Magnetic cellulose nanoparticles coated with ionic liquid as a new material for the simple and fast monitoring of emerging pollutants in waters by magnetic solid phase extraction

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ABSTRACT

Magnetic cellulose nanoparticles (MCNPs) coated with 1-butyl-3-methylimidazolium hexafluoro phosphate [C_4MIM][PF_6] ionic liquid (IL) through electrostatic interactions are proposed for the first time as sorbents in a magnetic solid phase extraction (MSPE) method for the determination of paracetamol (PAR), ibuprofen (IBU), naproxen (NAP) and diclofenac (DIC) in natural waters. The parameters that affect adsorption (dispersive solvent, amount of IL, pH and salt content) and desorption (desorption solvent, type of energy and time) were studied. The values that provided the maximum adsorption efficiency and extraction recovery were selected as optimum conditions for adsorption and desorption, respectively. Under the optimum conditions, the adsorption and desorption of all analytes was simultaneous and quantitative. High performance liquid chromatography (HPLC) with ultra violet (UV) and fluorescence (FL) detector was used after the sample preparation. The precision, expressed as relative standard deviation was between 1.4 and 7.6%. Limits of detection and quantification were in the range 3.2–7.2 μg L^{-1} and 11–24 μg L^{-1}, respectively. Moreover, the proposed method provides enrichment factors from 29.0 to 34.2. Recovery studies on 10 mL of spiked tap, river and dam water samples at 50 and 100 μg L^{-1} were carried out. The extraction recoveries were from 85 to 116%, and were in a comparable range regardless of the type of water. The method is simple, rapid, and environmentally friendly.

1. Introduction

The growing use of pharmaceutical products in general has turned into an environmental problem. They can enter the environment during their manufacture, the disposal of unused or expired drugs, and through human and animal excretions [1,2]. Analgesic and nonsteroidal anti-inflammatory drugs (NSAIDs) are the most commonly used group of drugs around the world [3] and that is why their load in the water bodies is high. The elimination of these pharmaceutical compounds during wastewater treatment processes is rather low and as a result, they have been found in surface, ground and drinking waters at levels from ng L^{-1} to μg L^{-1} [4,5]. Although these levels are low to pose an acute risk for humans, other receptors in non-target organisms, like aquatic organisms, might be sensitive to individual pharmaceutical residues, or their mixtures [6].

Because of the low levels of analgesic and NSAIDs and the intrinsic complexity of the water samples, sample preparation is required in the analytical methods so as to provide adequate selectivity and sensitivity. Solid phase extraction (SPE) has been traditionally used prior to chromatographic separation with satisfactory analytical figures, but it is time consuming and can be relatively expensive [7].

In recent years, material science and nanotechnology have provided new tools that avoid these setbacks. This is the case of magnetic nanoparticles (MNPs), which can be used in magnetic solid phase extraction (MSPE) [8]. This evolution of SPE is based on the use of magnetic or magnetizable adsorbents, which can be readily isolated from sample matrix with an external magnet. Thus, the overall method is quite simple because it does not require centrifugation or filtration to separate the magnetic material from the sample once extraction has been accomplished. Among the magnetic materials available, the use of magnetic cellulose nanoparticles (MCNPs) holds great promise in MSPE because they exhibit negative charge on the surface, which gives way to electrostatic interactions and could make the functionalization easy and rapid. An additional advantage of MCNPs is that the raw material, cellulose, is the most abundant renewable polymer, it is non-toxic and exhibits favourable biodegradability [9]. MCNPs have been used for the adsorption of inorganic [10] and organic analytes [11,12].

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The specific functionalization of the MNPs is necessary to increase the selectivity and affinity of the analytes [13]. Among the currently available coating materials, ionic liquids (ILs) are promising options. They have unique properties, such as low volatility, good chemical and thermal stability, and solubility in both organic and inorganic solvents. ILs have gained popularity in sample preparations that involve extraction because only tens to hundreds of microliters are necessary and also because they are less toxic, volatile, and contaminating than organic solvents [14]. All this makes them increasingly interesting to enhance extraction efficiency of target analytes.

Up to present, different types of IL-modified MNPs have been used for the extraction and preconcentration of alkylbenzene sulfonates [15], endocrine disrupting compounds [16] and Congo red dye [12], but long and complicated synthesis processes are involved. However, the combination of ILs with MCNP through the amphiphilic characteristics of the ILs and their electrostatic interaction with the magnetic nanomaterial has never been used. This approach would result in a simple and rapid setup of a hybrid sorbent material with very interesting analytical characteristics for extraction and also the advantages of being environmentally friendly.

The aim of this work is to study IL modified MCNPs as a sorbent for MSPE in the determination of some frequently occurring pharmaceuticals in waters, by taking advantage of the electrostatic interaction between MCNPs and the IL 1-butyl-3-methylimidazolium hexafluoro phosphate $[C_4MIM][PF_6]$ in order to save time and improve simplicity.

2. Experimental

2.1. Standards, solvents and reagents

All reagents used were of analytical grade. Ibuprofen (IBU), diclofenac (DIC), naproxen (NAP), and paracetamol (PAR) were obtained from Sigma-Aldrich (St. Louis, USA). Stock standard solutions of all analytes were prepared in methanol (MeOH) at a concentration of 100 mg L^{-1} and stored at 4 °C. Working solutions of 10 mg L^{-1} of all analytes were prepared daily by appropriate dilution of the corresponding stock solution with ultrapure water (18.2 MΩ cm at 25 °C).

LC-MS grade water, MeOH, acetonitrile (MeCN), hydrochloric acid (HCl), phosphoric acid (H_3PO_4), sodium dihydrogen phosphate (NaH_2PO_4), sodium hydroxide (NaOH), acetone and isopropanol were purchased from Scharlab (Barcelona, Spain). Ferric chloride ($FeCl_3 \cdot 6H_2O$), ferrous chloride ($FeCl_2 \cdot 4H_2O$), 1-butyl-3-methylimidazolium hexafluoro phosphate $[C_4MIM][PF_6]$ (≥97%) and cellulose microcrystalline (~50 μm particle size) were purchased from Sigma-Aldrich (St. Louis, USA).

2.2. Instruments

An Agilent 1200 SL HPLC system (Agilent Technologies, Wilmington, DE, USA) was used. The HPLC equipment included a binary pump, a thermostated column compartment, a UV–Visible and a FL detector. The analytical column employed was a reversed-phase C_{18} of 125 × 4.6 mm I.D. and 5 μm particle size (Agilent). The mobile phase was filtered using a vacuum filtration system through 0.2 μm polyamide membrane filters (Sartorius Stedim Biotech GmbH, Göttingen, Germany). Gradient separation was carried out using water (containing 0.1% acetic acid, v/v) and MeCN, as A and B solvents, respectively. The gradient program started as: 20% of B, constant for 0 min, then increased to 100% at t = 4 min, kept constant for 8 min. The flow rate was 1 mL min^{-1} and the injection volume was 10 μL. Data analysis was carried out using Agilent Chemstation software (Agilent Technologies). DIC, NAP and PAR were monitored and quantified at their wavelengths of maximum absorption, 275, 227 and 243 nm respectively. IBU was determined using a FL detector set at 220 and 290 nm as excitation and emission wavelengths, respectively.

A NdFeB magnet (Eclipse Magnetics Ltd., UK), a Crison 2001 pH-meter and a Selecta ultrasonic bath were used throughout the work.

2.3. Synthesis of IL-MCNPs

MCNPs were synthesized as reported elsewhere [17] with some slight modifications. Briefly, 20 mg of microcrystalline cellulose were swelled for 15 min in 200 mL of aqueous solutions of $FeSO_4$ and $CoCl_2$ with a molar ratio of [Fe]/[Co] = 2. The system was heated to 90 °C for 3 h to transform soluble iron/cobalt hydroxides into insoluble iron/cobalt oxyhydroxide complex. The nanocellulose network was then transferred into 200 mL of a 1.32 mol/L NaOH solution with KNO_3 ($[Fe^{2+}]/[NO_3^-] = 0.44$) at 90 °C for 8 h. The MCNPs were then washed thoroughly, immersed in liquid nitrogen and freeze dried to generate the ferromagnetic aerogel nanocomposites. The modification of MCNPs with IL was as follows. 50 mg of MCNPs were washed with 1 mL of ultrapure water three times and then with 1 mL of MeCN two times for activation. After that, 150 μL mixture of $[C_4MIM][PF_6]$ (50 μL) and MeOH (100 μL) were added to 50 mg of activated MCNPs in a 15 mL vial. The mixture was vortexed at room temperature for 5 min in order to form a homogenous dispersion of IL coated MCNPs.

2.4. Sample preparation

The sample preparation is depicted in Fig. 1. 10 mL of sample and 1 mL of 0.5 M of phosphoric acid (pH 1.5) were added to the vial containing the IL-MCNPs as described in Section 2.3, vortexed for 5 min and allowed to stand for 2 min. The IL-MCNPs were separated from the solution by an external magnet, and the solution was discarded. The desorption of the analytes was carried out in 250 μL of 0.5 M phosphate buffer (pH 12) after sonication for 10 min. Finally, the liquid phase was injected into the chromatographic system.

2.5. Optimization of the adsorption and desorption parameters

The optimization of the parameters that affect adsorption and desorption was carried out one by one while maintaining the rest of the conditions. The selected IL was $[C_4MIM][PF_6]$. The interval studied and the selected conditions are listed in Table 1. The optimization of the adsorption and desorption conditions was performed using standards of 10 mg L^{-1} of all analytes in ultrapure water with vortex stirring. All results were obtained from the mean value of three experiments.

Adsorption efficiency (AE), which was selected for monitoring the adsorption process, was calculated as follows:

$$AE = \left(1 - \frac{c_a}{c_0}\right) \times 100$$

where c_a is the concentration of the analyte in the aqueous phase after adsorption and c_0 is the initial concentration.
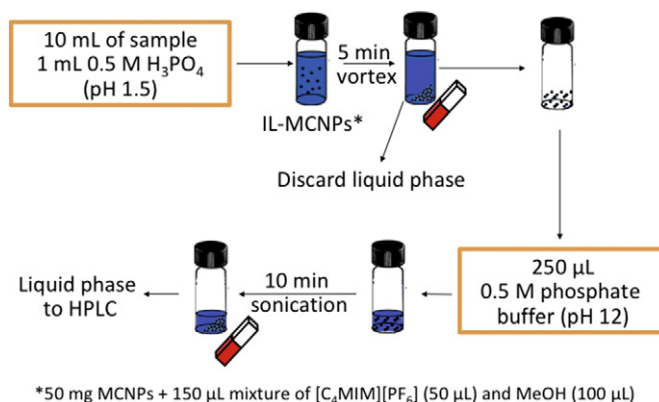

Fig. 1. Scheme of the analytical method.

Table 1
List of the variables studied, interval tested and optimum conditions. IL: [C₄MIM][PF₆].

Variable		Interval	Optimum
Adsorption	Dispersive solvent	MeCN, MeOH	MeOH
	Volume of dispersive solvent (μL)	100–1000	100
	Volume of IL (μL)	0–100	50
	pH	1.5, 2.5, 7.0	1.5
	NaCl (g L⁻¹)	0–20	0
	Vortex time (min)	0–10	5
	Sample volume (mL)	5–20	10
	Amount of MCNP (mg)	20–100	50
Desorption	Solvent	MeCN, MeOH, NaOH, buffer[a]	Buffer[a]
	Volume of solvent (mL)	0.25–5	0.25
	Type of energy	Vortex, sonication	Sonication
	Time (min)	5–20	10

[a] Phosphate buffer 0.5 M at pH 12.

Extraction recovery (ER) was calculated as the percentage of total amount of analyte which was desorbed, following this equation:

$$ER = \frac{c_f \times V_f}{c_0 \times V_0} \times 100$$

where c_f and c_0 are the concentration of the analyte in the extract after desorption and the initial concentration in the sample, respectively. The same applies to the volumes V_f and V_0.

2.6. Water samples

Tap water was sampled from our lab after allowing for 10 min to flow. Dam and river waters were obtained from Toledo province (Spain). In all cases, the sampling bottle was rinsed three times with water before it was filled up. The concentration of all the analytes was below the LODs in all samples. Then, two independent aliquots of each sample were spiked at 50 μg L⁻¹ and other two at 100 μg L⁻¹, and each aliquot was analysed by duplicate with the optimized MSPE procedure (Section 2.4).

2.7. Quality control

Student's "t" test was used for the assessment of the intercepts of the calibration curves. Procedural blanks consisting of ultrapure water were submitted to the analytical methodology for quality control purposes at the same time and with the same sorbent as samples in all experiments.

3. Results and discussion

3.1. Adsorption

The pKₐ values of IBU, DIC and NAP are about 4.2 and that of PAR is 9.5, so the analytes should be uncharged below pH 4.2. ILs are amphiphilic molecules with a somehow unpredictable behaviour towards analytes of different polarity [18]. Thus, adsorption was evaluated at pH 1.5 and 7.0. The results showed that AE at pH 1.5 were significantly
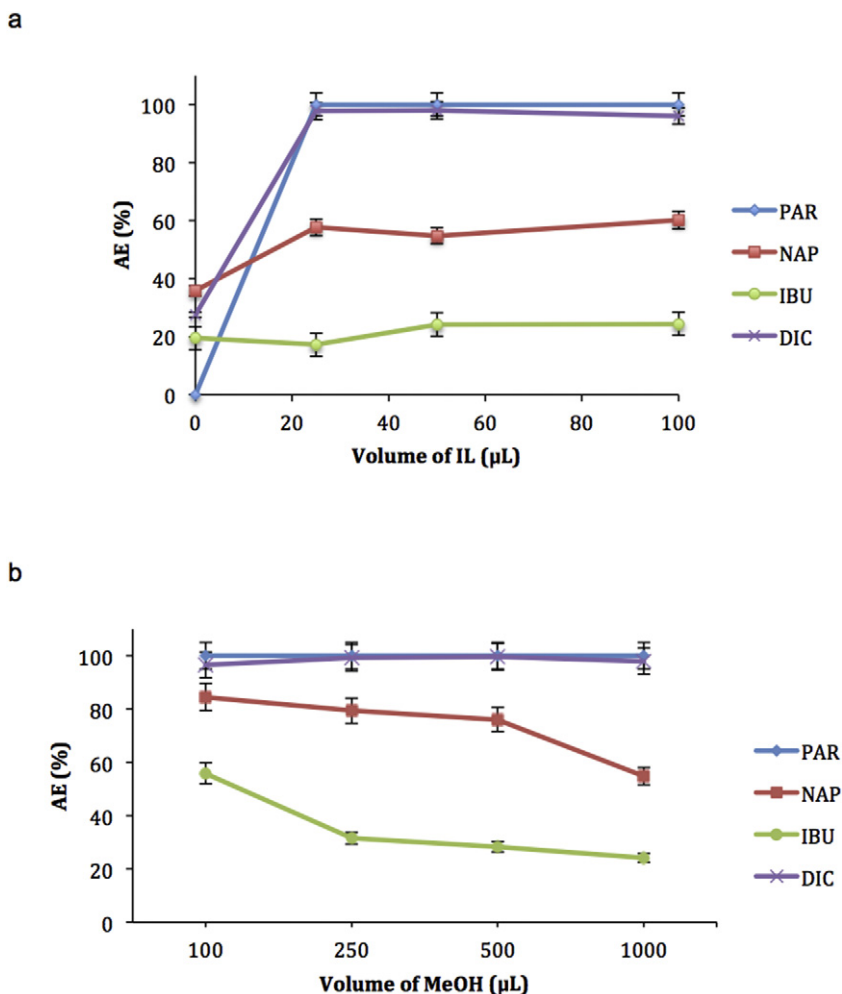

Fig. 2. Influence of the (a) volume of IL [C₄MIM][PF₆] and (b) volume of MeOH on IL-MCNP adsorption efficiency of a standard solution of PAR, NAP, IBU and DIC at 10 mg L⁻¹. Standard deviations are plotted as error bars.
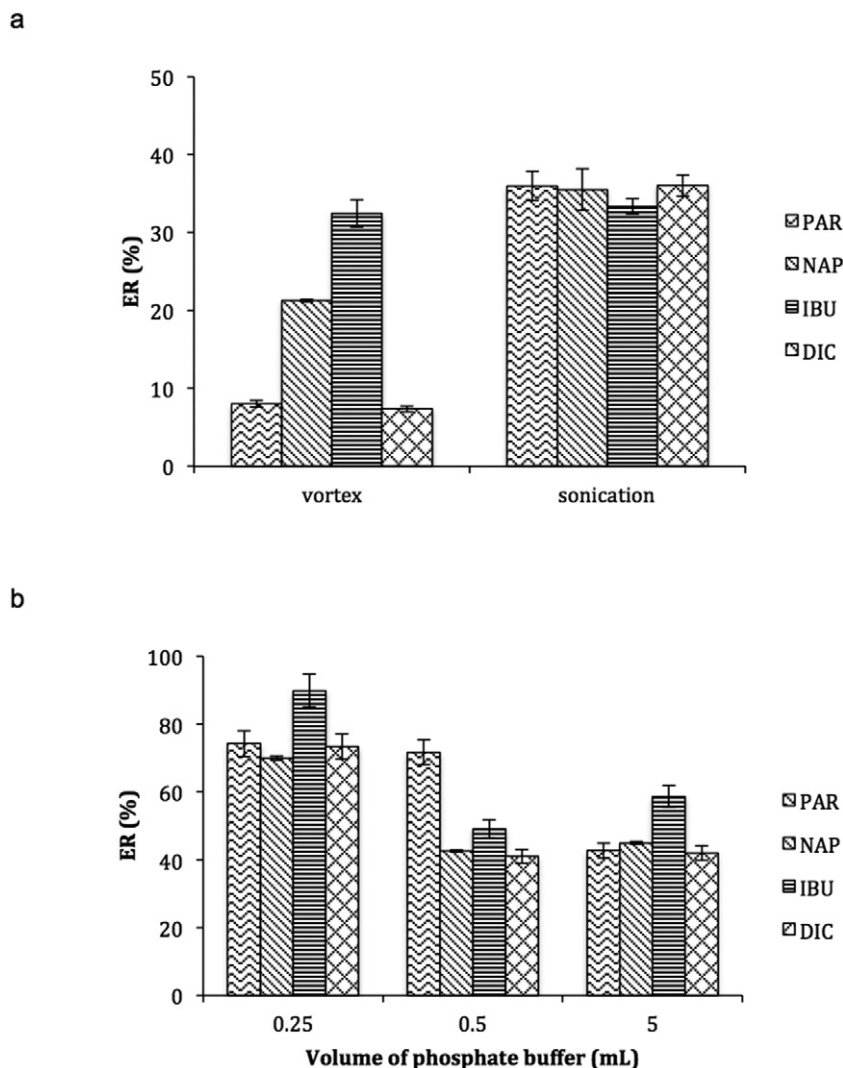
a

b

Fig. 3. Influence of (a) type of energy (5 min in 0.5 M phosphate buffer at pH 12) and (b) volume of 0.5 M phosphate buffer (pH 12) desorption solution (10 min sonication) on extraction recovery of a standard solution of PAR, NAP, IBU and DIC at 10 mg L^{-1}. Standard deviations are plotted as error bars.

higher than at 7.0, which means that [C$_4$MIM][PF$_6$] interacts best with the uncharged species of the analytes. Therefore, pH 1.5 was selected as suitable.

Interactions of the IL with the analytes are known to increase when a solvent helps IL disperse in the aqueous solution. Methanol and MeCN were tested as dispersive solvents with similar results but MeOH was used throughout the work.

The modification of MCNPs with IL did not affect greatly the adsorption of IBU or NAP, as shown in Fig. 2a. On contrary, a sharp increase in the adsorption of DIC and PAR was found. In this last case, the adsorption only took place in IL modified MCNPs. The maximum AE of PAR and DIC (~100%) was at 25 μL and remained constant beyond this point. However, 50 μL of IL was selected as suitable volume to be within a reasonable safety margin.

In the study of the influence of the volume of MeOH on the adsorption, the results showed that the maximum AE occurred with 100 μL of MeOH and that the adsorption decreased with larger volumes for NAP and IBU (Fig. 2b).

In general, the addition of salt reduces the solubility of the analytes in the aqueous sample and enhances the extraction of neutral species in organic solvents. However, the opposite effect can also occur when an IL is used as extractant solvent [19]. In this work, the effect of ionic strength on AE was evaluated by increasing the concentration of NaCl in the aqueous phase from 0 to 20 g L^{-1} with the result that AE decreased as the concentration of NaCl increased. Consequently, it was decided not to add NaCl.

Also the effect of the vortex time was studied from 0 to 10 min. The adsorption of PAR and DIC increased sharply up to 1 min and then the increase was mild for longer times. As for NAP and IBU, the AE increased up to 5 min and then decreased with longer time. Consequently, a vortex time of 5 min was selected.
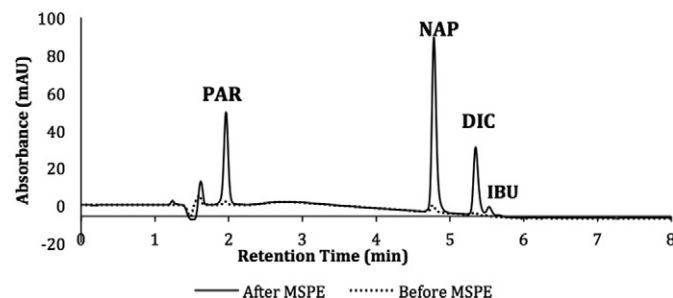

Fig. 4. Chromatogram of a standard solution of PAR, NAP, IBU and DIC at 500 μg L^{-1} before and after the MSPE process with IL-MCNP.

Table 2
Analytical figures of merit.

	LOD ($\mu g\ L^{-1}$)	LOQ ($\mu g\ L^{-1}$)	R^2	RSD (%)[a]
IBU	4.3	15	0.9997	5.3/3.5
DIC	3.2	11	0.9997	7.6/6.2
NAP	7.2	24	0.9985	1.4/4.9
PAR	5.8	19	0.9986	7.0/7.1

[a] Values for standards of 50 and 100 $\mu g\ L^{-1}$, respectively.

Finally, the amount of MCNP and the initial volume of sample were studied. AE increased sharply with the amount of MCNP from 20 to 50 mg and beyond this point, up to 100 mg, it remained constant for DIC and PAR and decreased moderately for IBU and NAP. Consequently, 50 mg was the selected amount of MCNP. As for initial volume, it was studied for 5, 10 and 20 mL and the maximum AE was for 10 mL.

3.2. Desorption

The main feature for desorption is to provide the maximum ER. Methanol and MeCN were initially tested as they are commonly used for this purpose. However, the analytes could not be desorbed. Then, NaOH and phosphate buffer solutions, both at pH 12, were also tested because at this pH, the analytes are anionic compounds, which would increase solubility in the desorption phase. The analytes were only desorbed in 5 mL of 0.5 M phosphate buffer (pH = 12) after vortexing for 5 min, but the ER were variable and below 10% for PAR and DIC (Fig. 3a).

In order to increase ER, sonication was evaluated for desorption. As shown in Fig. 3a, the use of 5 min sonication instead of vortex increased the ER of the analytes uniformly (33–36%). Then, the sonication time was studied from 5 up to 20 min. The best extraction recoveries (42–59%) were obtained for 10 min.

Another key feature is the desorption volume, which should be the lowest possible to allow the highest preconcentration factor (PF), which is the ratio of the initial to the final volume. As shown in Fig. 3b, the ER increased as the final volume was reduced. The minimum volume that can be handled comfortably was 250 μL and so it was selected. Since the initial volume of sample was set at 10 mL and the final volume was 250 μL, the analytes could ideally be concentrated 40 times. A chromatogram of a standard of 500 $\mu g\ L^{-1}$ is shown in Fig. 4 and compared with the same standard after being submitted to the optimized MSPE process.

3.3. Analytical figures of merit

The present method was characterized in terms of sensitivity, linearity and precision. The limits of detection (LOD) were calculated from a chromatogram corresponding to a standard of 50 $\mu g\ L^{-1}$ after the MSPE process. The LODs, which were defined using a signal-to-noise (S/N) ratio of three, are listed in Table 2 and varied from 3.2 $\mu g\ L^{-1}$ (DIC) to 7.2 $\mu g\ L^{-1}$ (NAP). The calibration graphs were constructed for each analyte using aqueous standards between the limit of quantification (LOQ), calculated as the concentration that provides an analytical signal ten times higher than the S/N ratio, and 1000 $\mu g\ L^{-1}$. The

determination coefficients (R^2) were in the range 0.9985–0.9997 for all analytes (Table 2). The intercepts were not statistically different from zero, according to the Student's "*t*" test. The precision of the method was studied by duplicate injection of two sets of six standards at two concentrations (50 and 100 $\mu g\ L^{-1}$) after they were submitted to the MSPE method. The relative standard deviations (RSD) varied between 1.4% (NAP) and 7.6% (DIC) for 50 $\mu g\ L^{-1}$, and between 3.5% (IBU) and 7.1% (PAR) for 100 $\mu g\ L^{-1}$. Therefore, the precisions obtained for both levels are adequate and comparable.

The LODs reported in this paper are in the low $\mu g\ L^{-1}$ range, like in other papers about similar compounds in water using IL modified MNPs [16]. Since levels up to 10 and 13.8 $\mu g\ L^{-1}$ of IBU in surface water and wastewater effluents, respectively, have been reported [20], these LODs are suitable. As for precision, in similar papers, the reported RSDs have been below 7.96% [15] and 8.3% [16].

3.4. Analysis of water samples

The proposed method was applied to the determination of the analytes in tap, river and dam water samples as explained in Section 2.6. Enrichment factors (EFs) were defined as the ratio of the concentration of the analyte in the extract after desorption to the initial concentration in the sample. Average EFs ($n = 12$) were calculated in spiked aliquots of the river, dam and tap water samples, and were 29.0 (NAP), 29.2 (DIC), 29.3 (PAR), and 34.2 (IBU). The quantification was carried out by means of the calibration curve and the application of the average EFs. As shown in Table 3, the ERs were from 85 to 116%, and were in a comparable range regardless of the type of water. In other works reporting the determination of emerging pollutants in water using IL modified MNPs, recoveries of 86.3–107.5% [15] and >87% [16] were obtained, which are in the same range as the ones obtained in the present study.

Additionally, in order to assess the reusability of the sorbent, two tap water samples spiked at 50 and 100 $\mu g\ L^{-1}$ each, were analysed four times successively with the same sorbent. After each use, the sorbent was washed with 2 × 1 mL of ultrapure water with vortex agitation for 1 min and dried at 80 °C. In both levels, the ERs were over 85% for all analytes in the first two uses. In the third use, the extraction recoveries were over 85% for IBU, DIC and PAR. In the fourth cycle, the ERs were all under 85%.

4. Conclusion

The use of MCNPs modified with [C$_4$MIM][PF$_6$] IL for the determination of emerging pollutants in natural waters offers some advantages over existing MSPE methods. Firstly, the modification of the magnetic material is generated in a simple manner thanks to the electrostatic interaction between MCNPs and the IL, which avoids long anchoring processes that occur in other MNPs. Secondly, the present method provides limits of detection in the low $\mu g\ L^{-1}$ range, adequate EFs, and quantitative recoveries in a short time. MCNPs can be reused twice with quantitative ERs of all analytes. Finally, this approach is environmentally friendly because cellulose is a renewable material, the IL is not toxic, and little volume of organic solvent (100 μL of MeOH) is required.

Table 3
Extraction recovery (ER), expressed as average $\pm$ standard deviation ($n = 4$), in water samples spiked with the analytes at 50 and 100 $\mu g\ L^{-1}$.

	ER (%) at 50 $\mu g\ L^{-1}$			ER (%) at 100 $\mu g\ L^{-1}$		
	Tap	River	Dam	Tap	River	Dam
IBU	116.2 ± 5.0	104.8 ± 3.7	96.6 ± 6.5	112.6 ± 1.0	96.2 ± 3.7	95.5 ± 1.4
DIC	102.9 ± 2.2	94.7 ± 8.5	96.0 ± 2.6	108.7 ± 1.8	92.7 ± 5.4	96.0 ± 7.1
NAP	97.4 ± 3.1	99.2 ± 7.5	95.4 ± 1.5	115.7 ± 1.9	103.2 ± 2.4	95.7 ± 1.0
PAR	92.3 ± 1.7	94.5 ± 9.9	85.7 ± 4.1	107.6 ± 1.3	85.4 ± 3.3	84.7 ± 1.7

Acknowledgments

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