Adsorption
https://doi.org/10.1007/s10450-018-9953-2

Nickel ferrite nanoparticles for removal of polar pharmaceuticals from water samples with multi-purpose features

Valeria Springer[1] · Luisa Barreiros[2] · Marcelo Avena[1] · Marcela A. Segundo[2]

Received: 27 March 2017 / Revised: 1 April 2018 / Accepted: 7 May 2018

Abstract
This paper reports the removal of two widely used pharmaceuticals, namely dipyrone and diclofenac, by magnetic nickel ferrite nanoparticles. A method combining nickel ferrite nanoparticles and high-performance liquid chromatography was applied for the simultaneous monitoring of these polar compounds. The adsorption process of the target compounds on nickel ferrite nanoparticles was performed by using only 800 mg L^{-1} of the adsorbent at pH 5.8. From the experimental adsorption isotherms, maximum adsorption resulted 31.2 mg g^{-1} for dipyrone and 16.8 mg g^{-1} for diclofenac, with dipyrone having a slightly higher affinity for the surface than diclofenac. The presence of dissolved salts in water samples affected the adsorption with removal efficiency remaining between 30–42% for diclofenac and 40–60% for dipyrone. On the other hand, desorption of the drugs was achieved using methanol for diclofenac and ascorbic acid for dipyrone. This research provides the understanding of the adsorption behavior of polar pharmaceuticals on bare nickel ferrite nanoparticles, which promotes the large-scale application of these magnetic nanoparticles to the removal of pharmaceuticals from water samples and their further selective recovery.

Keywords Diclofenac · Dipyrone · Emerging pollutants · Magnetic nanoparticles · Selective desorption

1 Introduction

Nonsteroidal anti-inflammatory drugs (NSAIDs) are widely used for the treatment of fever (antipyretic), pain (analgesic) and inflammation (anti-inflammatory) in human and veterinary medicine due to the blocking of the cyclo-oxygenase enzyme and inhibition of the synthesis of prostanoids (Cashman 1996). Due to their extensive use, some of these substances and their active metabolites have been reported in natural water (surface and groundwater), wastewater treatment plants and, to a minor extent, drinking water (Fernández et al. 2010; Larsson et al. 2014). Although the concentrations of NSAIDs in surface water are relatively low (from ng L^{-1} to mg L^{-1} levels), continuous release and chronic exposure to these substances can produce adverse effects on aquatic life and potential risk to human health (Parolini et al. 2011). For these reasons, their monitoring and control is very important in order to provide safe aquatic environment. Conventional water treatments include biological processes, reverse osmosis, ozonation, advanced oxidation technologies and adsorption processes (World Health Organization 2011; Xiao et al. 2015), including polymeric sorbents or functionalized organic sorbents (Paíga et al. 2015).

In the last years, special attention has been paid on the application of micro- and nanosized adsorbents to remove pollutants from aqueous media. As an example, carbon nanotubes have been applied for adsorption of pharmaceuticals and personal care products in water samples (Ncibi and Sillanpää 2015; Wang et al. 2016). Nevertheless, carbon-based materials are highly hydrophobic and their synthesis and/or surface modification imply high production cost, limiting the large-scale application in water treatments. Another example is constituted by magnetic nanoparticles, which

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10450-018-9953-2) contains supplementary material, which is available to authorized users.

✉ Valeria Springer
valeria.springer@uns.edu.ar

[1] INQUISUR, Departamento de Química, Universidad Nacional del Sur (UNS)-CONICET, Av. Alem 1253, 8000 Bahía Blanca, Argentina

[2] LAQV, REQUIMTE, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, R. Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal

Published online: 11 May 2018

have become increasingly popular because they combine high surface area with magnetic properties, making possible high adsorption yields and easy recovery from the aqueous solution by applying a magnetic field (Zhang et al. 2017). In this regard, nickel ferrite nanoparticles (NFNPs) have been recently applied for removal of some organic and inorganic pollutants from water samples (Ali 2012; Wang et al. 2012; Zhang et al. 2011). This nanomagnetic adsorbent showed important adsorption properties and potential environmental applications. However, it was never used for the simultaneous removal of polar NSAIDs from aqueous solutions.

In this work, the adsorption capacity of NFNPs toward highly polar pharmaceuticals is evaluated. Dipyrone (DIP), a common NSAID that has been banned in some countries due to its potential association with agranulocytosis disease (Hedenmalm and Spigset 2002), and the extensively used diclofenac (DC), assigned as emerging pollutant in EU (Decision (EU) 2015), have been selected as target compounds based on their widespread occurrence in domestic sewage and environment (Ahmad et al. 2016; Dai et al. 2015; Feldmann et al. 2008; Kostopoulou and Nikolaou 2008). In fact, DC has been recently reported in concentrations up to 0.1 mg L^{-1} in surface water and sediments (Agunbiade and Moodley 2016) and DIP at 1.0 mg L^{-1} in effluents (Gómez et al. 2007). To the best of our knowledge, there are no reports where DIP and DC are simultaneously adsorbed onto this type of adsorbent and then selectively desorbed. This research aims to achieve a general approach for the removal of these polar emerging pollutants by employing a low cost and effective nanomagnetic adsorbent.

2 Materials and methods

2.1 Reagents and solutions

All reagents used were of analytical grade with no further purification. Water from Arium water purification system (Sartorius, Goettingen, Germany; resistivity > 18 MΩ cm) was used for the preparation of all solutions. LC grade methanol obtained from Merck (Darmstadt, Germany) and phosphoric acid 85% v/v (Fluka, Buchs, Switzerland) were employed for mobile phase preparation. Stock solutions of DIP and DC (1 g L^{-1}) were separately prepared by dissolving accurately weighed amounts of the solid drug (Sigma Aldrich, St. Louis, MO, USA) in methanol. Working solutions were prepared by appropriate dilution of the stock solutions in mobile phase or water when required. All solutions were stored at 4 °C and filtered through a 0.45 µm filter (Corning, Flintstone, UK) prior to usage. $FeCl_3$ and $NiCl_2$ solutions (0.05 M each) and 0.01 M EDTA ($C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$) solution were prepared by dissolving weighed amounts of the solid compounds (Fluka, Buchs, Switzerland) and used for evaluating the possible interaction of metallic cations with DIP in aqueous solution. Ascorbic acid and potassium persulfate were obtained from Sigma Aldrich and their solutions were prepared in ultrapure water by dissolving the solid compounds. NaOH and HCl solutions (2.0 and 0.1 M, respectively) were used for adjusting the pH of solutions whenever required.

NaCl (2.45 g), $MgCl_2{\cdot}6H_2O$ (1.11 g), Na_2SO_4 (0.40 g), $NaHCO_3$ (0.02 g) and KCl (0.07 g) supplied by Fluka, were weighed to prepare 100 mL of artificial sea water (ASTM Standards D1141 2013), aiming to evaluate the matrix effect arising from ionic strength and co-existing ions on the adsorption process.

The mobile phase for separation of DIP and DC was filtered through a 0.45 µm filter (reversed cellulose, Corning, Flintstone, UK) and degassed using ultrasound radiation for 15 min before use.

2.2 Synthesis and characterization of NFNPs

NFNPs were synthesized by a co-precipitation method at room temperature (Maaz et al. 2009). Briefly, ferric chloride and nickel chloride aqueous solutions were mixed in a 1:2 molar ratio and constantly stirred. Then, a 2.0 M NaOH solution was added dropwise at a flow rate of 1.0 mL min^{-1} to the above solution while monitoring the pH. This co-precipitation reaction was carried out at room temperature (22 °C ± 2 °C) and a brown colored precipitate was obtained at pH level of 10–11. The obtained solid was washed with water until the pH of the slurry became 6 and the conductivity was 272 µS cm^{-1}(Hanna HI 99300 conductimeter, Buenos Aires, Argentina). The wet slurry was dried at 105 °C and then it was grounded in a mortar and subjected to calcination at 600 °C for 5 h.

The structural and morphological characterization of the nanocrystalline powder was performed with a X-ray diffractometer (Philips PW 1710, Cu Kα λ = 1.54059 Å, graphite monochromator operated at 45 kV, 30 mA and 25 °C at a scan rate of 2° θ s^{-1}; Westborough, MA, USA), a transmission electron microscope (JEOL 100 CX II, 100 kV; Tokyo, Japan) and N_2 adsorption isotherms (Quantachrome Nova 1200e instrument, temperature: 77.4 K; Florida, USA), while the magnetic characterization was done with a vibrating sample magnetometer (VSM-7404, magnetic field: 1900 Oe, room temperature; Westerville, OH, USA). The electrophoretic mobility of the obtained NFNPs was measured with a Zetasizer Nano ZS90 instrument (Malvern Instruments Ltd., Worcestershire, UK) at 25 °C and the zeta potential was calculated based on the Smoluchowski equation (Leroy et al. 2011). Stock suspensions of NFNPs (200 mg L^{-1}) in 0.01 M NaCl as supporting electrolyte were used to measure the electrophoretic mobility in the pH range between 2.5 and 9.5.

2.3 Chromatographic determination of DIP and DC

Chromatographic separation was carried out using an analytical HPLC system (Jasco, Easton, USA) comprising: pump (PU-2089), automatic injector (AS-2057), multi-wavelength array detector (MD-2015), LC-Net II/ADC controller and equipped with a monolithic Chromolith RP-18e column (100 mm × 4.6 mm i.d., Merck). The Chrom-Nav® software was used for control and data processing. DIP and DC were detected at 254 and 279 nm, respectively. The optimized separation was carried out using a gradient elution: solvent A (0.1% v/v phosphoric acid: methanol, 90:10) and solvent B (0.1% v/v phosphoric acid: methanol, 30:70) at a flow rate of 0.8 mL min^{-1}. The gradient elution was performed as follows: 0–6.0 min, 100% A; 6.0–8.0 min, 100–0% A; 8.0–20.0 min, 100% B; 20–24 min, 100–0% B; 24–28 min, 100% A. The calibration solutions were prepared in ultrapure water and injection volume was 50 µL. The auto-sampler was operated at 4 °C and the auto-sampler needle was rinsed before and after aspiration of the sample using mobile phase.

2.4 Adsorption experiments

Adsorption batch experiments were carried out in 25 mL polypropylene tubes containing 10 mL of aqueous solution at pH 5.8 ± 0.2. For adsorption isotherms and kinetic experiments, the concentration of NFNPs was set at 800 mg L^{-1} and ionic strength fixed at 0.01 M with NaCl. The process was assisted by ultrasonic irradiation (60 W, 50 Hz). After a given contact time between the particles and DIP or DC, NFNPs were decanted using a Nd magnet and an aliquot from the supernatant was analyzed by high-performance liquid chromatography (HPLC–UV). For adsorption isotherms, the initial concentrations of analytes ranged from 1.0 to 200 mg L^{-1} and measurements were conducted after 24 h. All experiments were performed in duplicate. Additionally, control experiments (without adsorbent) were simultaneously performed in order to verify whether the analytes were stable throughout the experimental time and under the working conditions.

The uptakes of DIP and DC by the NFNPs were calculated as follows:

$$q_{eq} = \frac{V(C_o - C_{eq})}{m} \quad (1)$$

where C_o and C_{eq} (mg L^{-1}) represent the initial concentration and the concentration in the solution at equilibrium, respectively. V (L) is the volume of solution and m (g) is the mass of the adsorbent.

In the same way, the uptake of each analyte at each time, q_t (mg g^{-1}), was calculated using Eq. 2:

$$q_t = \frac{V(C_o - C_t)}{m} \quad (2)$$

where C_t (mg L^{-1}) represents the concentration in the solution at time t (min).

Several substances were tested as DC and DIP desorbing agents, including non-aqueous polar solvents, such as ethanol and methanol, and aqueous solutions of ascorbic acid and sodium persulfate. Desorption studies were performed with 3 mL of desorbing agents and assisted by ultrasonic irradiation for 15 min.

3 Results and discussion

3.1 Physicochemical characterization of NFNPs

Figure 1 shows the results obtained from X-ray diffraction (XRD), transmission electron microscopy (TEM) and magnetic measurements. The XRD pattern corresponded to a pure nickel ferrite with a face centered cubic structure (He et al. 2013). The average crystallite size (D_{311}) was estimated to be 16.6 nm from the Scherrer's formula (Klug and Alexander 1974) and resulted comparable to data reported in the literature for NFNPs obtained by calcination (Shanmugavel et al. 2015). These results were confirmed by TEM micrographs, where polyhedral particles with a size of around 20 nm were observed. The synthesized NFNPs showed satisfactory magnetic properties with a saturation magnetization (Ms, 26 emu g^{-1}) smaller than that of the bulk material (55 emu g^{-1}) and exhibiting ferromagnetic behavior (Goldman 2006).

The isoelectric point (IEP) of the nanomagnetic particles was 6.5, as obtained from electrophoretic mobility versus pH data, in agreement with the IEP reported in the literature (Plaza et al. 2001), whereas surface area and average pore volume were 49 m^2 g^{-1} and 0.33 cm^3 g^{-1}, respectively. Table 1 summarizes the physical characterization of NFNPs.

The results show that the used co-precipitation method allowed obtaining nanomagnetic particles of nickel ferrite with a narrow size distribution, similar to the particles obtained by other co-precipitation methods (Joshi et al. 2014). Their magnetic properties enable their removal from a dispersion using simply a magnet (see below).

3.2 Evaluation of adsorption of DIP and DC on NFNPs

Typical HPLC–UV chromatograms for DIP and DC solutions used for calibration are shown as Supporting Information (Fig. S1). Well-defined chromatographic peaks were obtained for DIP and DC with retention times (Rt) of 4.8 and 16.3 min, respectively. Calibration curves (peak area vs. concentration) were constructed in the range 1.0–10 mg L^{-1} for DIP [Y = 53,404 (± 789)X − 23,845 (± 4211), $R^2 = 0.997$] and DC [Y = 177,000 (± 3689)X − 36,329 (± 20,273),

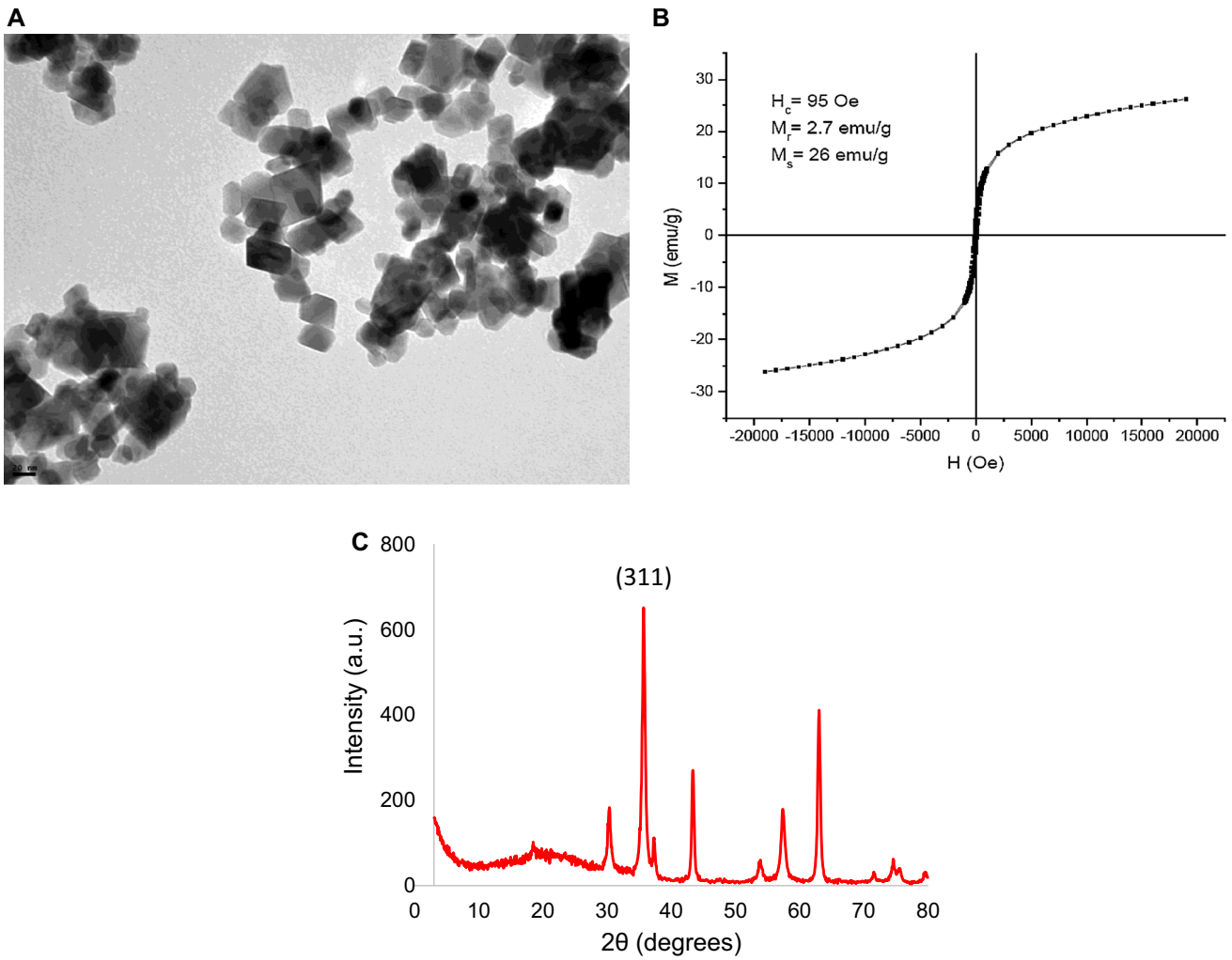

Fig. 1 Physicochemical characterization of the synthesized NFNPs. (**a**) TEM micrograph (×270,000), (**b**) magnetization curve, (**c**) XRD pattern

Table 1 Characterization of NFNPs

Physical characterization	Experimental data	Characterization technique
Specific surface area		
BET surface area (A_{BET})	49.63 m^2 g^{-1}	Nitrogen sorption isotherms
Average pore volume	0.33 cm^3 g^{-1}	
Size		
Average diameter	16.6 nm	X-ray diffraction (XRD)
	20 nm	Transmission electron microscopy (TEM)
Isoelectric point		
pH_{PZC}	6.5	Electrophoretic mobility
Magnetic properties		
Ms	26 (emu g^{-1})	
Mr	2.7 (emu g^{-1})	Vibrating sample magnetometer
Hc	95 (Oe)	

$R^2 = 0.995$]. Limits of detection (LODs), calculated as three times the standard deviation of the regression line/slope (Miller and Miller 2010), were 0.3 and 0.4 mg L^{-1} for DIP and DC, respectively.

Figure 2 shows an example of the chromatograms obtained for a DIP solution before and after being in contact with NFNPs in an adsorption experiment. The peak area corresponding to DIP decreased significantly in the second case, evidencing an important adsorption on the particles. Besides this, an extra peak (Rt: 4.3 min) appeared after being in contact with the particles. Although small, this peak may affect quantification if corresponds to an unknown species containing DIP, and thus some extra experiments were performed in order to assign it. The more plausible candidates for these species are soluble Fe^{3+}–DIP or Ni^{2+}–DIP complexes, because the solid particles can release some Fe^{3+} and Ni^{2+} ions to the aqueous media and because DIP is a good ligand for transition metal ions due to the presence of its sulfonate group (Loginova and Konovalova 2008; Pierre et al. 2007; Suarez et al. 2011; Teixeira and Dadamos 2009). Chromatograms obtained for synthetic solutions containing DIP + Fe^{3+} or DIP + Ni^{2+} are shown in Fig. 2b. They clearly show the presence of the peak at 4.3 min in both cases. In Fig. 2c, in addition, it is shown that the peak becomes very small after adding 0.01 M EDTA to the mixture. EDTA is a very strong ligand for metal ions and should displace DIP from the Fe^{3+}–DIP or Ni^{2+}–DIP complexes. The results confirm the presence of a relatively small amount of metal–DIP complexes in the supernatants of the adsorption experiments. These complexes should be taken into account in an accurate quantification. Moreover, the fact that DIP can form complexes with iron and nickel ions in solution is a very good indication that the substance can form surface complexes with iron and nickel ions belonging to the surface of NFNPs and adsorb significantly.

The same set of experiments was performed with DC, but no extra peaks were observed. It is known that Fe^{3+}–DC complexation can occur in aqueous solutions (Agatonovic-Kustrin et al. 1997), although it seems to take place at undetectable concentrations in our conditions.

3.2.1 Adsorption kinetics

Kinetic experiments were performed with 800 mg L^{-1} of NFNPs suspension and a sample volume of 10 mL at pH 5.8 ± 0.2 (22 °C). At this pH, DC and DIP are mainly in their anionic form, and they can act as good ligands to bind Fe^{3+} and Ni^{2+} at the surface (Table S1). Ultrasonic irradiation

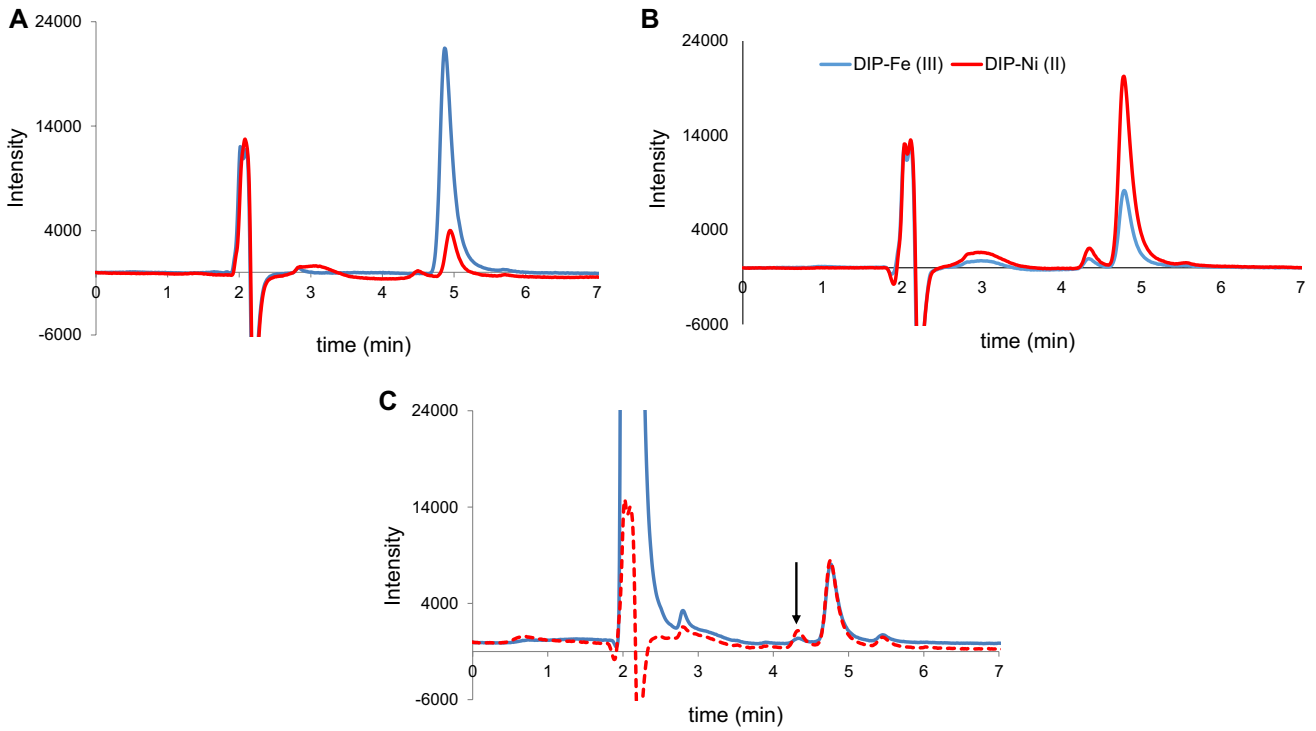

Fig. 2 Chromatograms of the following aqueous solutions: (**a**) 5 mg L^{-1} DIP before (blue line), and after contact with NFNPs in an adsorption experiment (red line). Experimental conditions: sample volume, 10 mL; NFNPs amount, 8 mg; ionic strength, 0.01 M; temperature, 22 °C; pH, 5.8; contact time, 30 min (**b**) 5 mg L^{-1} DIP + 6.8 mM Fe^{3+} (diluted 1:2 prior to analysis, blue line), and 5 mg L^{-1} DIP + 3.4 mM Ni^{2+} (red line). (**c**) DIP + 3.4 mM Ni^{2+} (dashed line), and the same mixture containing also 0.01 M EDTA (blue line). (Color figure online)

was preferred to mechanical assistance for the removal of both drugs from the aqueous solution because ultrasonic assistance can induce major dispersion of NFNPs and thus improve the adsorption. Kinetic data obtained for DIP and DC are shown in Fig. 3. The q_t versus time t curves show that most of the adsorption occurs during the first 20 min. Hence, 20 min were enough to achieve rather invariable adsorption values. The results are in agreement with those reported in the literature when acidic pharmaceuticals, including DC, were removed from aqueous solution (Gil et al. 2018).

3.2.2 Adsorption isotherms

The adsorption isotherms of DIP and DC onto NFNPs are depicted in Fig. 4. At low equilibrium concentrations the isotherms run closely for both substances, with DIP having a slightly higher affinity for the surface than DC. At high concentrations, however, the differences between the isotherms become stronger, reaching maximum adsorption values of around 31.2 mg g^{-1} for DIP and 16.8 mg g^{-1} for DC. The results suggest that the sulfonate group of DIP behaves as a better ligand than the carboxylate group of DC (see molecular structures in Table S1). The strong differences at high concentrations may arise from the different chemical structures of the analytes, leading to different conformations of the molecules at the surface, and thus to different effective surface areas occupied by them. It has been recently proposed that π–π interactions and C–H···π hydrogen bonds between DC molecules can generate possible micelle-like aggregates in water (Kozlowska et al. 2018). These molecule–molecule interactions could also affect differently the adsorption of DC and DIP. In addition, it has been also proposed a possible steric hindrance of the carboxylic group of DC due to the interaction with water molecules even in diluted solutions (Levina et al. 2018). Either molecule–molecule interactions or steric hindrance could affect DC adsorption as compared to DIP adsorption, but there is no clear information on this so far. The shape of the DC isotherm is similar to the shape of the isotherms reported in the literature when this drug was adsorbed onto

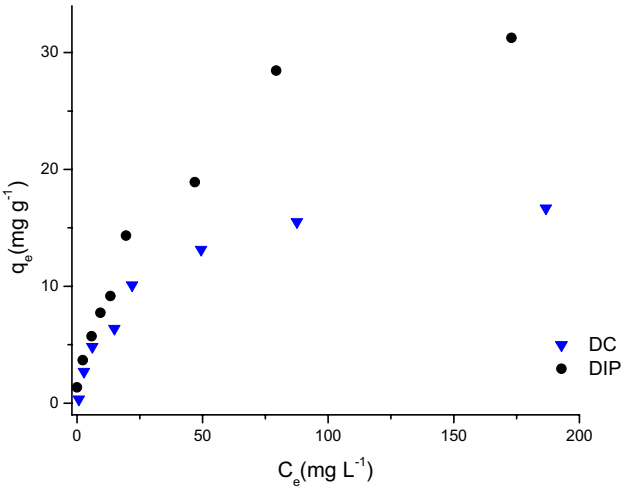

Fig. 4 Equilibrium adsorption isotherms of DIP and DC onto NFNPs at pH 5.8

hybrid-sericite support (Tiwari et al. 2015) or activated carbon (de Franco et al. 2018). Concerning DIP, there are not detailed information in the literature to compare the adsorption under equilibrium conditions.

3.2.3 Competitive adsorption of DIP and DC in binary mixtures

Adsorption experiments were also performed in binary mixtures of DIP and DC aiming to evaluate their influence on the adsorption process for further application in practical situations. Drugs were mixed in 0.5, 1.0 and 2.0 molar ratio and contact time was set as 20 min, considering that after this time the systems were close to equilibration, as shown for single systems (Fig. 3). The removal efficiency (%) was calculated as follow:

$$R(\%) = \frac{(Co - C)}{C_o} \times 100\% \quad (3)$$

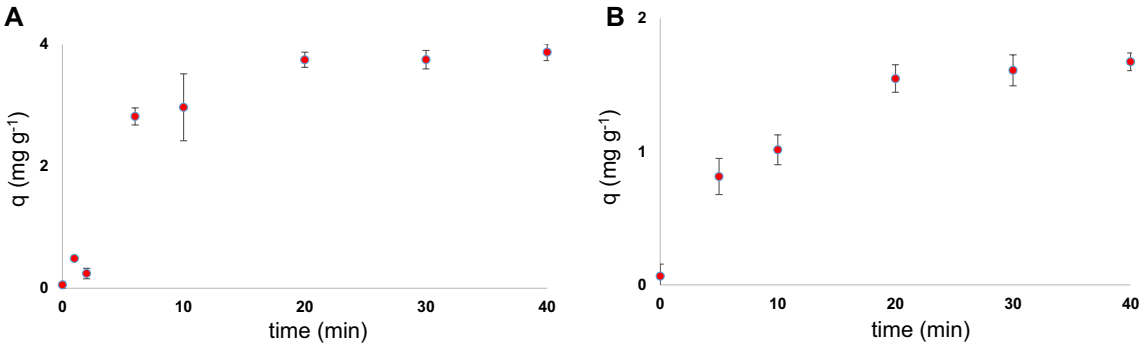

Fig. 3 Adsorption kinetic data for (**a**) DIP, initial concentration of 5 mg L^{-1} and (**b**) DC, initial concentration of 3 mg L^{-1}

where Co is the initial concentration (mg L^{-1}) and C is the remaining concentration after adsorption. The adsorption of DC was significantly decreased by the presence of DIP, e.g., when the initial concentration of DIP was twice the initial concentration of DC (molar ratio 2), DC adsorption was seven times smaller than in absence of DIP (Fig. 5a). On the contrary, the adsorption of DIP was virtually not affected by the presence of DC in the solution (Fig. 5b). Thus, the higher affinity of DIP for the surface becomes evident with this type of experiments.

3.3 Evaluation of desorption of DIP and DC

Based on the previous results and the stable adsorption of both drugs on NFNPs, adsorbent regeneration and/or recovery of analytes was evaluated. Two different organic solvents, methanol and ethanol, and two different solutes in water, ascorbic acid and potassium persulfate were tested. The results are listed in Table 2. The highest desorbed fraction was observed for DC when using methanol (60% of pre-adsorbed mass), while DIP was not recovered in the extract when using organic solvents. It can be associated to the differences in the solubility of both pharmaceuticals in the solvents and the specific interactions with the adsorbent (Table S1). In this case, DIP was properly released by 2% m/v aqueous ascorbic acid as desorbing agent (35% of pre-adsorbed mass).

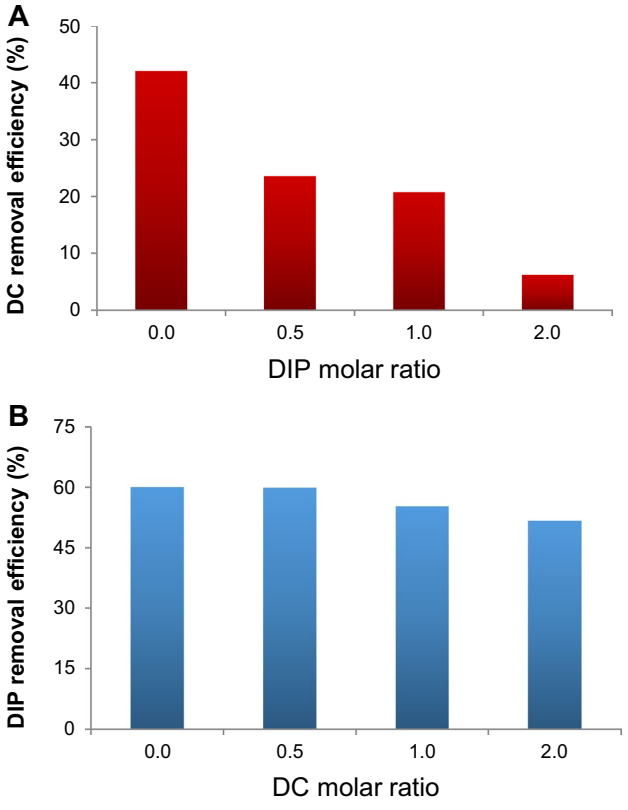

Fig. 5 Evaluation of simultaneous adsorption of DIP and DC on NFNPs (Concentration of each analyte: 3 mg L^{-1}), (**a**) removal efficiency (%) for DC and (**b**) removal efficiency (%) for DIP

Table 2 Recovery of pre-adsorbed analytes using different desorbing agents (experimental conditions: 800 mg L^{-1} of NFNPs; 10 mL of DIP–DC mixture, 5.0 mg L^{-1} of each drug; 3 mL of eluting solvent; agitation time of 15 min)

Analyte	Desorption efficiency (%)[a]			
	Potassium persulfate (2% m/v)	Ascorbic acid (2% m/v)	Methanol	Ethanol
DIP	10.2 ± 1.1	35.6 ± 1.3	–	–
DC	–	9.5 ± 0.6	60.5 ± 1.7	21.9 ± 2.1

[a]Mean of three replicates (n = 3)

Ascorbic acid (vitamin C, AH_2) is a water-soluble ketolactone with two ionizable hydroxyl groups. It has two pKa values (pK1: 4.2 and pK_2: 11.6) being ascorbate (AH^-) the dominant specie at near neutral pH condition. It is known that this molecule is a good ligand for transition metal ions (Boatright 2016; Davis 1992; Gorman and Clydesdale 1983; Harel 1994) and that it readily adsorbs on iron oxides, such as magnetite nanoparticles and magnetite entrapped calcium–alginate beads (Sonmez et al. 2016; Sreeja et al. 2015). Thus it should compete with DIP for adsorption sites and displace it from the nickel ferrite surface.

Hence, the obtained results show that it is possible the selective desorption of analytes by performing a sequential rinsing procedure with the selected solvents. This procedure was checked applying the following rinsing protocol: (1) NFNPs were mixed with 3 mL of methanol and sonicated during 15 min for desorption of DC. After magnetic recovery of the adsorbent, the extract was directly analyzed by HPLC–UV. Then, the same procedure was performed with 3 mL of ascorbic acid solution to release DIP from the NFNPs. As can be seen in Fig. 6, the chromatographic peaks for DC and DIP were selectively obtained after implementation of the protocol.

The reusability of the sorbent was also evaluated after rinsing it with 3 mL of deionized water during 5 min, aiming to remove traces of methanol and ascorbic acid. The results indicate that the adsorbent maintained its performance for four cycles and then it decreased dramatically (Fig. S2). This can be attributed to the strong binding of ascorbic acid to the NFNPs surface (Sreeja et al. 2015), which affects the available sorption sites.

3.4 Evaluation of matrix effect on DIP and DC adsorption and comparison with other sorbents

Regarding the evaluation of matrix effects, that is the components of a sample other than the analyte, expected

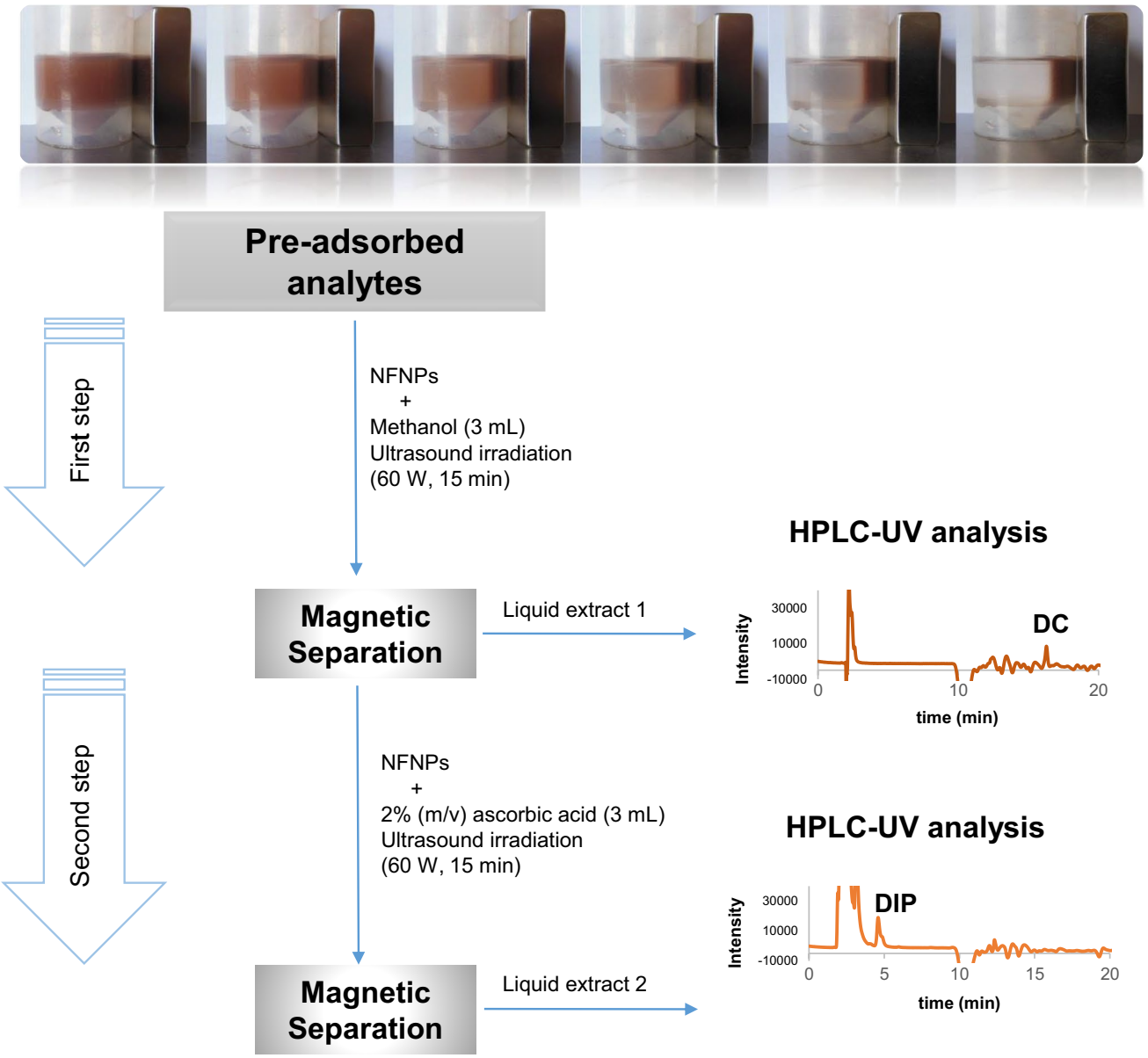

Fig. 6 Selective desorption of analytes using methanol (DC desorption) and 2% m/v ascorbic acid (DIP desorption). Inset: sequential pictures for the capture of NFNPs in aqueous solution by an external magnetic field (Nd magnet)

to be present in more complex water samples, adsorption experiments were performed in tap water and artificial sea water aiming to evaluate the effect of co-existing ions, such as chloride, carbonate, phosphate and sulfate on the adsorption process. Figure 7 shows that the adsorption of both analytes decreased significantly when the sample became more complex ($t_{calc} > 4.76$; $t_{tab} = 2.31$; $\alpha = 0.05$; $\nu = 8$). In fact, a decrease of c.a. 10% was observed for tap water (TW) and c.a. 35% for artificial sea water (SW) when compared to the adsorption in ultrapure water (UW). The effects are attributed in both cases to the possible competition for the sorption sites that takes place in this type of adsorbent (Chunming 2017).

Up to now, DIP and/or metabolites have been only retained on polymeric reversed phase sorbents (Gyenge-Szabó et al. 2014; Szabó et al. 2013) or with mixed-mode reversed phase/anionic exchange sorbent (Paíga et al. 2015). Concerning DC, many papers have been published in the literature where the central aim was to evaluate the ability of different materials for removal of this drug from aqueous solution. For example, adsorption capacities lower than 1 mg g^{-1} have been achieved when using sericite-hybrid

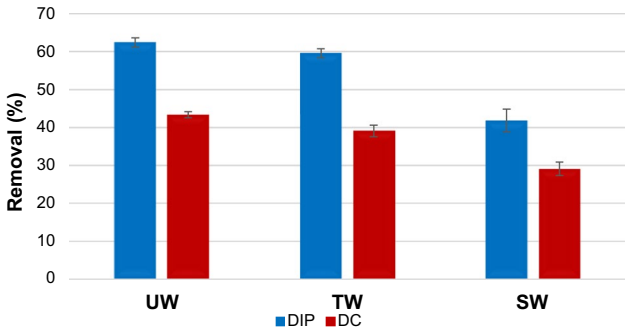

Fig. 7 Removal efficiency of DIP and DC from different water samples under optimal conditions (*UW* ultrapure water, *TW* tap water, *SW* sea water)

materials (adsorbent dosage 2.0 g L^{-1}) (Tiwari et al. 2015) and hybrid-materials such as organoclays prepared with two long-alkyl chains cationic surfactants (De Oliveira et al. 2017). In the same way, this compound has been recently removed using both, a column packed with activated carbon (adsorbent dosage 1.0 g) and batch conditions (adsorbent dosage 12.5 g L^{-1}) with an adsorption capacity of 1 mg g^{-1} at 25 °C when the equilibrium concentration was 100 mg L^{-1} (de Franco et al. 2018). In fact, DC has been successfully removed from aqueous solution only using modified-multiwalled carbon nanotubes (Hu and Cheng 2015) and by carbon nanotubes/Al_2O_3 composites (Wei et al. 2013). Nevertheless, the cost of carbon nanotubes is higher than the proposed material as pointed out in the literature (Wang et al. 2016), which represents an important factor for large-scale applications. As can be seen, the bare NFNPs used in this study allows obtaining satisfactory results if compared with these recently published works where more sophisticated adsorbent materials were employed.

4 Conclusion

In the present work NFNPs were used, for the first time, for the simultaneous removal of two polar pharmaceutical compounds, DIP and DC, from aqueous solution. The NFNPs are easy to synthesize and simple to recover due to its magnetic properties which represent an economic alternative to the traditional sorbents. Adsorption on these nanoparticles was found to be a favorable process for both drugs. Additionally, it is possible the controlled release of the adsorbed molecules by using a sequential rinsing protocol with methanol and ascorbic acid. It makes possible the reuse of NFNPs for successive dynamic processes. From the present study, the application of these bare NFNPs could be extended toward the removal of other polar pharmaceutical compounds in aqueous solution.

Acknowledgements V. Springer acknowledges the National Scientific and Technical Research Council (CONICET, Argentina) and Universidad Nacional del Sur (Argentina) for the financial support from a research fellowship program. Funds from CONICET, FONCyT and SGCyT-UNS are acknowledged. This work received financial support from the European Union (FEDER funds POCI/01/0145/FEDER/007265) and National Funds (FCT/MEC, Fundação para a Ciência e Tecnologia and Ministério da Educação e Ciência) under the Partnership Agreement PT2020 UID/QUI/50006/2013. L. Barreiros thanks FCT and POPH (Programa Operacional Potencial Humano) for her Post-Doc grant FCT SFRH/BPD/89668/2012.

References

Agatonovic-Kustrin, S., Zivanovic, L., Zeevi, M., Radulovic, D.: Spectrophotometric study of diclofenac-Fe (III) complex. J. Pharm. Biomed. Anal. **16**, 147–153 (1997)

Agunbiade, F.O., Moodley, B.: Occurrence and distribution pattern of acidic pharmaceuticals in surface water, wastewater, and sediment of the msunduzi river,kwazulu-natal, south africa. Environ. Toxicol. Chem. **35**, 36–46 (2016)

Ahmad, S.M., Almeida, C., Neng, N.R., Nogueira, J.M.F.: Bar adsorptive microextraction (BAE) coated with mixed sorbent phases—enhanced selectivity for the determination of non-steroidal anti-inflammatory drugs in real matrices in combination with capillary electrophoresis. J. Chromatogr. B **1008**, 115–124 (2016)

Ali, I.: New generation adsorbents for water treatment. Chem. Rev. **112**, 5073–5091 (2012)

ASTM Standards D1141-Standard Practice for the Preparation of Substitute Ocean Water, ASTM International. http://www.astm.org/Standards/D1141.htm. Accessed 2 Feb 2017

Boatright, W.L.: Oxygen dependency of one-electron reactions generating ascorbate radicals and hydrogen peroxide from ascorbic acid. Food Chem. **196**, 1361–1367 (2016)

Cashman, J.N.: The mechanisms of action of NSAIDs in analgesia. Drugs **52**, 13–23 (1996)

Chunming, S.: Environmental implications and applications of engineered nanoscale magnetite and its hybrid nanocomposites: a review of recent literature. J. Hazard. Mater. **322**, 48–84 (2017)

Dai, G., Wang, B., Huang, J., Dong, R., Deng, S., Yu, G.: Occurrence and source apportionment of pharmaceuticals and personal care products in the Beiyun River of Beijing, China. Chemosphere **119**, 1033–1039 (2015)

Davis, M.B.: Reactions of L-ascorbic acid with transition metal complexes. Polyhedron **11**, 285–321 (1992)

Decision (E.U.): 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council. Off. J. Eur. Union L78, 40–42

De Franco, M.A.E., de Carvalho, C.B., Boneto, M.M., Soares, R.P., Féris, L.A.: Diclofenac removal from water by adsorption using activated carbon in batch mode and fixed-bed column: isotherms, thermodynamic study and breakthrough curves modeling. J. Clean. Prod. **181**, 145–154 (2018)

De Oliveira, T., Guégan, R., Thiebault, T., Milbeau, C.L., Muller, F., Teixeira, V., Giovanela, M., Boussafir, M.: Adsorption of diclofenac onto organoclays: effects of surfactant and environmental (pH and temperature) conditions. J. Hazard. Mater. **323**, 558–566 (2017)

Feldmann, D.F., Zuehlke, S., Hebere, T.: Occurrence, fate and assessment of polar metamizole (dipyrone) residues in hospital and municipal wastewater. Chemosphere **71**, 1754–1764 (2008)

Fernández, C., González-Doncel, M., Pro, J., Carbonell, G., Tarazona, J.V.: Occurrence of pharmaceutically active compounds

in surface waters of the Henares-Jarama-Tajo river system (Madrid, Spain) and a potential risk characterization. Sci. Total Environ. **408**, 543–551 (2010)

Gil, A., Santamaría, L., Korili, S.A.: Removal of caffeine and diclofenac from aqueous solution by adsorption on multiwalled carbon nanotubes. Colloid Interface Sci. Commun. **22**, 25–28 (2018)

Goldman, A.: Modern Ferrites Technology, 2nd edn. Springer, New York (2006)

Gomez, M.J., Malato, O., Ferrer, I., Aguera, A., Fernández-Alba, A.R.: Solid-phase extraction followed by liquid chromatography–time-of-flight–mass spectrometry to evaluate pharmaceuticals in effluents. A pilot monitoring study. J. Environ. Monit. **9**, 718–729 (2007)

Gorman, J.E., Clydesdale, F.M.: The behavior and stability of iron-ascorbate complexes in solution. J. Food Sci. **48**, 1217–1225 (1983)

Gyenge-Szabó, Z., Szoboszlai, N., Frigyes, D., Záray, G., Mihucz, V.G.: Monitoring of four dipyrone metabolites in communal wastewater by solid phase extraction liquid chromatography electrospray ionization quadrupole time-of-flight mass spectrometry. J. Pharm. Biomed. Anal. **90**, 58–63 (2014)

Harel, S.: Oxidation of ascorbic acid and metal ions as affected by NaCl. J. Agric. Food Chem. **42**, 2402–2406 (1994)

He, L., Zhao, Z., Zhang, Y.: Synthesis of nickel ferrite precursors from low-grade nickel matte. Trans. Nonferrous Met. Soc. China 23, 2422–2430 (2013)

Hedenmalm, K., Spigset, O.: Agranulocytosis and other blood dyscrasias associated with dipyrone (metamizole). Eur. J. Clin. Pharmacol. **58**, 265–274 (2002)

Hu, X., Cheng, Z.: Removal of diclofenac from aqueous solution with multi-walled carbon nanotubes modified by nitric acid. Chin. J. Chem. Eng. **23**, 1551–1556 (2015)

Joshi, S., Kumar, M., Chhoker, S., Srivastava, G., Jewariya, M., Singh, V.N.: Structural, magnetic, dielectric and optical properties of nickel ferrite nanoparticles synthesized by co-precipitation method. J. Mol. Struct. **1076**, 55–62 (2014)

Klug, H.P., Alexander, L.E.: X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, 2nd edn. Wiley, New York (1974)

Kostopoulou, M., Nikolaou, A.: Analytical problems and the need for sample preparation in the determination of pharmaceuticals and their metabolites in aqueous environmental matrices. TrAC Trends Anal. Chem. **27**, 1023–1035 (2008)

Kozlowska, M., Rodziewicz, P., Utesch, T., Mroginski, M.A., Kaczmarek-Kedziera, A.: Solvation of diclofenac in water from atomistic molecular dynamics simulations—interplay between solute–solute and solute–solvent interactions. Phys. Chem. Chem. Phys. (2018). https://doi.org/10.1039/C7CP08468D

Larsson, E., al-Hamimi, S., Jönsson, J.: Behaviour of nonsteroidal anti-inflammatory drugs and eight of their metabolites during wastewater treatment studied by hollow fiber liquid phase microextraction and liquid chromatography mass spectrometry. Sci. Total Environ. **485–486**, 300–308 (2014)

Leroy, P., Tournassat, C., Bizi, M.: Influence of surface conductivity on the apparent zeta potential of TiO_2 nanoparticles. J. Colloid Interface Sci. **356**, 442–453 (2011)

Levina, E.O., Penkov, N.V., Rodionova, N.N., Tarasov, S.A., Barykina, D.V., Vener, M.V.: Hydration of the carboxylate group in anti-inflammatory drugs: ATR-IR and computational studies of aqueous solution of sodium diclofenac. ACS Omega 3, 302–313 (2018)

Loginova, L.P., Konovalova, O.Y.: Test films for test-determinations on the base of reagents, immobilized in gelatinous gel. Talanta **77**, 915–923 (2008)

Maaz, K., Karim, S., Mumtaz, A., Hasanain, S.K., Liu, J., Duan, J.L.: Synthesis and magnetic characterization of nickel ferrite nanoparticles prepared by coprecipitation route. J. Magn. Magn. Mater. **321**, 1838–1842 (2009)

Miller, J.N., Miller, J.C.: Statistics and Chemometrics for Analytical Chemistry, 6th edn. Pearson Education Limited, New York (2010)

Ncibi, M.C., Sillanpää, M.: Optimized removal of antibiotic drugs from aqueous solutions using single, double and multi-walled carbon nanotubes. J. Hazard. Mater. **298**, 102–110 (2015)

Paíga, P., Lolić, A., Hellebuyck, F., Santos, L.H.M.L.M., Correia, M., Delerue-Matos, C.: Development of a SPE–UHPLC–MS/MS methodology for the determination of non-steroidal anti-inflammatory and analgesic pharmaceuticals in seawater. J. Pharm. Biomed. Anal. **106**, 61–70 (2015)

Parolini, M., Binelli, A., Provini, A.: Chronic effects induced by ibuprofen on the freshwater bivalve *Dreissenapolymorpha*. Ecotoxicol. Environ. Saf. **74**, 1586–1594 (2011)

Pierre, S.C., Schmidt, T., Brenneis, C., Michaelis, M., Geisslinger, G., Scholich, K.: Inhibition of cyclooxygenases by dipyrone. Br. J. Pharmacol. **151**, 494–503 (2007)

Plaza, R.C., de Vicente, J., Gómez-Lopera, S., Delgado, A.V.: Stability of dispersions of colloidal nickel ferrite spheres. J. Colloid Interface Sci. **242**, 306–313 (2001)

Shanmugavel, T., Gokul Raj, G., Ramesh Kumar, G., Rajarajan, G., Saravanan, D.: Cost effective preparation and characterization of nanocrystalline nickel ferrites ($NiFe_2O_4$) in low temperature regime. J. King Saud Univ. Sci. **27**, 176–181 (2015)

Sonmez, M., Verisan, C., Voicu, G., Ficai, D., Ficai, A., Oprea, A.E., Vlad, M., Andronescu, E.: Extended release of vitamins from magnetite loaded polyanionic polymeric beads. Int. J. Pharm. **510**, 457–464 (2016)

Sreeja, V., Jayaprabha, K.N., Joy, P.A.: Water-dispersible ascorbic-acid-coated magnetite nanoparticles for contrast enhancement in MRI. Appl. Nanosci. **5**, 435–441 (2015)

Suarez, W.T., Pessoa-Neto, O.D., Vicentini, F.C., Janegitz, B.C., Faria, R.C., Fatibello-Filho, O.: Flow injection spectrophotometric determination of dipyrone in pharmaceutical formulations using Fe(III) as reagent. Anal. Lett. **44**, 340–348 (2011)

Szabó, Z., Szoboszlai, N., Jámbor, É, Gulyás, G., Lóránd, T., Ohmacht, R., Záray, G., Mihucz, V.G.: Determination of four dipyrone metabolites in Hungarian municipal wastewater by liquid chromatography mass spectrometry. Microchem. J. **107**, 152–157 (2013)

Teixeira, M.F.S., Dadamos, T.R.L.: An electrochemical sensor for dipyrone determination based on nickel-salen film modified electrode. Procedia Chem. **1**, 297–300 (2009)

Tiwari, D., Lalhriatpuia, C., Lee, S.-M.: Hybrid materials in the removal of diclofenac sodium from aqueous solutions: batch and column studies. J. Ind. Eng. Chem. **30**, 167–173 (2015)

Wang, L., Li, J., Wang, Y., Zhao, L., Jiang, Q.: Adsorption capability for Congo red on nanocrystalline MFe2O4 (M = Mn, Fe, Co, Ni) spinel ferrites. Chem. Eng. J. **181–182**, 72–79 (2012)

Wang, Y., Ma, J., Zhu, J., Ye, N., Zhang, X., Huang, H.: Multi-walled carbon nanotubes with selected properties for dynamic filtration of pharmaceuticals and personal care products. Water Res. **92**, 104–112 (2016)

Wei, H., Deng, S., Huang, Q., Nie, Y., Wang, B., Huang, J., Yu, G.: Regenerable granular carbon nanotubes/alumina hybrid adsorbents for diclofenac sodium and carbamazepine removal from aqueous solution. Water Res. **47**, 4139–4147 (2013)

World Health Organization Press: Pharmaceuticals in drinking-water, WHO/HSE/WSH/11.05, Switzerland (2011)

Xiao, J., Xie, Y., Cao, H.: Organic pollutants removal in wastewater by heterogeneous photocatalytic ozonation. Chemosphere **121**, 1–17 (2015)

Zhang, L., Liu, X., Guo, X., Su, M., Xu, T., Song, X.: Investigation on the degradation of brilliant green induced oxidation by NiFe2O4 under microwave irradiation. Chem. Eng. J. **173**, 737–742 (2011)
Zhang, C., Li, Y., Jiang, Y., Wang, T.J.: Size-dependent fluoride removal performance of a magnetic Fe_3O_4@Fe–Ti adsorbent and its defluoridation in a fluidized bed. Ind. Eng. Chem. Res. **56**, 2425–2432 (2017)