

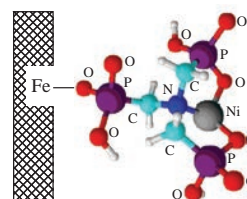
Organophosphonate-functionalized nanosized magnetic iron oxides as sorbents for heavy metal cations

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The surface of synthetic magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles was modified with phosphonic chelating compounds, 1-hydroxyethane-1,1-di(phosphonic acid) and nitrilotris(methylenephosphonic acid). The sorption affinity of functionalized magnetic iron oxides towards Ni^{II} under acidic conditions was increased by one order of magnitude.



The widespread and non-toxic magnetic iron oxides (MIO), magnetite Fe_3O_4 and maghemite $\gamma\text{-Fe}_2\text{O}_3$, can be used as sorbents for toxic metal ions. The use of nanosized MIO for the efficient removal of Pb^{II} , Cd^{II} , Cu^{II} , Hg^{II} , Zn^{II} , Ni^{II} , Co^{II} , Cr^{III} , Cr^{IV} , As^{III} , etc. from aqueous systems (natural waters/waste waters) has been reported.^{1,2} The major advantage of MIO as compared to other inorganic sorbents is the facile magnetic separation from an aqueous phase by applying an external magnetic field, which significantly reduces the overall cost of water treatment. The sorption and magnetic characteristics of MIO depend on their particle size and stability towards aggregation, which may be controlled by the particle preparation method, including the type and amounts of coating/stabilizing agents.^{3,4} To further enhance sorption characteristics, the $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ surface modification was performed with different organic molecules/biopolymers, which contain ligand functional groups (COOH, SH, OH, and NH_2).^{1,5,6} Although the strong binding affinity of phosphonic acids and their derivatives to different metal oxides is well-known,^{7,8} these modifiers have rarely been applied for the functionalization of MIO surfaces.⁹ Thus, the present work was aimed at the development of method for the covalent binding of chelating compounds *via* reactive phosphonic group(s) to synthetic nanosized Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ and at the characterization of sorption capability of modified MIO. We have selected Ni^{II} for sorption experiments, since it is a typical hazardous heavy metal cation found in the polluted aqueous systems.

Synthetic Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were obtained by the co-precipitation method[†] according to the known procedures.¹⁰ The morphology of MIO nanoparticles was examined by SEM method (Figure S1, Online Supplementary Materials). The crystallography identity of synthesized MIO was confirmed by the powder X-ray diffraction spectra (Figure S2). The mean particle

size calculated according to the Scherrer equation using the broadening of the most prominent peak (*ca.* $\theta = 20^\circ$) was 30.2 ± 0.1 nm for both Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$. The BET surface areas measured by four-point N_2 sorption at 77 K were: 36.8 ± 4.1 $\text{m}^2 \text{g}^{-1}$ (Fe_3O_4) and 35.7 ± 3.3 $\text{m}^2 \text{g}^{-1}$ ($\gamma\text{-Fe}_2\text{O}_3$).[‡]

For the surface modification of MIO, two phosphonic chelators were used: 1-hydroxyethane-1,1-diphosphonic acid (HEDP, H_4L) and nitrilotris(methylenephosphonic acid) (NTP, H_6L).[§] Chemical modification and further sorption studies were performed for both Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ to reveal the influence of the possible Fe_3O_4 oxidation on the obtained results. HEDP/NTP-modified $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$, similar to the parent unmodified oxides, can be easily separated from aqueous suspensions by a hand-held magnet. The phosphonate modification layer with a coverage of $0.2\text{--}0.4$ mmol g^{-1} (3–6 groups per nm^2) was stable at $\text{pH} < 8$. According to the thermal analysis (Figure S4), surface-bound phosphonate was decomposed at temperatures above $200\text{--}250$ °C.

The FTIR spectra[¶] of HEDP/NTP-modified MIO, as distinct from that of pure MIO, contains a strong absorbance in the region of $800\text{--}1300$ cm^{-1} , where the phosphonic groups $\text{PO}(\text{OH})_2$ are active (Figures 1 and S5). The bands were assigned on the basis of ATR-FTIR results reported previously for HEDP/NTP in an aqueous solution and bound to aluminium oxides.^{11,12} A significant difference in the number and position of bands was observed between free and surface-bound HEDP/NTP. The detected characteristic bands of phosphonic groups of pure HEDP/NTP are due to the phosphoryl $\text{P}=\text{O}$ vibrations [1170 cm^{-1} (HEDP)

[‡] The BET surface areas were measured using a Sorbi-M[®] analyzer.

[§] Commercially available HEDP and NTP (Zschimmer and Schwarz, Cublen[®] seria, Product K 60 and AP 1) were used. The weighted amount of MIO was treated with a 20 mM aqueous solution of phosphonic acid (1 mmol of HEDP/NTP per 1 g of MIO) under different conditions: incubation time from 30 min to 24 h, temperatures $20\text{--}80$ °C, and solution acidity ($\text{pH} 2\text{--}11$). The amount of surface-bound phosphonate was calculated by determining the remaining concentration of phosphonate in the solution after MIO treatment using the spectrophotometric method (blue-molibdenum test for inorganic phosphate after organophosphonate oxidative digestion). The highest surface was achieved at $60\text{--}80$ °C for 2–6 h at $\text{pH} 2\text{--}3$ (Figure S3).

[¶] The FTIR spectra were recorded at room temperature in KBr tablets using an FSM 2201 spectrometer.

[†] Magnetite Fe_3O_4 was prepared by mixing hot (75 °C) alkaline solution of KNO_3 (0.3 g of KNO_3 and 4.0 g of KOH in 300 ml of water) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (10.0 g in 750 ml of water) followed by heating at 90 °C for 10 min ($3\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{KNO}_3 + 6\text{KOH} = \text{Fe}_3\text{O}_4 + \text{KNO}_2 + 24\text{H}_2\text{O} + 3\text{K}_2\text{SO}_4$). Black precipitate was washed with distilled water, filtered and dried at 75 °C. Further heating of magnetite at 350 °C for 2 h resulted in a brown-colored maghemite ($4\text{Fe}_3\text{O}_4 + \text{O}_2 = 6\gamma\text{-Fe}_2\text{O}_3$). Both oxides can be easily separated from an aqueous solution using a permanent hand-held magnet.

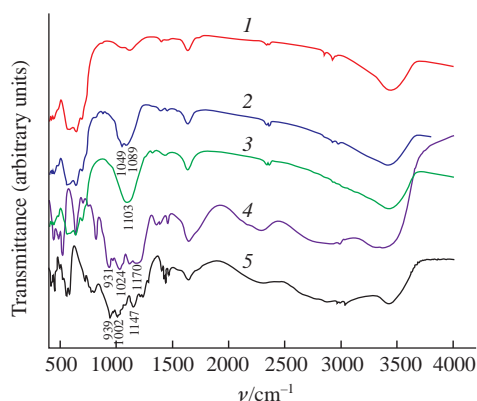


Figure 1 FTIR spectra of (1) γ - Fe_2O_3 , (2) HEDP- γ - Fe_2O_3 , (3) NTP- γ - Fe_2O_3 , (4) HEDP, and (5) NTP.

and 1147 cm^{-1} (NTP)], vibrations of P–O bonds in PO_3^{2-} and HPO_3^- (series of bands near $\sim 1000\text{ cm}^{-1}$), and P–OH vibrations [931 cm^{-1} (HEDP) and 939 cm^{-1} (NTP)]. Upon HEDP/NTP binding onto the surface of MIO, P=O and P–OH bands disappeared and a band assigned to P–OFe vibrations [1049 , 1089 (HEDP), and 1103 cm^{-1} (NTP)] of deprotonated PO_3^{2-} group arised instead of them. Thus, all the phosphonic groups of HEDP/NTP are equivalent in dried samples (KBr tablets) and bound to the MIO surface.

The acid–base properties^{††} of modified MIO were different from those of unmodified MIO (Figures 2 and S6). In the case of pure Fe_3O_4 , the calculated acidity constants (non-electrostatic surface model) for the dissociation of surface OH groups (Table 1) and zero point charge ($\text{pH}_{\text{ZPC}}\ 7.6 \pm 0.1$) were in good agreement with published data.¹⁰ Titration curves for HEDP/NTP-modified MIO can be successfully modelled assuming the mononuclear monodentate binding of the phosphonic group to a surface $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ atom. The obtained results (see Table 1) revealed that the basicity of Fe_3O_4 -bound phosphonic acids is decreased by one unit as compared to their solution behavior. Thus, the titration results suggest that the binding of HEDP/NTP to the MIO surface in an aqueous environment occurs only *via* the one phosphonic group, while other functional group(s) are available for protonation and complexation reactions. A similar conclusion was made for HEDP/NTP adsorbed on goethite [α - $\text{FeO}(\text{OH})$]¹³ and boehmite [γ - $\text{AlO}(\text{OH})$].¹⁴

The new functional groups on the modified MIO surface were expected to promote the binding of metal cations, since the

Table 1 Equilibrium constants describing the acid–base properties of Fe_3O_4 and modified Fe_3O_4 .

Surface dissociation reaction ^a	pK		
	Fe_3O_4	HEDP- Fe_3O_4	NTP- Fe_3O_4
$\equiv\text{FeOH}_2^+ \rightleftharpoons \equiv\text{FeOH} + \text{H}^+$	5.4 ± 0.1		
$\equiv\text{FeOH} \rightleftharpoons \equiv\text{FeO}^- + \text{H}^+$	9.9 ± 0.1		
$\equiv\text{Fe-LH}_5 \rightleftharpoons \equiv\text{FeLH}_4 + \text{H}^+$			4.5 ± 0.2
$\equiv\text{Fe-LH}_4 \rightleftharpoons \equiv\text{FeLH}_3 + \text{H}^+$			7.1 ± 0.2
$\equiv\text{Fe-LH}_3 \rightleftharpoons \equiv\text{FeLH}_2 + \text{H}^+$		6.6 ± 0.1	8.5 ± 0.2
$\equiv\text{Fe-LH}_2 \rightleftharpoons \equiv\text{FeLH} + \text{H}^+$		7.6 ± 0.1	9.5 ± 0.1
$\equiv\text{Fe-LH} \rightleftharpoons \equiv\text{FeL} + \text{H}^+$		9.3 ± 0.1	10.4 ± 0.1

^a The charge of surface $\equiv\text{Fe-LH}_i$ is omitted for simplicity. The symbol ' $\equiv\text{Fe}$ ' used herein designates a Fe atom belonging to the surface of a nanoparticle.

^{††} The suspension of MIO (1 g dm^{-3} , 25 ml) in a 0.1 M KNO_3 solution was slowly titrated potentiometrically with a 0.01 M KOH solution under constant stirring with the simultaneous recording of pH values. The Hyperquad 2008 software was used for the mathematical processing of the obtained titration data.

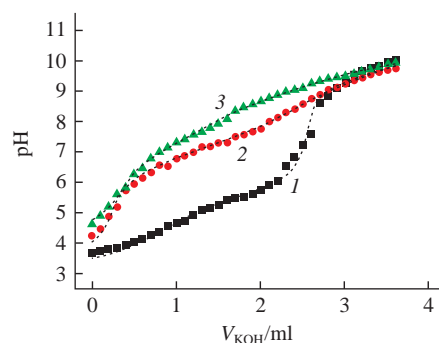


Figure 2 Acid–base titration curves for (1) Fe_3O_4 , (2) HEDP- Fe_3O_4 , and (3) NTP- Fe_3O_4 . These curves are drawn using the constants indicated in Table 1.

utilized phosphonic acids are well-known metal chelators in the solutions.¹⁵ Sorption experiments were performed with Ni^{II} as a model cation representing other metal contaminants of water.^{††} The pH-effect revealed that Ni^{II} sorption onto Fe_3O_4 is small at $\text{pH} < \text{pH}_{\text{PZC}}$ (Figure 3). A further sharp increase in Ni^{II} sorption was observed inside a narrow pH-range ($\text{pH}\ 6\text{--}8$) due to the formation of inner-sphere surface complex $\equiv\text{FeONi}(\text{OH})_2^-$ as was previously found from modelling of Ni^{II} sorption on the Fe_3O_4 surface.¹⁶ The affinity of Ni^{II} to the magnetite surface is much weaker in comparison with other heavy metals. This can be deduced from the pH values for 50% sorption,¹⁷ which increase in the series of Pb^{II} ($\text{pH}_{50}\ 4.8$) > Cu^{II} ($\text{pH}_{50}\ 5.3$) > Cd^{II} ($\text{pH}_{50}\ 6.3$) > Ni^{II} ($\text{pH}_{50}\ 6.8$). In the case of HEDP/NTP-modified Fe_3O_4 at $\text{pH}\ 5\text{--}7$, Ni^{II} sorption was much stronger as compared to the unmodified sorbent (up to a tenfold increase in the distribution coefficient). A similar increase in Cu^{II} and Cd^{II} sorption was earlier observed for NTP-modified Fe_3O_4 and γ - Fe_2O_3 .¹⁷ Thus, the modified MIO at optimal acidic pH can be used in real systems (natural/industrial waters) to separate heavy metal cations from Ca^{II} and Mg^{II} , which are not adsorbed under these conditions and commonly present at high concentrations. The maximum adsorption capacity of modified MIO towards the investigated heavy metals estimated from sorption isotherms (Figure S7) is $0.2\text{--}0.4\text{ mmol g}^{-1}$, which is comparable to other metal oxides applied for metal removal.^{1–3}

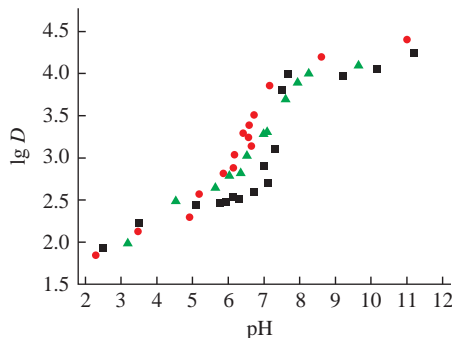


Figure 3 Distribution coefficient ($\lg D$) for Ni^{II} ions as a function of the solution pH for (■) Fe_3O_4 , (●) HEDP- Fe_3O_4 , and (▲) NTP- Fe_3O_4 .

^{††} A sorbent (20 mg) was placed into an aqueous solution (20 ml) containing $\text{Ni}(\text{NO}_3)_2$ (0.1 mM) and KNO_3 (0.1 mM). The mixture was then adjusted to a certain pH by adding KOH or HNO_3 and shaken for 60 min (this equilibration time was determined from preliminary investigations). After removal of the sorbent with a magnet, the final pH was measured and the concentration of Ni^{II} was determined spectrophotometrically (Ni^{III} dimethylglyoximate formation in alkaline solution). The distribution coefficient of Ni^{II} ($D/\text{cm}^3\text{ g}^{-1}$) was calculated from the degree of sorption [$R = (C_0 - C)/C_0$, where C_0 and C are the initial and remaining after sorption concentrations, respectively] and known values of sorbent mass (m) and solution volume (V): $D = RV[(1-R)m]^{-1}$.

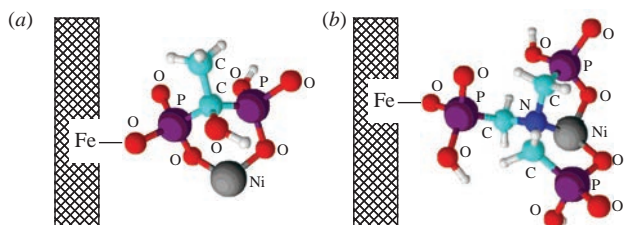


Figure 4 Schematic representation for Ni^{II} binding to modified magnetic iron oxides, (a) HEDP–MIO and (b) NTP–MIO.

All the obtained results suggest that phosphonic group(s) of HEDP/NTP-modified Fe₃O₄/γ-Fe₂O₃ may participate in complexation reactions in an aqueous environment. HEDP- or NTP-modified MIO may act as effective chelating sorbents to coordinate metal cations *via* the formation of stable 5- or 6-membered rings, respectively (Figure 4).

In conclusion, the modification of surface of Fe₃O₄ and γ-Fe₂O₃ synthetic nanoparticles with chelating organophosphonates enhances their sorption capability towards heavy metal cations under acidic conditions. This is a promising approach to resolve an urgent problem of the easy and selective recovery of toxic heavy metals from natural waters/waste waters. These new, easy synthesized complexing sorbents demonstrate a great advantage over similar known sorbents (ligand-modified silica, chelating resins, *etc.*) due to the opportunity to easily perform magnetic separation for their recycling or regeneration. The developed method for the surface functionalization of magnetic iron oxides with chelating molecules may also be employed for design of new MIO materials for other applications.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.05.040.

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