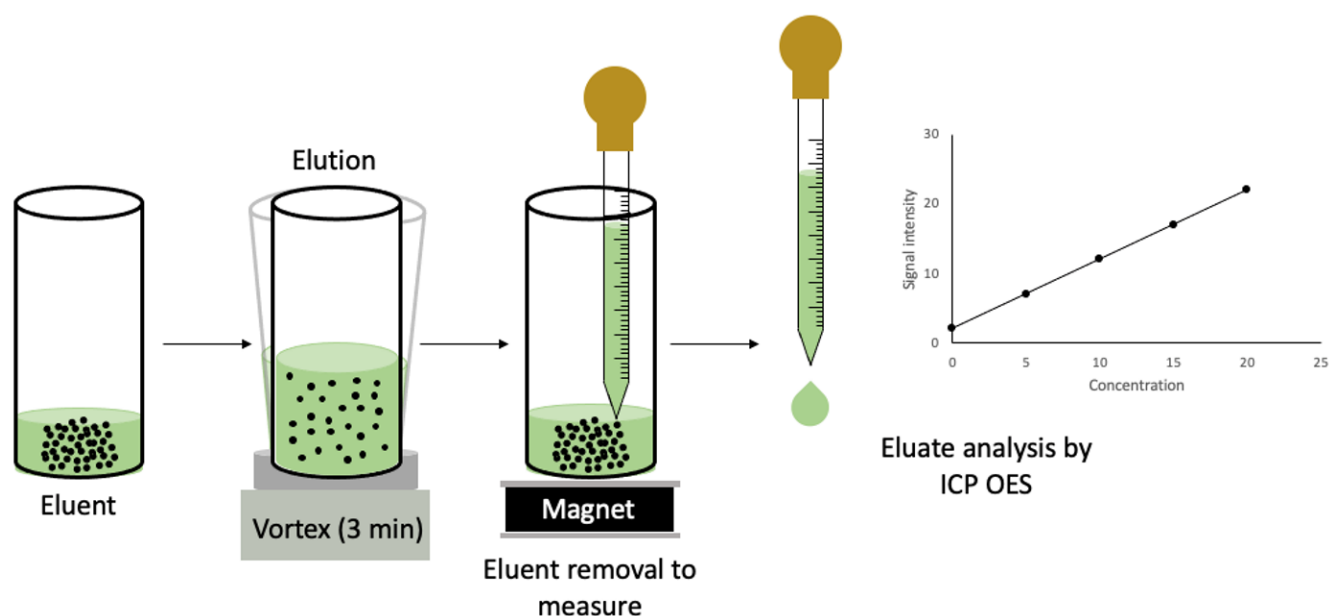


Figure 1. Schematic representation of MDSPE for preconcentration of trace metals using the optimized experimental conditions (i.e., (i) sample weight, 10 g; (ii) sample pH, 7.6; (iii) amount of sorbent, 10 mg; (iv) dispersion mode, vortex; (v) complexing agent concentration, 0.5%; (vi) ionic concentration, 0%; (vii) eluent, HCl; (viii) eluent concentration, 0.5 M; (ix) eluent volume, 300 μL ; (x) extraction time, 3 min; (xi) elution time, 3 min).

3. Result and Discussion

3.1. Characterization of ZIF67C_900_1

As presented in Figure S1, three diffraction peaks appear at 44.2° , 51.5° , and 75.9° in the XRD pattern, which could be indexed to Co(0) (JCPDS card No. 15-0806). Moreover, the peak found at 25.85° could be assigned to the (002) plane of graphite (JCPDS card No. 89-8487). In all cases, well-defined peaks can be observed, which indicate that both carbon and cobalt are crystalline, but there are crystallite sizes of less than 100 nm, since the peaks are very broad.

The N_2 adsorption isotherm (Figure S2) of the original carbon and the washed one are very similar; in both cases, they show a very wide distribution of porosity, which is easily deduced from the wide shoulder that shows the adsorption. Although the specific surface area is not very high in either case (400 and $480 \text{ m}^2 \text{ g}^{-1}$), the washed sample has an area that is 20% higher. It should also be noted that it presents a certain hysteresis (desorption branch above the adsorption branch); this indicates that we have ink-bottle-type pores that have been generated by acid washing the carbon due to the extraction of the unbound cobalt particles [76].

The secondary electron micrograph (Figure 2) shows the cobalt-doped carbon crystallites. The microstructure reminds us of the original ZIF, where there has simply been a contraction of the particles without losing their original cubo-octahedral shape [80]. In addition, it is possible to observe from the secondary electron micrograph that the particle size of the ZIF is $1 \mu\text{m}$.

The XPS spectra shown in Figure S3 are very revealing. Firstly, we will analyze Co. The XPS spectrum shows the $2p_{1/2}$ transition where a peak associated with Co(0) and a peak at higher energy associated with Co(II) can be clearly seen. The presence of the satellites is unequivocal that we have Co(II) and not Co(III). A fact to highlight is that the presence of Co(0), which is what we have seen by other techniques, indicates that we only have a small nanometric layer of cobalt oxide. Regarding the nitrogen spectrum, we observe the $1s$ transition, where three peaks can be seen that we can associate with three N positions in the graphene sheet, as indicated in the figure.

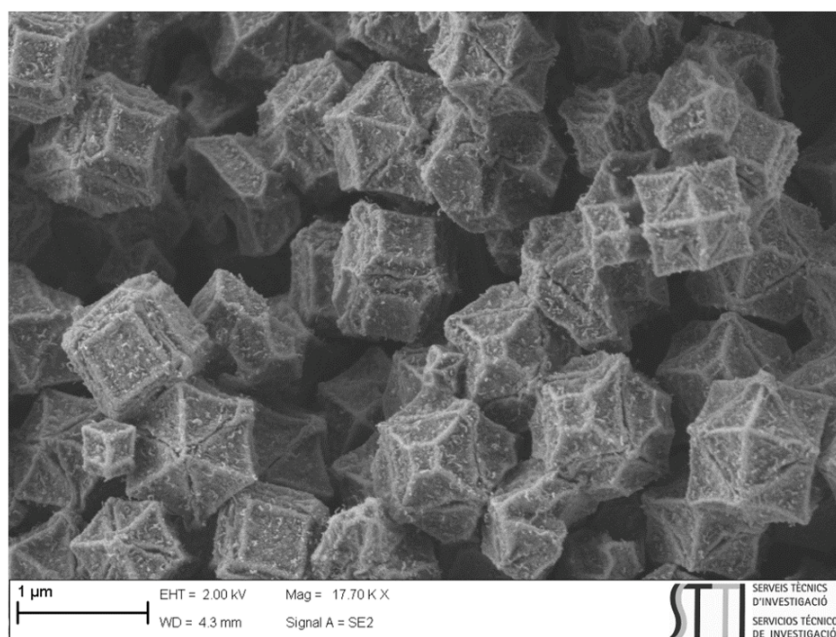


Figure 2. Secondary electron micrograph of ZIF67C_900_1.

The Raman spectrum shows four easily identifiable bands [81] as shown in Figure S4. First of all, highlight the two bands called G and 2D, which indicate that the carbon is not turbostratic but rather graphitic, as the intensity of the G band is much higher than that of the carbon. The 2D band indicates that there are stacks of more than 10 layers. The presence of the D band, also called the defects, is indicative that the graphene sheets have a considerable number of defects, and that there are areas where the carbon is not perfectly ordered.

Figure S5 shows the magnetic susceptibility of the studied ZIF67C_900_1 material at 300 K in a magnetic field that ranges from -30 to 30 kOe. At the magnetization curve it is possible to observe a sigmoid shape that passes approximately through the origin having an extremely narrow hysteresis loop. In addition, the coercivity field (H_C) and residual magnetization (M_R) values are significantly small while saturation magnetization (M_s) is relatively high, the values are 200 kOe, 3.91 emu g^{-1} , and 15.34 emu g^{-1} , respectively, showing a ferromagnetic behavior [82].

To investigate the surface charges of the ZIF67C_900_1 in the same matrix sample performed the MDSPE procedure, their zeta potentials were measured at different sample pH. The zeta potential of ZIF67C_900_1 as function of the sample pH of the suspension is given in Figure S6. In the suspension with an initial pH of 4.0 the zeta potential was 20.3 mV. As can be seen it continuously decreases when the pH is increased up to a pH value of 7.0 , where the zeta potential is stabilized; the isoelectric point of the magnetic material is 5.0 . Therefore, the surface of the magnetic material is positively charged at pH values below the isoelectric point and negatively charged above this point. The negative charge surface of the magnetic sorbent is of great importance, since it affects the extraction process of positively charged metals. For that reason, the optimum pH value was 7.6 (Section 3.2) where the charge was negative (i.e., the material was deprotonated), increasing the interactions with metals and, thus, increasing the extraction efficiency.

3.2. MDSPE Multivariate Optimization

Since MDSPE is affected by many experimental variables, it is necessary to optimize the entire extraction process. Many experiments would have been necessary to optimize all experimental variables if they had been done through univariate optimization, increasing the consumption of sample, reagents, energy and time. To overcome this fact, multivariate optimization has recently emerged as an alternative to univariate optimization, since the

number of experiments was significantly reduced. For that reason, a multivariate optimization design has been employed in order to obtain the optimal experimental conditions, considering the simultaneous determination of all analytes. The optimization process was carried out using a Plackett–Burman design as a screening approach to distinguish between significant and non-significant factors, followed by a central composite design (CCD) in order to obtain the optimal values of the significant factors. To perform the MDSPE optimization experiments a standard of $500 \mu\text{g L}^{-1}$ containing the elements was used. Then, the analytical signals obtained measuring with ICP OES were individually used as response function for optimization. In this way, individual optimum conditions were obtained for each analyte. In order to obtain a global optimum condition for all the analytes, a desirability function was employed to extract all the analytes with the best conditions.

3.2.1. Screening Study

The eleven factors that affect the MDSPE were selected based on previous experience and experiments carried out by our research group. The factors evaluated in the Plackett–Burman design were the following: (i) sample weight, (ii) sample pH, (iii) amount of sorbent, (iv) dispersion mode, (v) complexing agent concentration, (vi) ionic concentration, (vii) eluent, (viii) eluent concentration, (ix) eluent volume, (x) extraction time, and (xi) elution time. The positive and negative levels of each factor are shown in Table S2. A matrix of twelve experiments was constructed and randomly performed in order to obtain the analytical signals.

Once the obtained signals were used in the Plackett–Burman design, Pareto charts were constructed, showing the significant and non-significant factors (Figure S7). The length of each bar in these Pareto charts is related to the relative importance of that factor in the MDSPE approach. Furthermore, the bars to the right show a positive effect in the response, when the value of the factor is increased from the lower to the upper level. On the other hand, the bars to the left indicate a negative effect. Additionally, the bars that surpass reference vertical lines (dashed lines) are 95% likely to be significant [83].

Regarding the results in Figure S7, it can be seen that only the eluent (i.e., HCl), the dispersion mode (i.e., vortex), the sample pH, and the eluent volume significantly affect the metal extraction procedure for the majority of the analytes that were evaluated. In addition, MDSPE is favored with the positive effects of the sample weight (10 g), the amount of sorbent (10 mg), and the extraction and elution time (3 min). On the other hand, it is favored with the negative effect of the complexing agent concentration (0.5%), the ionic concentration (0%), and the eluent concentration (0.5 M). Among the four factors that significantly affect the MDSPE, two of them are binary (i.e., dispersion mode and eluent) and the others are continuous (i.e., sample pH and eluent volume). Therefore, the binary and the non-significant factors have been directly fixed at the most favorable levels for the central composite design.

3.2.2. Central Composite Design (CCD)

Once the significant parameters affecting the MDSPE were determined, a central composite design (CCD) was formulated to obtain the optimum sample pH and eluent volume for each element. In this design, there were five levels (Table S3). The response surfaces obtained are shown in Figure S8 and the optimum conditions for each element are shown in Table S4.

3.2.3. Desirability Function

Due to the different results obtained in the sample for the optimum pH and eluent volume for each element, it is necessary to find the same optimum conditions for all the analytes evaluated. For that reason, the desirability function was employed to obtain a common set of optimum extraction conditions to facilitate the experimental procedure. Figure 3 shows the optimum values of sample pH and eluent volume for all the elements by applying the desirability function. In the graphics obtained using this function, the closest

result to a value of 1 is the best fit for all the elements. Therefore, once the desirability function was applied, the obtained optimized conditions for simultaneous extraction of all evaluated metals were the ones shown in Table S5. It was possible to observe that the optimum pH value obtained (i.e., 7.6) was above the isoelectric point (i.e., pH = 5), as predicted in Section 3.1. This was due to the fact that, above the isoelectric point, the material was negatively charged; this affects the extraction process by increasing the affinity for metals (i.e., positively charged).

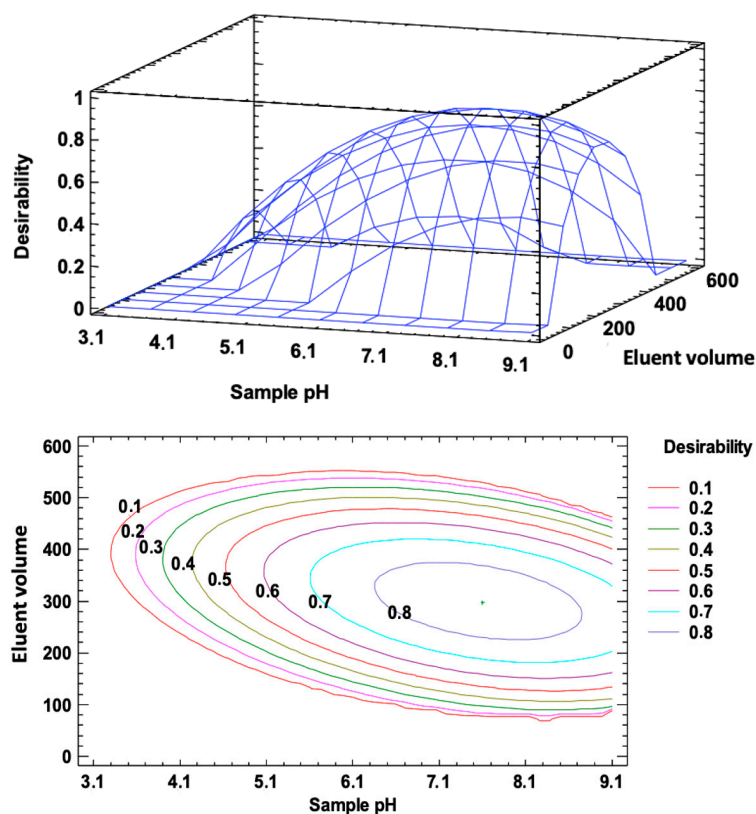


Figure 3. Graphics with obtained optimum results of sample pH and eluent volume applying the desirability function. Experimental fixed conditions: (i) sample weight, 10 g; (ii) amount of sorbent, 10 mg; (iii) dispersion mode, vortex; (iv) complexing agent concentration, 0.5%; (v) ionic concentration, 0%; (vi) eluent, HCl; (vii) eluent concentration, 0.5 M; (viii) extraction time, 3 min; (ix) elution time, 3 min.

3.3. Sorbent Reutilization Study

The possibility of reusing the sorbent was also studied. To that end, five consecutive extractions were carried out in triplicate, employing the same MDSPE procedure; then, the magnetic sorbent was washed three times with 1 mL of ultrapure water. Finally, the magnetic composite was dried at 130 °C for 1 h after each extraction process in order to eliminate the excess water. The experiments were performed using a standard of 5 $\mu\text{g L}^{-1}$. As shown in Figure 4, the signal intensity decreases after each extraction, which may be due to the corrosive nature of the acid used in the elution process and the washing out of the functional groups. In addition, the phase separation using the magnet took longer time after each extraction. For these reasons, the material cannot be used more than once. Nonetheless, the synthesis of ZIF67C_900_1 is very simple and inexpensive. Thus, the disadvantage of not being able to reuse the material is not a limiting factor in carrying out the developed method. In addition, new synthesis routes are currently being investigated in our laboratory to provide a reusable material with the same extraction efficiency.

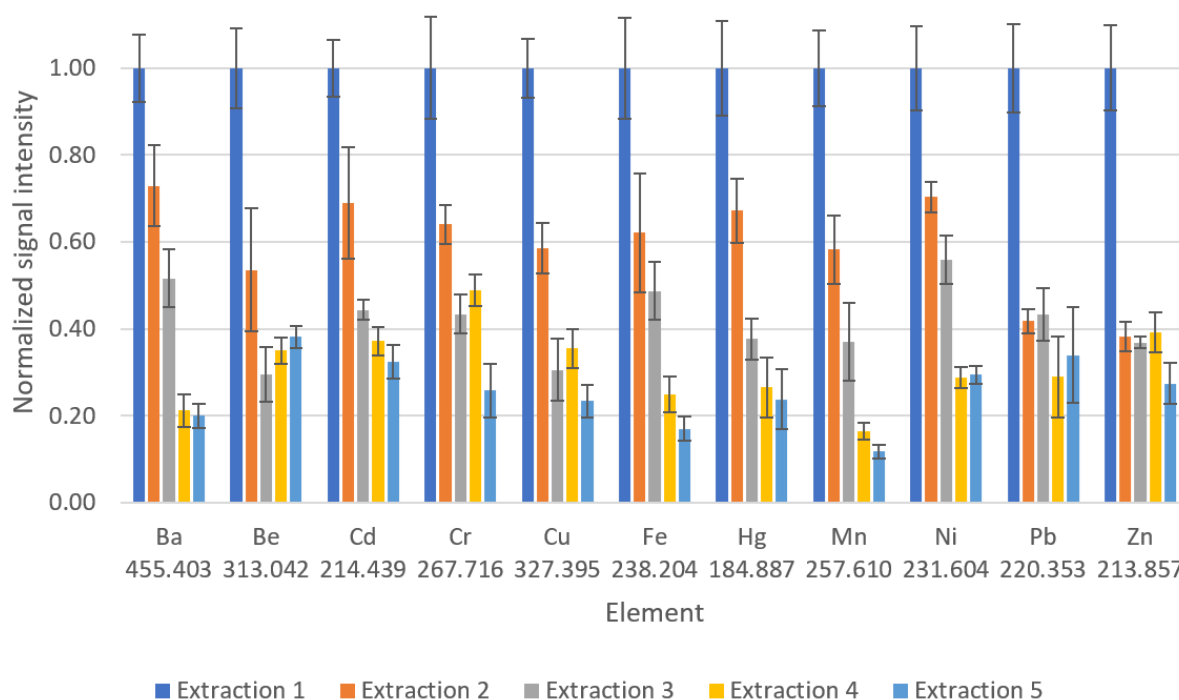


Figure 4. Study of sorbent reusability using the same sorbent in five consecutive extractions of $5 \mu\text{g L}^{-1}$ standard solution. The sorbent was washed three times with 1 mL of ultrapure water and heated at 130° for 1 h; it was dried between each extraction. The error bars were evaluated through the standard deviation of three replicates. Experimental conditions used: (i) sample weight, 10 g; (ii) sample pH, 7.6; (iii) amount of sorbent, 10 mg; (iv) dispersion mode, vortex; (v) complexing agent concentration, 0.5%; (vi) ionic concentration, 0%; (vii) eluent, HCl; (viii) eluent concentration, 0.5 M; (ix) eluent volume, $300 \mu\text{L}$; (x) extraction time, 3 min; (xi) elution time, 3 min.

3.4. Method Validation

All the analytical figures of merit of the proposed method (Table 1) were assessed under optimum conditions, as shown in Table S5. For the purposes of comparison, the proposed method (i.e., MDSPE-ICP OES) was contrasted with the direct ICP OES analysis (i.e., without the MDSPE procedure). In the case of the proposed method, the calibration curves showed coefficients of determination (R^2) that ranged from 0.993 to 0.9996 (i.e., $N = 7$), demonstrating good linearity. In the direct ICP OES analysis, good linearities were also obtained (i.e., 0.98–0.9994). Five independent measurements of samples spiked at 25 and $300 \mu\text{g L}^{-1}$ of each target element were used to assess the repeatability of the proposed method. The obtained relative standard deviations were between 4 and 8%. The sensitivity was also evaluated for both methods and compared through the enrichment factor. Sensitivities ranged between 0.39 and $877 \text{ cps } \mu\text{g}^{-1} \text{ L}$ in the direct ICP OES analysis. A significant increase in the sensitivity was observed in the proposed method, obtaining values that ranged from 3.03 to $7103 \text{ cps } \mu\text{g}^{-1} \text{ L}$. Finally, in order to compare the sensitivity values, the enrichment factor was calculated using the ratio between the obtained sensitivities with and without the MDSPE procedure; the results of enrichment factors were between 3.2 and 13. These values of the enrichment factor enhanced the significant increase in the sensitivity of the applied extraction method.

Table 1. Analytical figures of merit for direct ICP OES and the MDSPE-ICP OES method, developed for the analysis of water samples.

Direct ICP OES							
Emission Line (nm)	Working Range ($\mu\text{g L}^{-1}$)	R ²	Sensitivity ^a (cps μg^{-1} L)	Repeatability (RSD%)	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	EF
Ba 455.403	250–1000	0.998	534 ± 17	-	2.6	8.8	-
Be 313.042	250–1000	0.998	877 ± 28	-	0.39	1.3	-
Cd 214.439	250–1000	0.998	8.3 ± 0.2	-	1.5	5.0	-
Cr 267.716	250–1000	0.9994	11.37 ± 0.19	-	1.3	4.4	-
Cu 327.395	250–1000	0.998	11.0 ± 0.4	-	1.2	3.9	-
Fe 238.204	250–1000	0.998	9.1 ± 0.2	-	9.8	33	-
Hg 184.887	250–1000	0.9991	2.86 ± 0.06	-	5.1	17	-
Mn 257.610	250–1000	0.996	34.3 ± 1.6	-	0.82	2.7	-
Ni 231.604	250–1000	0.98	1.24 ± 0.12	-	9.9	33	-
Pb 220.353	250–1000	0.98	0.39 ± 0.04	-	21	70	-
Zn 213.857	250–1000	0.992	25.0 ± 1.6	-	0.81	2.7	-

MDSPE-ICP OES ^d								
Emission line (nm)	Working range ($\mu\text{g L}^{-1}$)	R ²	Sensitivity ^a (cps μg^{-1} L)	Repeatability (RSD%) ^b		LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	EF ^c
				25 ($\mu\text{g L}^{-1}$)	300 ($\mu\text{g L}^{-1}$)			
Ba 455.403	0.5–500	0.9991	7103 ± 93	5	5	0.085	0.29	13
Be 313.042	0.5–500	0.997	5638 ± 131	7	6	0.073	0.24	6.4
Cd 214.439	0.5–500	0.993	84 ± 3	6	4	0.12	0.41	10
Cr 267.716	0.5–500	0.998	50.2 ± 1.0	7	6	0.14	0.45	4.4
Cu 327.395	0.5–500	0.998	85.9 ± 1.5	6	6	0.10	0.34	7.8
Fe 238.204	5–500	0.997	64.6 ± 1.8	8	5	1.3	4.3	7.1
Hg 184.887	0.5–500	0.997	33.8 ± 0.8	7	6	0.13	0.43	12
Mn 257.610	0.5–500	0.997	109 ± 3	6	6	0.11	0.37	3.2
Ni 231.604	5–500	0.998	8.23 ± 0.16	7	7	1.1	3.8	6.6
Pb 220.353	5–500	0.9996	3.03 ± 0.03	8	7	1.1	3.8	7.9
Zn 213.857	1–500	0.998	92.2 ± 1.6	8	6	0.22	0.75	3.7

^a Slope of the calibration curve ± standard deviation (N = 7). ^b Repeatability of the method evaluated at two levels through the RSD (n = 5). ^c Enrichment factor (EF): ratio between the slope with and without the MDSPE procedure. ^d Experimental conditions used: (i) sample weight, 10 g; (ii) sample pH, 7.6; (iii) amount of sorbent, 10 mg; (iv) dispersion mode, vortex; (v) complexing agent concentration, 0.5%; (vi) ionic concentration, 0%; (vii) eluent, HCl; (viii) eluent concentration, 0.5 M; (ix) eluent volume, 300 μL ; (x) extraction time, 3 min; (xi) elution time, 3 min.

Limits of detection (LODs) and limits of quantification (LOQs) were calculated according to the guidelines established by Eurachem [84], from the value of the standard deviation of 10 measurements of the blank signal. This value is divided by the sensitivity (i.e., slope of the calibration line) and multiplied by factor k . The k value established by the IUPAC is 3 for the limit of detection and 10 for the limit of quantification. As can be seen, the LOD values were found to be between 0.073 and 0.22 $\mu\text{g L}^{-1}$ for all the analytes except for Fe, Ni, and Pb, with a LODs of 1.3, 1.1 and 1.1 $\mu\text{g L}^{-1}$, respectively. The limits of detection obtained in direct ICP OES analysis ranged from 0.39 to 21 $\mu\text{g L}^{-1}$. In other words, the LOD values obtained performing the MDSPE procedure were 14 times lower on average in comparison with those obtained through direct ICP OES analysis. In addition, the LOD values obtained with the developed method are on average 17 times lower than those established in the official method of the Environmental Protection Agency (EPA) (i.e., method 200.7). Finally, a certified reference material (ERM-CA713) was analyzed using the optimal conditions of the developed method in order to evaluate the method validation. The certified reference material analysis obtained recovery values between 90 and 109%; these results demonstrate the reliability of the method which was developed for the analysis of trace metals in wastewater samples. Table 2 shows the results of the certified reference material analysis.

Table 2. Results of certified reference material analysis ^a.

Analyte	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb
Certified value ($\mu\text{g L}^{-1}$) ^b	5.09 ± 0.20	20.9 ± 1.3	101 ± 7	445 ± 27	1.84 ± 0.11	95 ± 4	50.3 ± 1.4	49.7 ± 1.7
Found value ($\mu\text{g L}^{-1}$) ^c	4.8 ± 0.4	21.6 ± 1.3	94 ± 8	424 ± 33	1.66 ± 0.14	90 ± 2	55 ± 3	50 ± 4
Recovery (%)	95 ± 8	103 ± 6	93 ± 8	95 ± 7	90 ± 8	95 ± 2	109 ± 5	100 ± 7

^a Experimental conditions used: (i) sample weight, 10 g; (ii) sample pH, 7.6; (iii) amount of sorbent, 10 mg; (iv) dispersion mode, vortex; (v) complexing agent concentration, 0.5%; (vi) ionic concentration, 0%; (vii) eluent, HCl; (viii) eluent concentration, 0.5 M; (ix) eluent volume, 300 μL ; (x) extraction time, 3 min; (xi) elution time, 3 min. ^b Certified value ± expanded uncertainty. ^c Found value ± expanded uncertainty (coverage factor of 2).

3.5. Method Applicability

Real wastewater sample was analyzed and recovery studies were carried out to assess the applicability of the proposed method. Real sample was spiked at two different levels (i.e., 5.05 and 25.4 $\mu\text{g L}^{-1}$) and analyzed in triplicate. All the measurements of the real sample were performed under optimal conditions. As can be seen in Table 3, the results show recovery values ranging between 94 and 108%, with standard deviations from 2 to 8% demonstrating that the developed method is valid for applications in performing analyses of real wastewater samples.

Table 3. Results of recovery study on spiked real sample ^a.

		Analyte										
Added Value ($\mu\text{g L}^{-1}$)		Ba	Be	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Found value ($\mu\text{g L}^{-1}$) ^b	-	<LOQ	<LOQ	<LOQ	308.4 ± 0.5	53.6 ± 1.0	62.6 ± 1.3	1.27 ± 0.05	2.41 ± 0.02	<LOQ	<LOQ	108.4 ± 1.4
	5.05	5.4 ± 0.2 (106 ± 4)	5.2 ± 0.2 (101 ± 6)	5.02 ± 0.16 (99 ± 3)	313.8 ± 0.4 (108 ± 8)	58.4 ± 0.3 (95 ± 6)	67.6 ± 0.2 (98 ± 4)	6.1 ± 0.2 (94 ± 3)	7.2 ± 0.2 (94 ± 5)	5.2 ± 0.2 (103 ± 4)	5.2 ± 0.2 (103 ± 4)	113.4 ± 0.3 (98 ± 6)
	25.4	26.1 ± 1.1 (102 ± 5)	24.0 ± 0.9 (94 ± 3)	24.0 ± 0.8 (94 ± 4)	334.2 ± 1.4 (101 ± 5)	79.6 ± 1.9 (102 ± 6)	88.8 ± 0.7 (103 ± 3)	27.0 ± 1.4 (100 ± 7)	26.5 ± 0.8 (95 ± 3)	27.2 ± 0.7 (107 ± 2)	27.2 ± 1.3 (107 ± 4)	133.4 ± 0.8 (98 ± 4)

^a Experimental conditions used: (i) sample weight, 10 g; (ii) sample pH, 7.6; (iii) amount of sorbent, 10 mg; (iv) dispersion mode, vortex; (v) complexing agent concentration, 0.5%; (vi) ionic concentration, 0%; (vii) eluent, HCl; (viii) eluent concentration, 0.5 M; (ix) eluent volume, 300 μL ; (x) extraction time, 3 min; (xi) elution time, 3 min. ^b Found value \pm standard deviation. Recovery (%) \pm standard deviation is shown in parentheses.

3.6. Comparison with Other Methods

A comparison between this work and previously described procedures that combined different SPE techniques and spectrochemical detection methods for the determination of trace metals in water and environmental samples is shown in Table S6. As can be seen, the developed method has the shortest extraction time (i.e., 3 min) and the lowest sorbent and sample amounts (i.e., 10 mg and 10 g, respectively) compared with previous studies. This is a great advantage according to the second (i.e., minimal sample size and minimal number of samples are goals), fifth (i.e., automated and miniaturized methods should be selected), and ninth (i.e., the use of energy should be minimized) principles of Green Analytical Chemistry (GAC) [85]. In addition, the developed method in this work has been evaluated for use with a higher number of analytes compared with the rest of the experimental studies; this is in accordance with the eighth principle of GAC (i.e., multi-analyte or multi-parameter methods are preferred versus methods using one analyte at a time). In some cases, the differences are outstanding: for example, in the method developed by Dogru et al. [1], a duration of at least 85 min was needed in order to prepare the column and perform the solid-phase extraction. In addition, the sorbent amount required in the proposed method was found to be between 2 and 25 times lower than other methods presented in the literature (Table S6), reducing the consumption of reagents and the cost of the MDSPE procedure. On the other hand, this work provides LOD values (i.e., 0.073–0.22 $\mu\text{g L}^{-1}$) that are lower or comparable with previous ICP OES-based studies; except for Fe, Ni, and Pb, where the limits of detection were 1.3, 1.1, and 1.1 $\mu\text{g L}^{-1}$, respectively.

4. Conclusions

The developed MDSPE-ICP OES method has been successfully applied for the pre-concentration, separation, and determination of trace metals (i.e., Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) in wastewater samples. The proposed sorbent is a new carbon material that contains magnetic cobalt; it was prepared using controlled pyrolysis of a ZIF-67. This magnetic material combines the excellent extraction properties of zeolites with the simple handling of the magnetic sorbent in the presence of an external magnetic field. Using this method, high enrichment factors (i.e., between 3.2 and 13) and lower limits of detection and quantification have been obtained compared with those obtained by direct ICP OES analysis. The limits of detection obtained in the developed method range from 0.073 to 1.1 $\mu\text{g L}^{-1}$; these values are, on average, 17 times lower than the values established in the official method of the Environmental Protection Agency (i.e., method 200.7). In addition, the MDSPE-ICP OES has been validated through the analysis of a certified reference material; this analysis obtained recovery values ranging from 90 to 109% of the certified value. Furthermore, the applicability of the method was evaluated using recovery experiments at two different spiking levels (i.e., recovery values from 94 to 108%) in a real wastewater sample. The magnetic nature of the sorbent material enables the separation through the application of an external magnetic field; this permits the centrifugation step to be avoided and reduces the consumption of energy and time used in the analysis. In addition, the proposed method has been developed for a high number of elements, and the sample and sorbent amounts required have been reduced compared with previous studies; these difference meet the requirements outlined by the GAC principles and ensure that this method is an ecofriendly option. Moreover, the synthesis of the magnetic sorbent is inexpensive, and can be disposed of after a single use. For all these reasons, the developed method is a fast, reliable, multi-elemental, and ecofriendly alternative to conventional SPE methods for use in the analysis of trace metals in wastewater samples. Furthermore, taking into account all the extraction properties and the low synthesis cost, the developed magnetic material and the new analytical method could comprise a potential option to perform the extraction of analytes in industrial wastewater treatment in comparison with current materials.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/separations10110563/s1>, Figure S1: XRD pattern of ZIF67c_900_1; Figure S2: N₂ adsorption isotherm of the original carbon (i.e., ZIF67c_900) and the washed material ZIF67c_900_1; Figure S3: XPS spectra of cobalt and nitrogen in ZIF67c_900_1; Figure S4: Raman spectrum of ZIF67c_900_1; Figure S5: Magnetization curve of ZIF67c_900_1: (a) representation of the magnetization curve (i.e., X axis from −25,000 to 25,000 Oe); (b) amplified representation of the magnetization curve (i.e., X axis from −2000 to 2000 Oe); Figure S6: Zeta potential of ZIF67c_900_1/DDTC complex as function of the pH value; Figure S7: Pareto charts obtained in the screening study of the factors affecting the MDSPE. Orange means significant effect while blue means non-significant effect on MDSPE; Figure S8: Response surface from CCD for each analyte evaluated; Table S1: Operational parameters employed in Agilent 720 ICP OES; Table S2: Considered experimental factors and levels in the Plackett–Burman design; Table S3: Considered experimental levels in CCD design; Table S4: Optimum sample pH and eluent volume for each determined element; Table S5: Optimum experimental conditions for MDSPE; Table S6: Comparison of analytical figures of merit of the proposed method and other published methods.

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