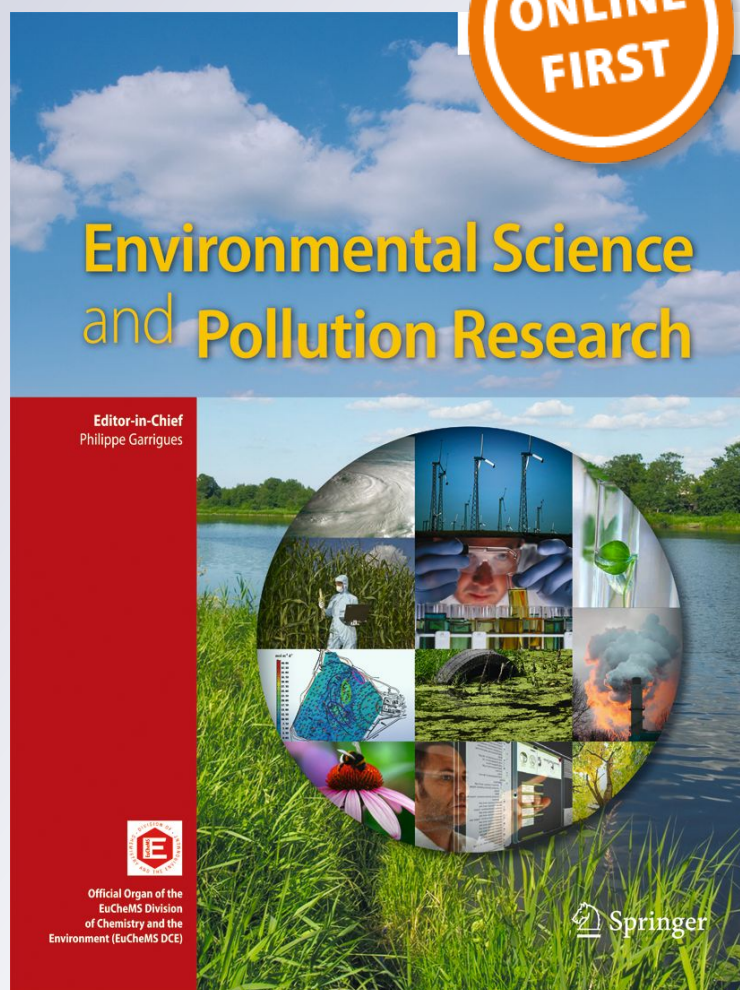# Magnetic nanotechnological devices as efficient tools to improve the quality of water: analysis on a real case

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Magnetic nanotechnological devices as efficient tools to improve the quality of water: analysis on a real case

Maria Fernanda Horst[1] · Aldana Pizzano[1] · Carla Spetter[2,3] · Verónica Lassalle[1]

Abstract

Magnetic nanoparticles (MNPs), based on iron oxide (magnetite) and ferrogel of gelatin and MNPs, were employed as efficient tools for the removal of heavy metals and nutrients from water samples from Bahia Blanca estuarine (BBE). An exhaustive adsorption performance of Cu, NO_3^-, and NO_2^- was conducted in batch using model solutions aiming to adjust the adsorption conditions. Adsorption studies using water simulating the real samples were also performed. Both kinds of nanomaterials demonstrated an efficiency between 60 and 80%, and 85% for the removal of heavy metals and NO_3^- and NO_2^-, respectively. Similar adsorption assays were performed using BBE water samples, employing the experimental conditions explored with model and simulated water. The reached efficiency was 30 and 45% for heavy metal and nutrient removal, respectively, using nanoparticles; meanwhile, ferrogels displayed a removal capacity around 50–60%. The nanoparticles showed structural instability by the leaching of iron to the medium after the adsorption processes. Ferrogels remained almost inalterable in terms of their integrity during the adsorption time. These materials showed satisfactory perspectives regarding their reuse possibilities. They were used for almost five repeated cycles of adsorption without losing efficiency on the adsorption. The results of this study suggest that MNPs and FGs appear as versatile and promising materials that may be considered as valid alternatives to the actual tools for the remediation of real water samples.

Keywords Estuarine water remediation · Heavy metals · Nutrients · Adsorbent nanomaterials · Ferrogels · Magnetic nanoparticles

Introduction

In recent decades, the world's accelerated economic development has led not only to rising income but also to a rapid urbanization and an uncontrolled population growth. The rapid industrialization has taken to an increased discharge of wastewater from the aquatic environment containing diverse contaminants such as heavy metals (i.e., Cr, Cd, Pb, Hg),

agrochemicals, bacteria, and arsenic. Besides, nitrate and phosphate are also largely released to aquatic systems either through the sewage discharge like of the mining, industrial, and agricultural activities (Kurniawan et al. 2012; Chih-Chang 2015). The excessive input of nutrients to water bodies would result in eutrophication causing depletion of dissolved oxygen, loss of aquatic vegetation and even fish mortality, among others. Particularly the nitrogen (N) and phosphorus (P) species are the principal responsible of these problems. Specifically, nitrate in bodies of freshwater for human consumption is also hazardous to human health; it may cause infant methemoglobinemia, the "blue baby" syndrome as well as generating nitrosamines and nitrosamides that are known to be carcinogenic (Bryan and Van Grinsven 2013). In the case of heavy metals, they rapidly bioaccumulate and pass through the different levels of the trophic chain (Vu et al. 2017; Zhang et al. 2017). They may become mobile in soils depending on soil pH and their speciation. Hence, a fraction of the total mass can leach to aquifers or may become bioavailable to living organisms. In estuarine and coastal regions, sediments have been regarded as both carriers and sinks of various

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contaminants originating from industrial, municipal, and agricultural processes (La Colla et al. 2015; Spetter et al. 2015).

Recent reviews have resumed the most actual technologies for heavy metal and nutrient removal from contaminated water (Hashim et al. 2011; Carolin et al. 2017). The treatment methodologies may be classified into three groups: (i) chemical treatment technologies, (ii) biological/biochemical/biosorptive treatment technologies, and (iii) physicochemical treatment technologies. In the case of chemical treatment, those are mostly applied for controlling large plumes of contaminants spread over a large area deep in the water. They are used to decrease the toxicity or mobility of metal contaminants by converting them to inactive states. Oxidation, reduction, and neutralization reactions may be used for this purpose. Meanwhile, biological treatment methods used natural biological processes involving plants and microorganisms as responsible for metal elimination from soil and groundwater. Biosorption is an emerging field of remediation technology. It is cost-effective, offers the possibility of metal recovery, and also generates minimum sludge. Permeable reactive barriers (PRBs) is recognized as one of the most practical solutions for remediating flowing groundwater. They incorporate the strength of other technologies such as adsorbents, ZVI (zero valent iron), and bacterial sulfate reduction (BSR). However, they are prone to serious problem regarding obstruction and reduction of permeability, leading to bypass of groundwater flow. Besides, these systems present the disadvantage of the exhaustion of reactivity also hinder their activity. This technology principally depends upon sorption, precipitation, and biological reduction processes. In particular, sorption process in the PRBs is achieved by employing the iron-based sorbents, activated carbons, zeolite materials, and biosorbents (Hashim et al. 2011).

The desired technology should be novel, reliable, cost-effective, and environmentally friendly. The approaches include avoiding the consumption of chemicals, minimizing the generation of sludge or secondary waste after treatment, and reducing energy consumption and treatment costs, while improving the quality of treated effluents based on the legislation requirements. In this context, nanomaterials of different nature have appeared as an attractive alternative during the last decade. Because of their small size, active surface, and eventually, high porosity, nanoadsorbents not only are capable of sequestering contaminants with varying molecular size, hydrophobicity, and speciation behavior, but also enable manufacturing process to efficiently consume raw materials without releasing extra toxics (Kurniawan et al. 2012). Particularly, magnetic nanoparticle (MNP) investigations have grown recently, and their applications have attracted the attention of both the researchers and industries devoted to environmental remediation (Jiang et al. 2013; Horst et al. 2016a; Iconaru et al. 2016; Wanna et al. 2016). For example, the use of MNPs for metal removal has been extensively

demonstrated by several published contributions. In our previous works, chitosan magnetic nanocomposites were synthetized by co-precipitating the iron oxide onto chitosan. The adsorption performance of the materials were tested in batch experiences by removal of heavy metals (Horst et al. 2016a). It demonstrated an efficiency of 188, 159, 72, and 46 mg of Me/g of nanocomposite for Cu, Cd, Zn, and Cr; respectively. In another study, ferrogels based on gelatin/gum Arabic and magnetite nanoparticles were synthetized and the behavior as adsorbent materials was evaluated by heavy metal adsorption using model aqueous solutions. In this work, an exhaustively analysis was performed by evaluating the effect of pH on heavy metal adsorption, the kinetics and initial concentration of heavy metal. Cadmium removal was successfully achieved reaching an efficiency of 90%. Besides, the material demonstrated great possibilities of reuse along four repeated adsorption cycles and the material could be regenerated (Horst et al. 2017).

Bahía Blanca estuary is located on the South Atlantic coast and there is established one of the most important ports of Argentina. The installation of several industries and cities (with more of 350,000 inhabitants) around this estuary has impacted on the quality of their water.

The Bahía Blanca estuarine is considered highly eutrophic (Popovich et al. 2008) and is polluted by untreated sewage discharge (Dutto et al. 2012), hydrocarbons (Arias et al. 2011), heavy metals (Botté et al. 2010; Fernández-Severini et al. 2013), and organotin compounds (Quintas et al. 2016).

In this scenario, it is clear that there persists a need for achieving more efficient and economically viable materials to solve the problems associated with the water quality. The aim of this work is to apply materials derived from nanotechnology to remove emergent contaminants of high impact, in general, in aqueous bodies. The main goal is to evaluate their performance in a real and concrete environment, such as the Bahía Blanca estuarine. To this end, nanoparticles based on magnetite and gum Arabic and ferrogel from gelatin and magnetite prepared and well characterized in our laboratory have been selected as adsorbents (Horst et al. 2016b, 2017). A reasonable sequence was followed and involved the following: (i) the evaluation of the nanomaterials against model aqueous solutions of the contaminants, though in batch experiences to gain insight into the kinetic and adsorption efficiency; (ii) the test of the nanomaterials using a water sample simulating a real one. This sample includes heavy metals and nutrients in its composition. (iii) The same assays were repeated using real seawater samples arising from the inner zone of Bahía Blanca estuarine. The data arising from this work may be useful for any researcher working in the remediation of aqueous sources of a different origin with alike nanomaterials. A representative scheme showing the sequence of assays is depicted in Fig. 1.
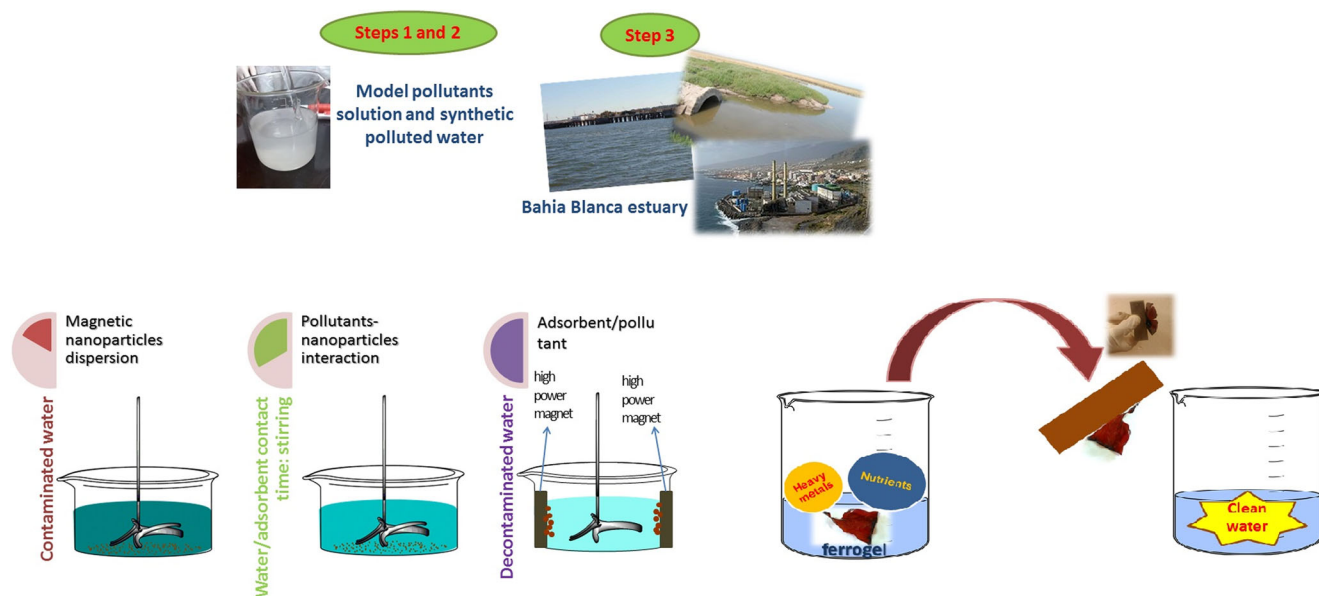
Fig. 1 Schematic of adsorption assays with model solution, synthetic water, and real water polluted

Materials and methods

Materials

Magnetite gum Arabic nanoparticles (GMNPs) were prepared and characterized in our laboratory following the methodology previously reported (Horst et al. 2016b). The hydro- and ferrogels (HGs and FGs, respectively) were prepared by freeze-thawing method with some modifications (Gonzalez et al. 2014; Horst et al. 2017). The synthesis and characterization of ferro- and hydrogel has been recently published (Horst et al. 2017).

Methods

Adsorption assays using model solutions of contaminants

Adsorption of Cu and Cd on GMNPs and FG Gum Arabic magnetic nanoparticles were employed in batch experiences for heavy metals adsorption. The adsorption experience was conducted using Cu ion as model heavy metal. To do this, 50 mg of adsorbent material was suspended in 50 mL of copper aqueous solution of 100 mg/L and maintained under magnetic stirring during 4 h at room temperature. The copper stock solution was a commercial one of 1000 mg/L; aliquots from this were taken to prepare solutions with the desired concentration. The pH value was previously adjusted to 6 (Monier et al. 2010). Then, aliquots of 1 mL were withdrawn to measure the remained copper ion in solution by atomic absorption spectroscopy using a GBC Avanta 932.

The adsorption performance of ferrogel was previously reported (Horst et al. 2017). In this experience, 100 mg of ferrogel was kept in contact with 100 mL of Cd, 100 mg/L

solution as model heavy metal. Cd stock solution was a commercial one of 1000 mg/L and aliquots of this were taken to prepare solutions with the desired concentrations. The pH was previously adjusted to 6. Aliquots of solution were withdrawn to measure the heavy metal ion unadsorbed by atomic absorption spectroscopy.

Adsorption of nutrients (NO_3^- and NO_2^-) A 100 mg/L stock standard solution of NO_3^- and NO_2^- was prepared by dissolving an appropriate amount of Na NO_3^- and Na NO_2^-, respectively in 500 mL of distilled water. Adsorption assays were determinant by batch experiences of 100 mg of GMNPs with 100 mL of NO_2^- or NO_3^- solutions. The suspensions were maintained under magnetic stirring for 3 h at room temperature. The pH value of the suspensions was maintained around 7 during the assays. The solid adsorbents were allowed to decant by an Nd magnet and aliquots of the supernatant were withdrawn at different times. The remained nutrients in solution were determined by colorimetric methods using a Technicon AA-II Autoanalyzer (Grasshoff et al. 1983).

For ferrogel adsorption assays, the experimental methodology was similar to GMNPs. In brief, 50 mg of FG was allowed to swelling in 50 mL 100 mg/L of NO_3^- solution during 3 h at room temperature. Aliquots of solution were withdrawn at different times and the remained NO_3^- ion was measured.

Adsorption using simulated water sample

Preparation of simulated water sample A water sample was prepared in our laboratory by adjusting the conditions and composition to simulate an aqueous sample from the Bahía Blanca estuary. The composition was as follows: 60.67 mg/L $NaNO_3$, 36.76 mg/L $CaCl_2.2H_2O$, 36.97 mg/L $MgSO_4.7H_2O$,

420.04 mg/L NaCO$_3$, 6.19 mg/L K$_2$HPO$_4$, 2.90 mg/L FeCl$_3$, 1.5 mg/L CuSO$_4$.5H$_2$O, 1.20 mg/L ZnSO$_4$.7H$_2$O, 2 mg/L Cd pattern solution, 0.147 mg/L MnCl$_2$.2H$_2$O, 3.5 mg/L Pb pattern solution, 1 mg/L HNO$_3$. The measured pH was around 6.44 and 4.98 mS of conductivity.

Adsorption assays The assays using GMNPs and FGs as adsorbents were performed at room temperature and pH = 6. This pH value was selected based on our previous studies (Horst et al. 2016a, 2017) considering the possible pH value found in a real water sample. Fifty milligrams of the adsorbents were incubated in 50 mL of synthetic wastewater under magnetic stirring. In the case of GMNPs, the incubation time was about 30 min; this time was selected based on previous studies with chitosan magnetic nanocomposites which exhibited similar active functional groups for heavy metal adsorption (Horst et al. 2016a). The adsorbent was isolated to the aqueous media by magnetic decantation whereas the supernatant was recovered to heavy metals measurements by absorption atomic spectroscopy.

The assays using ferrogels involved the swelling of the adsorbents in the water sample for 30 min. The remained heavy metals in solution were measured by absorption atomic spectroscopy. The final adsorption time was selected from the previous adsorption assays with model heavy metals (Horst et al. 2016a, 2017).

Adsorption assays using seawater samples

Surface estuarine water samples (~ 0.50 m depth) were collected in the inner zone of the Bahía Blanca estuary (BBE) (38° 48′ 45.04″ S and 62° 13′ 24.13″ O) with a 2.5-L Van Dorn sampler bottle, filtered through glass fiber grade F (0.7 μm) membranes and frozen until analysis to determine the concentrations of nitrite and nitrate by colorimetric methods (X, Y) using a Technicon AA-II Autoanalyzer. The limit of quantification of methods is 0.10 μM for NO$_3^-$ and 0.02 μM for NO$_2^-$. Simultaneously, temperature, conductivity/salinity, pH, turbidity, and dissolved oxygen (DO) concentration were in situ measured using a Horiba U-10 multisensor device. The conditions at the moment of sample collection were as follows: pH of 7.56, temperature 11.6 °C, salinity 29.1 psu, turbidity 99NTU, and OD 10.85 mg/L.

Adsorption kinetic assays were performed by suspended 100 mg of GMNPs in 100 mL of estuarine water sample during 30 min at room temperature. The adsorption time was fixed based on previous kinetic studies employing similar nanomaterials and gels (Horst et al. 2016a, 2017). The adsorbent was isolated by magnetic decantation and the supernatant reserved to measure heavy metals ion and nutrients. Similar procedure was performed using FGs as adsorbent. It is important to highlight that for nutrient determination, all the samples were frozen until the measurements in order to preserve the sample.

The methodology adopted for heavy metal removal from real water samples was taken from the studies performed using model solutions. In this case, the remained heavy metal was measured by using inductively coupled plasma spectrometer (ICP-AES) Shimadzu 9000 Simultaneous High Resolution according to EPA 200.7 standard.

Reusability assays

Reuse adsorption assays were performed using GMNPs in batch experience using NO$_2^-$ and NO$_3^-$ model solution and using FG in heavy metal model. To do this, 100 mg were incubated in 100 mL of model solutions during 30 min of contact time.

Characterization

Fourier transform infrared spectroscopy (FTIR) of adsorbent materials was recorder on a Thermo Scientific Nicolet iS50 FT-IR, modulo NIR: Thermo Scientific Nicolet iS50 NIR module with Integrating Sphere in the frequency range 4000–400 cm^{-1}.

Malvern Zetasizer was employed to measure the Z potential (ξ) and the average hydrodynamic diameter of particles by dynamic light scattering (DLS).

Results and discussion

Adsorption experiences of nutrients and heavy metals in model solution on GMNPs The adsorption kinetics of nitrites and NO$_3^-$ on GMNPs using model solutions is shown in Fig. 2. The data suggest that both species are efficiently adsorbed onto magnetic nanoparticles in relatively short times. In fact, equilibrium state is reached at almost 60 min. It is evident a higher affinity of the adsorbent for nitrites, removing 63% of the initially available concentration. These results suggest that other than electrostatic interactions are the responsible for the nutrient binding to the GMNPs surface (Miretzky and Cirelli 2010; Paulino et al. 2011; Monier 2012). The surface charge of raw GMNPs was − 15 mV at of the pH fixed for the adsorption experiences (Horst et al. 2016b). After NO$_2^-$ and NO$_3^-$ adsorption assays, the surface charge of GMNPs changed to − 35 ± 5.09 and − 29.37 ± 4.35 mV, respectively. These data not only confirm the effective adsorption of nutrients on GMNPs but also reinforce the hypothesis that other than electrostatic are the interactions implicated between anions and adsorbent. Other authors have reported similar findings studying similar adsorbents. One work deals with the use of magnetic multi-walled carbon nanotubes (MMWCNTs) for nitrate adsorption, conducting the assay at pH = 4 and obtaining a maximum of 97% removal
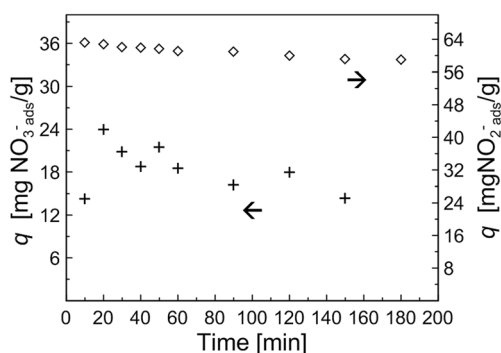
Fig. 2 Adsorption profiles of nitrates and nitrites adsorption on GMNps nanoparticles using a model solution

(Alimohammadi et al. 2016). They observed that increasing the pH values, the adsorption capacity decreased due to the negative surface charged of adsorbent at that pH. The authors also observed that, at higher pH, the negatively charged parts also increased, but the electrostatic repulsion from the negatively charged parts of the adsorbent does not favor absorption of nitrate. So they obtained lower adsorption capacity at higher pH.

In the current study, the influence of the pH was not explored because it was intended to emulate the pH corresponding to the real natural water samples. From a basic point of view, it would be possible that better adsorption levels could be obtained, adjusting the adsorption pH assays by inducing electrostatic interactions between the adsorbent and contaminants.

FTIR spectra of GMNPs before and after adsorption are depicted in Fig. 3. It can be observed that new bands appeared in the MNP spectra after NO_3^- and NO_2^- adsorption. In both spectra corresponding to MNPs post adsorption of model nutrient solution and real water sample could be distinguished two regions with new bands, one around 1700 cm^{-1} corresponds to overtone modes of nitrate vibrations (N=O) (Addison and Simpson 1965; Klingenberg and Vannice 1996). Besides, at 650 cm^{-1}, there appears bands due to NO_2 asymmetric bend (Addison and Simpson 1965). Therefore, from the FTIR spectra post adsorption, we could be assured that nitrate and nitrite moieties were adsorbed on GMNPs material. Then, it is possible to infer a mechanism of adsorption. As mentioned earlier, the adsorption assays were performed at pH = 6; considering the surface charge of GMNPs nanoparticles at this pH, the material displayed negative surface charge as it was previously reported (Horst et al. 2016b). In this condition, functional groups of GA mainly carboxylate are the responsible of the negative charge, in addition to the OH exposed groups of magnetite. Thus, the binding of NO_3^- and also NO_2^- could be achieved by replacing the OH^- with an anion; meaning an ion exchange process (Song et al. 2016).

The recovery of adsorbent materials for recycling is actually one of the most important aspects of research regarding the treatment of water and wastewater and one of the main advantages associated with the magnetic nature of the proposed materials. From the technological point of view, the reusability of the materials provides economic benefits. For this reason, NO_3^- and NO_2^- adsorption cycles were performed by using GMNP nanoparticles in batch experiences of model solutions. For the best of our knowledge, most of the bibliography articles report the regeneration of similar material by using an alkaline media, e.g., NaOH where OH^- ions exchange against the NO_3^- or NO_2^- or others (Kuzawa et al. 2006; Banerjee and Chen 2007; Drenkova-Tuhtan et al. 2013). However, almost any of them provides information regarding the final disposal of such residues. In the present work, the adsorption cycles were repeated each time without washing or using any solvent to regenerate the adsorbent material because of the lack of strategies to the disposal of the generated residues. Hence, the protocol was adjusted to avoid the generation of extra pollutants. An exhaustive study of such strategies is currently in development and will be matter on a separated work.

The effect of recycling time on GMNPs on nutrient adsorption performance was repeated four times, and the results are shown in Fig. 4. The adsorption experiences were performed at pH = 7 and 30 min was the contact time taking into account the previous adsorption assays. The results are presented in terms of adsorption capacity (expressed as % of adsorption) as function of each cycle. As it can be observed, GMNPs exhibited excellent adsorption efficiency for both pollutants (NO_3^- and NO_2^-) along all cycles of reuse. In the first adsorption assay, the efficiency for nitrite adsorption was around 60%; meanwhile, it was of 15% for NO_3^-, from the initial available anion concentration. This tendency was observed for the kinetics adsorption assays previously discussed, where nitrites displayed huge adsorption efficiency with the time. The NO_3^- adsorption displayed a slight increase for the third cycle, which is almost improbable since the tendency in these materials is the pollutant occupies the active sites causing saturation of the surface and the consequent decrease in adsorption. This behavior could be possibly caused by desorption of NO_3^- at the third reuse cycle.

Figure 5 shows the adsorption kinetics of copper ion as model of heavy metal, on gum Arabic magnetic nanoparticles. The kinetic profile appears to be similar than the observed in the nutrients removal, that is, a fast initial adsorption in the first 10 min, reaching the maximum heavy metal uptake at 30 min of contact time. The maximum Cu^{2+} adsorbed was 90% with respect to the initially available heavy metal. A partial Cu^{2+} desorption was observed after 240 min of contact time. The fast initial adsorption may be justified in terms of the available active sites present in the surface of the GMNPs at the pH of the experiences. As it was previously reported

Fig. 3 FTIR spectra of GMNPsnanoparticles before and after nutrient adsorption: **a** complete spectra and **b** a region of the spectra interest
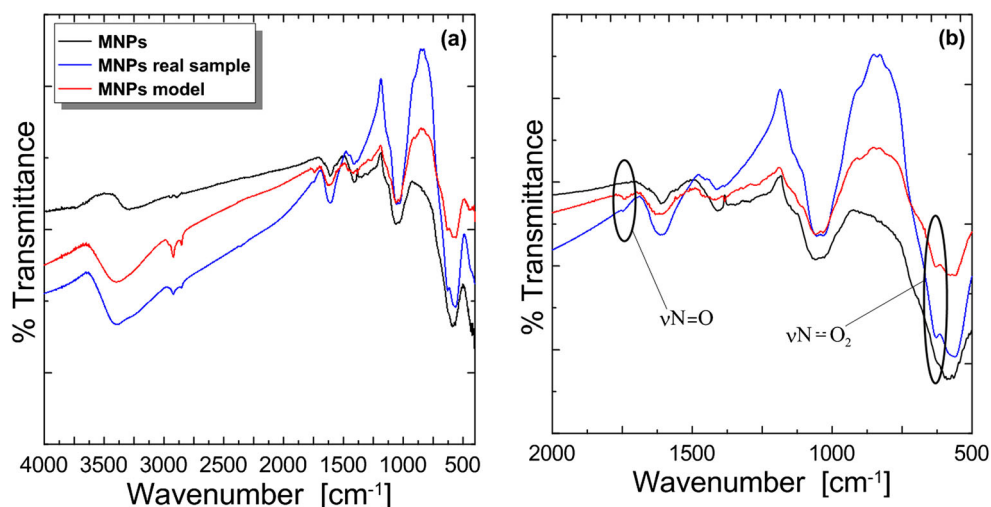

(Horst et al. 2016b), GMNPs nanoparticles display negative surface charge at pH > pH$_{pzc}$; then, strong electrostatic interactions are presumable ruling heavy metal adsorption on GMNPs adsorbent. Other authors observed an almost similar tendency by using comparable materials for heavy metal removal. For instance, Saravanan et al. (Saravanan et al. 2012) prepared gum Kondagogu-modified magnetic nanoparticles by co-precipitation method and tested them as adsorbent using a series of heavy metal ions. The adsorption assays were conducted at pH = 5 and 30 °C temperature. The efficiency adsorption for Cu^{2+} removal was around 94% for the available initial ions. Furthermore, in our previous published work, chitosan/magnetite nanocomposites were synthetized by co-precipitation methodology and the performance for heavy metal adsorption was tested using Cu, Cd, Zn, and Cr ions as heavy metal models. It was observed that adsorption efficiency depended on heavy metal assayed reaching an adsorption of 60% for Cu, Zn, and Cd, 39% for Cr. Besides, the

material demonstrated great possibilities of reuse for roughly eight cycles of heavy metal adsorption (Horst et al. 2016a).

Adsorption of heavy metals in synthetic wastewater of GMNPs In order to investigate the adsorption performance of GMNPs in a real polluted water sample, experimental adsorption assays were performed in a synthetic wastewater simulating its conditions. Table 1 shows the percentage of heavy metal ions adsorbed on GMNPs adsorbent.

From the data, it is evident that GMNPs is highly efficient in removing heavy metals from this simulated media. It is evident that the material displays a preference for the adsorption of certain heavy metal than others, which means there is a competition between the heavy metals for the active sites available on the material's surface. It was observed for Cu model adsorption an efficiency of 90% which diminishes to 70% in the presence of Cd, Zn, and Pb. The adsorption efficiency obtained for the other heavy metals showed

Fig. 4 Reuse of GMNPs nanoparticles on the adsorption of nutrient solution models
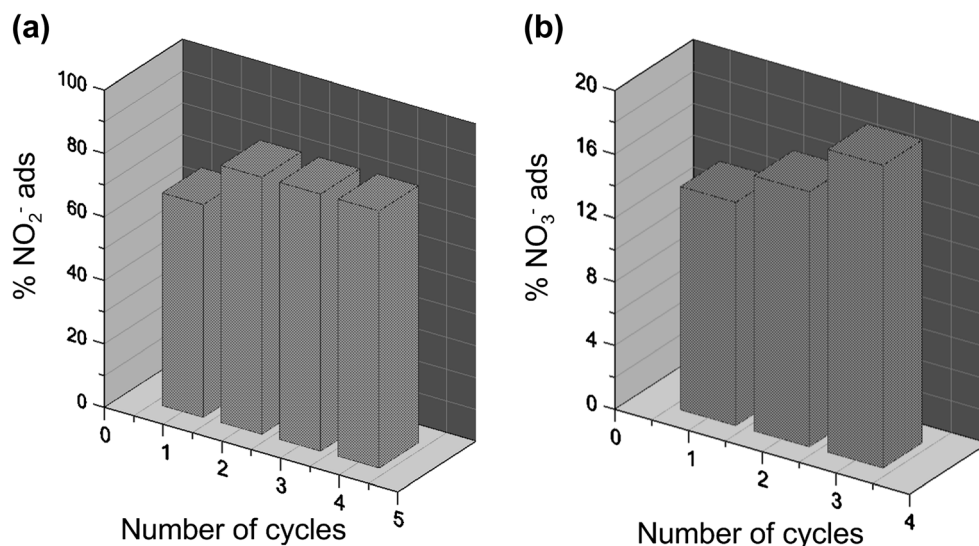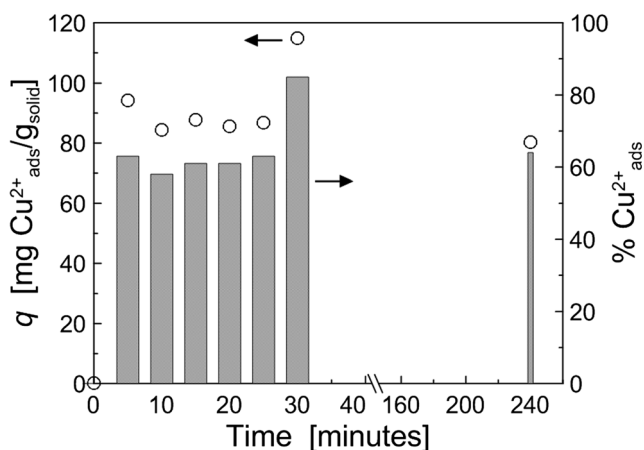
Fig. 5 Adsorption time profile of Cu on GMNPs nanoparticles using a model solution

appreciable differences so this is an evidence of the material selectivity for the heavy metals. The tendency of adsorption was as followed: Zn>Cu>Cd>Pb. Although the adsorption behavior for all single heavy metals was not presented in this study, it is evident that there is a combined action between such heavy metals which lead to a preferentially adsorption order of them. Some studies reported single and competitive adsorption in similar materials. For example, Zhu et al. (Zhu et al. 2012) studied the adsorption behavior of Pb, Cu, and Zn on xanthate-chitosan magnetic nanoparticles. The authors observed that the adsorption capacity followed the order Pb(II)>Cu(II)>Zn(II), which was consistent with the order in single system. In another study, a magnetic chitosan/cellulose microspheres were synthetized by sol-gel method and was tested for Pb, Cd, and Cu adsorption. The authors found the adsorption equilibrium reached at 60–80 min of contact time. And the order of selectivity for competitive conditions in multi-metal solution was Pb>Cd>Cu (Luo et al. 2015).

It is worth noting that the measured content of Fe after adsorption assays resulted higher than the initial concentration in the raw sample. This may be ascribed to a partial Fe release from the GMNPs under the assay conditions. Hence, even when the levels of adsorption reached using these GMNPs are highly suitable, the lack of stability under the assay conditions would considerably limit their practical implementation. Some strategies, such as crosslinking with a coupling

Table 1 Adsorption assays of simulated wastewater on GMNPs nanoparticles and FG

	Heavy metal	Cd	Cu	Pb	Zn	Fe
GA-MAG	% adsorption	60 ± 5	71 ± 2	11 ± 2	83 ± 1	*
FG	% adsorption	19 ± 5	nd**	nd**	4 ± 1	23 ± 3

nd not detected

*not reliable measurement, affected by the Fe leaching from GMNPs structure. **values reported by AA below the lower limit detectable

agent such as glutaraldehyde, may be performed to avoid or at least minimize the Fe leaching (Nicolás et al. 2014).

Adsorption of heavy metals and nutrient model solution on FG The adsorption performance of heavy metals in model solution on ferrogel was published and discussed in previously studies (Horst et al. 2017). From the obtained data, we can conclude that FG could be used as efficient material for heavy metal removal from water and wastewater. It was observed in the adsorption times assaying the material maintained its structure. There was no evidence of Fe leaching to the media in comparison with GMNPs. Some reports studied in similar systems found the adsorption of heavy metal, e.g., cadmium, and reported similar maximum values for Cd adsorption. For example, in chitosan and gum Arabic magnetic hydrogel, a Cd maximum adsorption of 50 m/g and 22 mg/g for maltodextrin magnetic hydrogel was reported (Paulino et al. 2011).

Figure 6 displays the adsorption kinetics of NO_3^- anion on ferrogel. A rapid adsorption during the first 5 min was observed, reaching the equilibrium state at already 30 min. The FG exhibited a great affinity for NO_3^- adsorption removing a maximum of 80% of the initial available anion. The kinetic profile observed in the NO_3^- removal is consistent with the corresponding to the heavy metal adsorption using FG (Horst et al. 2017). It is possible that absorption of NO_3^- was by diffusion inside the porous structure of the swelled ferrogel.

Adsorption of synthetic wastewater

The adsorption of synthetic wastewater on ferrogel is shown in Table 1. It can be observed that FG had satisfactory adsorption performance for heavy metal from this system. From the values obtained, it could be said that some heavy metal ions were adsorbed preferably for FG adsorbent. As well as for GA magnetic nanoparticles, there was a competition between the different species for the active sites of the ferrogel. Therefore, this could explain the relatively low values obtained for heavy metal comparing with model solutions. Besides, in the table, it can be observed from the reported (not detected) data that this could be explained by the low initial heavy metal concentration in simulated wastewater. The synthetic water was prepared emulating the probable heavy metal concentration found in real polluted water (that is low values), but after the adsorption process, the concentration of heavy metals could not be determined by the technique here employed, so nd values were reported. Although initial concentration could be determined, post-adsorption quantification was not possible.

The lower adsorption values found for heavy metals on FG in comparison with those obtained using GMNPs could be explained in terms of the physical structure of each adsorbent material. In GMNPs, the stabilization of magnetic nanoparticles due to the presence of coated-gum Arabic originates a
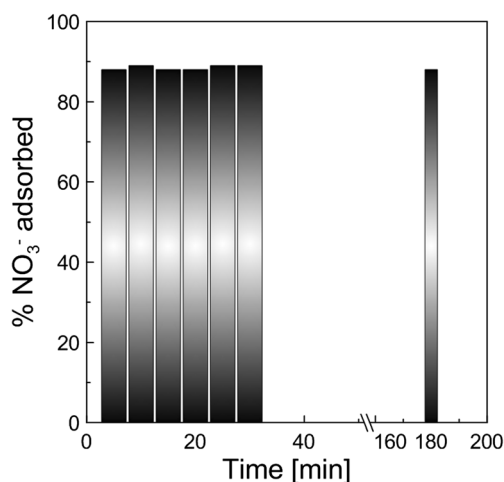
Fig. 6 Adsorption time profile of nitrates on FG using a model solution

Table 3 Nutrient determination in estuarine sample water and after adsorption assays

Pollutant	Initial concentration	FG % adsorbed	GMNPs % adsorbed
NO_2^-	0.43 (μmol L^{-1})	56	44
NO_3^-	0.24 (μmol L^{-1})	nd	29
Pb	0.022 (mg L^{-1})	47	36
Zn	0.016 (mg L^{-1})	–	44

nd not detected

well-water-dispersed material with wide possibilities to interact with the pollutants present in suspension, e.g., heavy metals. Besides, the hydrodynamic sizes in the nanoscale assure a higher contact surface area with the heavy metals in water (Ramimoghadam et al. 2014). As a difference, the entanglement structure of the FGs makes some active sites unavailable for heavy metal interactions. Besides, the presence of magnetic particles in the hydrogel matrix increases the degree of crosslinking and thereby hinders the diffusion of water-polluted heavy metal through the matrix gel (Paulino et al. 2011). This justifies the lower adsorption efficiency evidenced with FG in comparison with GMNPs. Although FGs displayed lower capacity for heavy metal removal from simulated polluted water, this material has the advantage that is more stable than GMNPs. The leaching of Fe was not registered after FG adsorption assays, whereas GMNPs provide different Fe concentrations to the aqueous solution after the period comprised in the assays. Table 2 displays comparative adsorption efficiency of different adsorbent materials with simultaneous heavy metals; the majority of the studies were performed by using a synthetic wastewater with heavy metal concentrations emulating real water.

Adsorption assays of seawater sample from Bahía Blanca estuary performed in FG and MNPs Anthropogenic activities frequently introduce elevated concentrations of heavy metals

and metalloids along with organic pollutants in the estuary. In particular, the BBE have been studied along the last decade regarding the incidence of pollutants present in the seawater, sediments, and environment (Popovich et al. 2008; Arias et al. 2011; Quintas et al. 2016).

Table 3 displays data regarding nutrients and heavy metal content in original water sample (seawater from BBE) and after adsorption assays using MNPs and FGs respectively. From the data, it is evident that both kinds of materials are efficient for the nitrite removal. The FG appears to be more efficient for nutrient removal. The NO_3^- values after FG adsorption remained lower than the detection limit suggesting a great efficiency of the adsorbent. The better capability of FG to eliminate the more critical contaminants from the BBE samples, in comparison to MNPs, seems to be contradictory regarding to the data obtained from adsorption assays employing model solutions. The justification is given by the additional species found in the real water sample that are unknown or not measured in the current work, but certainly may compete with nutrients or selected heavy metal for MNP interactions. This phenomenon mainly affected the behavior of MNPs because of their great reactivity in aqueous dispersion.

The conventional water treatments for estuarine ambient involves the bioremediation, such as phytoremediation, microalgae ponds, and photosynthetic bacteria treatment (Oyetibo et al. 2017). Most of these techniques lead to higher efficiency in comparison with the data arising from the materials here proposed. However, most of them involve high-associated fees and the generation of extra residues (Figueiredo and Quintelas 2014; Jadhav et al. 2014; Chen et al. 2015; Carolin et al. 2017; Meng et al. 2017).

Table 2 Comparative adsorption performance of some heavy metals by different materials in synthetic wastewater

Adsorbent material	Cu (%)	Pb (%)	Cd (%)	Zn (%)	Reference
Nanocrystals ZnS	99	90	66		(Fang et al. 2018)
Starch-PAA hydrogel	93	94	99		(Zhou et al. 2016a)
Polyampholyte hydrogel	31	99	99	44	(Zhou et al. 2016b)
Clinoptilolite-Fe	99			99	(Doula 2009)
Gum Arabic-Fe3O4 nanoparticles	71	11	60	83	This work
Ferrogel			19	4	This work

From a comparative point of view, the works in open literature devoted to the use of nanomaterials for water remediation employing real samples are very limited.

A recent study reported the use of coal cinders and zeolite powders with polyvinyl alcohol (PVA) for ammonia nitrogen and organic pollutants adsorption in aquaculture water in estuarine wetlands. The informed adsorption efficiencies ranged 70% for both parameters evaluated (Tian et al. 2016). Another recent work studied the use of zero valent iron nanoparticles for the remediation of soil and water of aquifer industrial area named Barreiro, located in Portugal, confirmed that the uses of this nanomaterial could reduce almost 60% of heavy metals (Zn, Cu, Pb, As), sulfates, and NO_3^- present in the soil and water (Gonçalves 2016). The commented researches reported results comparable with the values reached within this work, in terms of the efficiency of the prepared materials as adsorbents in real water samples.

Concluding remarks

Magnetic materials are presented as alternative to the traditional treatments of nutrients and heavy metals in water. Magnetic gum Arabic nanoparticles demonstrated to be more efficient adsorbent material of heavy metals from simulated polluted water than ferrogel. Besides, GMNPs could be instable during the adsorption process due to the leaching of Fe to the media. For this reason, ferrogel have adequate adsorption properties and great stability to be used for practical application. Despite this, ferrogel and magnetic nanoparticles demonstrated to be efficient for heavy metal and nutrient removal in estuarine water sample based on the obtained results arising between 40 and 60% of efficiency removal for heavy metals and nutrients. So the ferrogel and nanoparticles here designed appear as efficient and competitive, from the economical point of view, to contribute to the solution of a real local problem. The removal levels are comparable with those reached using more complex, less efficient, and more expensive technologies. As these materials are suitable for the removal of the mentioned pollutants of interest, they could retain other species or compounds that were not considered in this study. The possibility of reuse for repeated adsorption cycles without using any eluent offers great potential for water treatment plants.

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