Hybrid porous phosphate heterostructures as adsorbents of Hg(II) and Ni(II) from industrial sewage

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ABSTRACT

Porous phosphate heterostructures (PPH), functionalized with different ratios of aminopropyl and mercaptopropyl groups, labelled as $N_{x=5,25,50}$-PPH and $S_{x=5,25,50}$-PPH, respectively, were tested as adsorbents for Ni(II) and Hg(II) found in industrial sewage from electroplating processes and button battery recycling. X-ray diffraction was used to study the structures. The specific surface area of the pristine material (PPH) was $620\,m^2\,g^{-1}$, whereas the specific surface areas of the modified mercaptopropyl (S_5-PPH) and aminopropyl (N_5-PPH) were 472 and $223\,m^2\,g^{-1}$, respectively. The adsorption data were fitted to a Langmuir isotherm model. The S_5-PPH material was saturated by 120 mmol Hg(II) per 100 g of material, whereas for Ni(II) adsorption, N_{25}-PPH material displayed the highest adsorption with a saturation value of 43.5 mmol per 100 g. These results suggest that functionalized PPH materials may be promising toxic metal scavengers and that they may provide an alternative environmental technology.

1. Introduction

Environmental pollution due to toxic metals is a current concern. Although some metals are necessary in different life cycles, a high concentration in the water or soil may represent a serious threat to human health, natural resources and ecological systems [1], requiring an immediate solution. Certain industrial sectors, such as the metal finishing industry, are responsible for most of the environmental pollution by toxic metals. These metals are dangerous due to their persistence in the environment. The main contamination source is the emission of sewage, with relatively low concentrations of harmful metals including Cr(VI), Ni(II), Zn(II), Cu(II) and Cd(II). These metals must be removed from the sewage before their release into the environment being their selective clean-up an emerging area of interest [2].

Nowadays, new techniques are focused on adsorption processes because they are more economical than other previously employed, such as precipitation [3,4], ionic exchange [5–7], ultra-filtration [8] and reverse osmosis [9,10]. Adsorption processes also suppose an efficient approach for use in the heavy metal remediation of wastewaters. Granular activated carbon is widely used for water purification [11,12], as well as alumina [13,14]; however, they are not economically attractive due to their high operating costs.

Clays [15,16], zeolites [17,18], natural biopolymers such as chitosan [19,20], polypeptides [21], humic substances [22], and phytoremediation [23] are other alternatives which are currently under study, although their selectivity has been found to be low.

Another group of interesting adsorbents is that of functionalized mesoporous materials because of their attractive properties, such as a high level of heavy metal removal, large surface area, narrow pore size distribution and the specificity of the chelating agents inserted in the network. Among these materials, MCM-41 [24,25], MCM-48 [26], SBA-15 [27,28], and porous clay heterostructures (PCH) [29], strategically functionalized with organic groups are under study. The use of porous phosphate heterostructures (PPH) functionalized with different organic groups has been proposed for heavy metal removal. These porous solids are prepared by combining pillared layer structures (PLS) and MCM-41 mesoporous solid synthetic routes, where zirconium phosphate is previously expanded and later the formation of silica galleries takes place in the interlayer region.

Applications of PPH in environmental catalysis include the selective reduction of NO_x, hydro-treating processes and catalytic oxidation of H_2S to sulphur [30–32], to avoid their emission into the atmosphere. Other applications of PPH include the separation of propane and propene [33], and inorganic membranes [34].

In the present work, PPH materials were evaluated for the removal of Ni(II) and Hg(II) from the sewage of electroplating and button battery recycling industries.

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2. Materials and methods

2.1. Synthesis of N_x-PPH and S_x-PPH adsorbent materials

2.1.1. Synthesis of N_x-PPH

Cetyltrimethylammonium (CTMA)-expanded zirconium phosphate was prepared from a solution of CTMA-Br in 1-propanol, H_3PO_4 (85%) and zirconium(IV) propoxide (70%) according to previously reported procedures [35]. The cetyltrimethylammonium-ZrP (CTMAZrP) obtained was suspended in water ($10\,g\,L^{-1}$) and a solution of hexadecylamine in 1-propanol (0.145 M) was added as a co-surfactant. After one day of stirring, a solution (50%, v/v in 1-propanol) of tetraethylorthosilicate (TEOS) and the corresponding aminopropyl triethoxysilane (APTEOS) with TEOS/APTEOS (hereafter called TEOS/N) molar ratios of 5, 25 and 50 was added, and in each case the resulting suspension was stirred at room temperature for three days. Because of the fast hydrolysis of APTEOS, an alternative method of synthesis was carried out for the material with the lowest TEOS/N molar ratio by using 1-propanol as a solvent instead of water. Then, the obtained solids were centrifuged, washed with ethanol, and dried at room temperature. In this case, the surfactant molecules used as templates of silica galleries in the interlayer spaces could not be removed by calcinations in order to avoid degradation of the amino groups. Therefore, an acid extraction with HCl:ethanol (1:10 v/v) was performed three times to assure the total extraction of surfactants. After this, the solid was washed with ethanol and dried at room temperature. The solids were denoted as N_x-PPH, where x is the added TEOS/N molar ratio. All reagents used were purchased from Sigma–Aldrich.

2.1.2. Synthesis of S_x-PPH

The preparation of a hybrid porous phosphate heterostructure functionalized with a 3-mercaptopropyl group was carried out following a method to that described for N_x-PPH. In this case, as the hydrolysis rate of mercaptopropyl-trimethoxysilane (MPTMS) is similar to that of TEOS, only water was used as a solvent. Three solids were also obtained by varying the added TEOS/MPTEOS (hereafter called TEOS/S) molar ratios: 5, 25 and 50. The solids were denoted as S_x-PPH, where x is the added TEOS/S molar ratio.

2.2. Adsorption experiments for nickel and mercury in pure water and sewage samples

For the Ni(II) adsorption studies, the N_x-PPH materials were previously treated with NaOH (0.1 M) to reach pH 7, due to the fact that the resulting structures (see Section 2.1.1) with HCl:ethanol (1:10 v/v) the amino groups were protonated and became inactive as ligands for Ni(II) adsorption. Then, the solid was separated by centrifugation, washed twice with deionized water and dried at 333 K for 24 h. The Ni(II) adsorption was carried out by stirring

0.3 g of the adsorbent in an adequate volume of a Ni(II) aqueous solution 1.70 mM for a period of 24 h, at room temperature and in stoppered flasks in order to achieve equilibrium conditions. Different Ni/N ratios were used to test the sorption of Ni(II) by the adsorbents. As the next step, the solid was separated by centrifugation and the metal content adsorbed by the solid was determined using inductively coupled plasma spectrometry (ICP). For this purpose, the solids were dissolved in 0.2 mL of hydrofluoric acid (40%) at room temperature and diluted to an adequate concentration for ICP analysis. The same procedure was carried out for the wastewaters from the electroplating industry. All assays were carried out in triplicate and only the average values are presented. For the Hg(II) extraction, different Hg/S ratios were studied for the adsorption process of Hg(II) 0.1 mM in pure water, following the same procedure as for Ni(II).

2.3. Sewage samples

Wastewater from an electroplating industry (Progaelectric S.A. situated in Montilla, Córdoba (Spain)) was used to test the efficiency of N_5-PPH as a sorbent. The S_5-PPH sorbent was tested using wastewater from a button battery recycling company located in the same area.

2.4. Data analysis

The equilibrium adsorption isotherm data of M(II) at different concentrations were analyzed using the Langmuir adsorption expression (Eq. (1)):

$$\frac{C}{Q} = \frac{1}{bQ_0} + \frac{C}{Q_0} \tag{1}$$

where Q is the adsorption capacity (mmol/100 g), C is the equilibrium concentration of the M(II) solution (mM), Q_0 is the saturated adsorption capacity (mmol/100 g) and b is an empirical parameter ($L\,mmol^{-1}$).

3. Results and discussion

3.1. Characterization of the sorbent materials

After removal of the organic surfactants, a porous solid was generated with a porosity that is mainly due to the inner silica galleries. Several porous materials were obtained with physical and chemical properties depending of the nature and the amount of organosilyl derivative incorporated (Table 1). This can be explained by the different hydrolysis rates and the basicity of the respective precursors.

Table 1 also summarizes the d_{001} basal space obtained from the corresponding XRD data (Supplementary information). All the solids showed a reflection line at a low angle centered at 40 Å, which

Table 1
Characteristics of the different materials synthesised and Langmuir relationship.

Material	R group content (mmol/100 g)	d_{001} (Å)	S_{BET} ($m^2\,g^{-1}$)	Vp[a] ($cm^3\,g^{-1}$)	dp[a] (Å)	[b]M(II) taken up (mmol/100 g)	[c]Q_0 (mmol/100 g)	[c]b (L/mmol)	R_L^2
PPH	–	40	620	0.543	30.9	–	–	–	–
S_5-PPH	78.1	40	472	0.513	37.9	120.0	123.5	810	0.9995
S_{25}-PPH	18.0	40	506	0.521	37.8	28.4	29.7	421	0.9974
S_{50}-PPH	8.1	44	537	0.522	36.8	17.8	18.8	531	0.9971
N_5-PPH	156.4	–	223	0.411	63.9	28.1	25.6	2.49	0.9506
N_{25}-PPH	36.1	40	355	0.437	47.5	43.5	47.6	7.78	0.9978
N_{50}-PPH	21.7	42	556	0.618	37.4	37.6	43.9	5.85	0.9909

[a] Using Cranston and Inkley method (Supplementary information).
[b] M(II) = Hg(II) for S_x-PPH materials and Ni(II) for N_x-PPH materials.
[c] Langmuir parameters obtained at 298 K. Q_0 is the saturated adsorption capacity, b is an empirical parameter and R_L^2 the regression coefficient obtained from the Langmuir model.

indicated the separation between two zirconium phosphate layers occupied by the silica galleries. No diffraction peak was detected in the case of N5-PPH, which was probably due to an irregular formation of the silica galleries, caused by the large amount of APTEOS added and its fast hydrolysis. In the case of S$_x$-PPH, the structure is not affected due to the similar hydrolysis rate of MPTMS and TEOS and the lower incorporation of mercaptopropyl groups in comparison with the respective aminopropyl groups, as is deduced from the amount of each group present in the materials (see Table 1 and Fig. 4).

Textural parameters were obtained from the N$_2$ adsorption–desorption isotherms at 77 K. These isotherms were of type IV (Supplementary information), typical of mesoporous materials. In all cases, a decrease in the Brunauer–Emmett–Teller (BET) surface area was noted with respect to the pure silica PPH material (620 m^2 g^{-1}). The BET surface area decreased upon the incorporation of increasing amounts of the mercaptopropyl and aminopropyl groups. For example, the lowest BET surface areas were found for the solids with the highest contents of functionalized groups (S5-PPH: 472 m^2 g^{-1} and N5-PPH: 223 m^2 g^{-1}). This decrease in the BET surface area was more prominent in the case of aminopropyl groups, due to the resulting structures were less crystalline, as observed in the XRD diffractograms (Supplementary information). The average pore size values indicated that mesopores were present. This mesoporosity was derived from the silica galleries or from the large diameter of the pores formed by the stacked packets of layers.

These results indicate that different porous hybrid materials were obtained. As the corresponding organic groups were accessible, they could interact with different chemical species and thus be used as potential selective adsorbents. Thus, the adsorption of Ni(II) and Hg(II) was tested for N$_x$-PPH- and S$_x$-PPH type-materials, respectively, and their application on industrial wastewaters.

3.2. The adsorption isotherms of Ni(II) by N5-, N25- and N50-PPH

The behaviour of N5-, N25- and N50-PPH as adsorbents in the adsorption of Ni(II) at 25 °C was investigated. Fig. 1a and b shows the fitting of the experimental adsorption data to adsorption isotherms. The incorporation of an aminopropyl group on the silica galleries walls permits the adsorption of chemical species which can selectively interact with this amino group. This was the case for the Ni(II) cations, which easily formed complexes with the amino group displacing the water molecules from its coordination shell.

Table 1 summarizes the contents of the functional groups in mmol per 100 g for each solid. For each of the adsorbents, the Ni(II)/N molar ratios added of 0.1–5 were tested. The results are shown in Fig. 1a where, surprisingly, the sorbent with the highest amount of the aminopropyl group displayed the lowest adsorption.
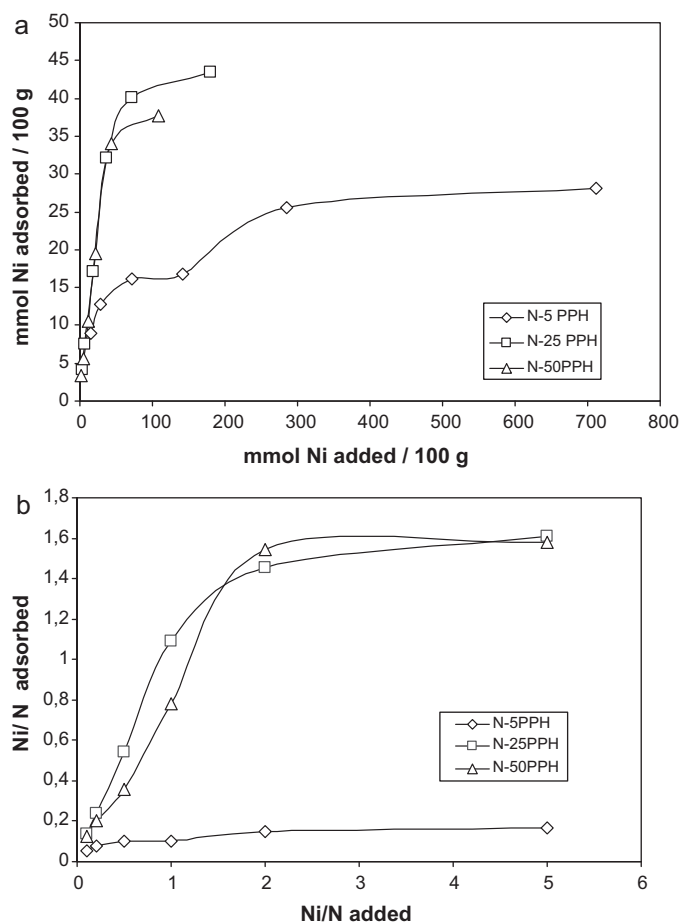

Fig. 1. (a) Ni(II) adsorption isotherms expressed in relation to mmol Ni(II) adsorbed for 100 g of sorbent. (b) Ni(II) adsorption isotherms expressed in relation molar ratio Ni/aminopropyl groups retained.

This fact can be explained considering the low BET surface area of this solid (Table 1). In contrast, a high number of aminopropyl groups were accessible to Ni(II) ions in the case of the N50-PPH sample, which had the highest BET surface area. Therefore, in the case of N5-PPH adsorbent, many of these organic groups could not retain Ni(II) because they were blocked in the inner pores. On the other hand, when the molar ratios of Ni(II)/N added are plotted versus the molar ratios of Ni(II)/N adsorbed (Fig. 1b), the value of the Ni(II)/N molar ration adsorbed is higher than 1 for N$_{x=25,50}$-PPH. This indicates that other ion exchange sites such as PO–H and SiO–H groups were available in the pores. As these acid sites were neutralized when a NaOH solution was added to activate the amino-
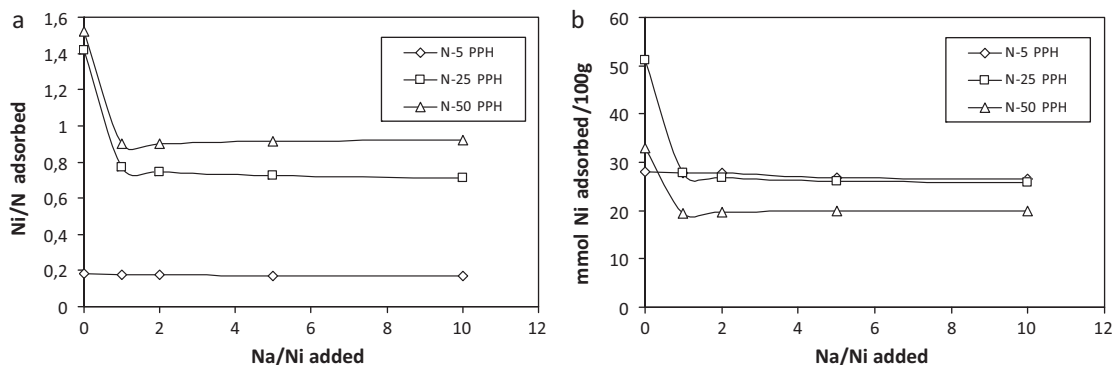

Fig. 2. (a) Effect of Na$^+$ addition in Ni/N molar ratio adsorbed. (b) Effect of Na$^+$ addition in the mmol Ni adsorbed/100 g sorbent.
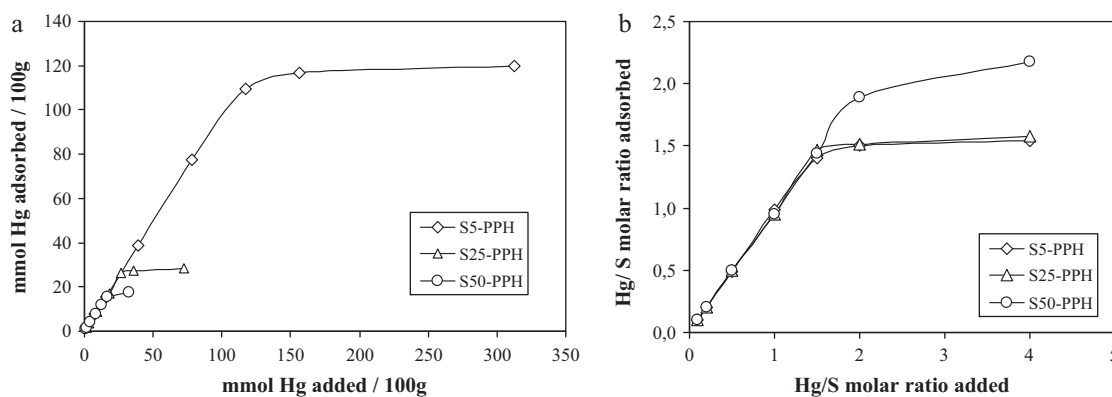
Fig. 3. (a) Hg(II) adsorption isotherms expressed in relation to mmol Hg(II) adsorbed for 100 g of sorbent. (b) Hg(II) adsorption isotherms expressed in relation to molar ratio Hg/mercaptopropyl group retained.
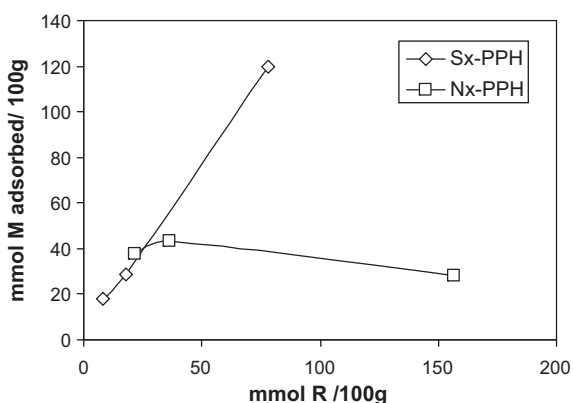

Fig. 4. Relation between Ni^{2+} and Hg^{2+} adsorption with the amount of organic groups(R) on N_x-PPH and S_x-PPH materials.

propyl group, these exchange centres became present as $Na^+ PO^-$ and $Na^+ SiO^-$. Unlike the aminopropyl groups, these exchange sites were not selective and when other cations were present (i.e. alkaline ions), they were also adsorbed by these sites, decreasing the Ni(II) adsorption capacity. In order to evaluate this effect on the cationic exchange capacity for Ni(II), different Na/Ni molar ratios were added for each adsorbent up to the Ni/N molar ratio saturation point. In this case, the Ni/N molar ratio adsorbed of samples N_{25}-PPH and N_{50}-PPH decreased from 1.6 to nearly 1.0 (Fig. 2a), whereas for N_5-PPH, it remained almost constant, around 0.15, indicating that for this latter material complexation was the main process for the Ni(II) adsorption. This aspect would be an important consideration for the application of these materials in wastewater treatment due to the presence of many chemical species together to Ni(II), as is the case for electroplating and Ni(II) bath plating wastewaters. Fig. 2b shows the mmol of Ni(II) adsorbed per 100 g as a function of the amount of Na^+ added. Ni(II) adsorption by N_5-PPH material is not influenced by Na^+ presence.

3.3. The adsorption isotherms of Hg(II) on S_5, S_{25} and S_{50}-PPH

The adsorption capacity of hybrid heterostructures functionalized with mercaptopropyl groups was tested against Hg(II) ions [36]. A similar adsorption procedure, as described in the previous section, was carried out. Table 1 shows the maximum values of Hg(II) obtained from the corresponding Hg(II) adsorption isotherm presented in Fig. 3a and b. In this case, the adsorption of Hg(II) was directly related to the content of the mercaptopropyl group in the solids (Fig. 4), unlike for the N_x-PPH materials. In this case, all of the materials presented high BET surface areas and, although a

decrease in the BET surface area was observed when the content of the organic group increased, this decrease was not as significant as for N_x-PPH described above. Saturation of S_5-PPH sample was achieved at 120 mmol Hg per 100 g material, which is within the order of similar sorbents such as the porous clay heterostructures (PCH) functionalized by co-condensation [36], where the Hg(II) adsorption capacity was in the range of 70–310 mmol per 100 g for sorbents containing thiol groups in a range of 0.7–2.9 mmol g^{-1}.

In the case of these S_x-PPH materials, cationic exchange with the PO–H and SiO–H groups was also observed, given that the Hg/S molar ratio was higher than 1.0 for the saturation values, as shown in Fig. 3b. This contribution of cationic exchange to the adsorption process was more evident for S_{50}-PPH, since this material had the lowest content of thiol groups and the highest BET surface area. For this material, the molar ratio between the Hg adsorbed and thiol groups present was 2.0. Therefore, these materials demonstrated their capacity to retain Hg(II) from a diluted solution of 0.1 mM Hg(II). The material with the highest Hg(II) adsorption capacity was tested for the removal of this heavy metal from the wastewater of a button battery recycling industry.

3.4. Application for Ni(II) extraction

In accordance with the results obtained previously, N_5-PPH was employed as an adsorbent material for treating wastewater from an electroplating industry (Progaelectric S.A., Montilla, Spain). The sewage from this type of industry contains traces of the metals ions used in the electroplating process and must be treated before it is released. The N_5-PPH material was tested as an adsorbent of aqueous Ni(II) present in the sewage. Fig. 5a shows the effect of the N_5-PPH material on the electroplating wastewater. In the electroplating industry, nickel baths are most commonly used to give a final coating. Other intermediate steps use other metallic finishes, such as gold or brass. After the application of the adsorbent material the Ni(II) initial concentration of ~0.850–1.022 mM, decreased to a final concentration of Ni(II) below the stipulated legal limit [37], which demonstrated their feasibility for use in metal ion removal from wastewater; the effect of pH in the range 1–7 is shown in the Supplementary information, where it is observed that optimal adsorption occurs between pH 6 and 7.

3.5. Application for Hg(II) extraction

The material S_5-PPH was also studied for removing Hg(II) from wastewater from an industry dedicated to the collection of button batteries, situated in Córdoba (south Spain). Table 2 shows the metal concentration of the solution. After partial neutralization with NaOH (1 M) to pH 5.1, a precipitate, mainly Fe(OH)$_3$, was
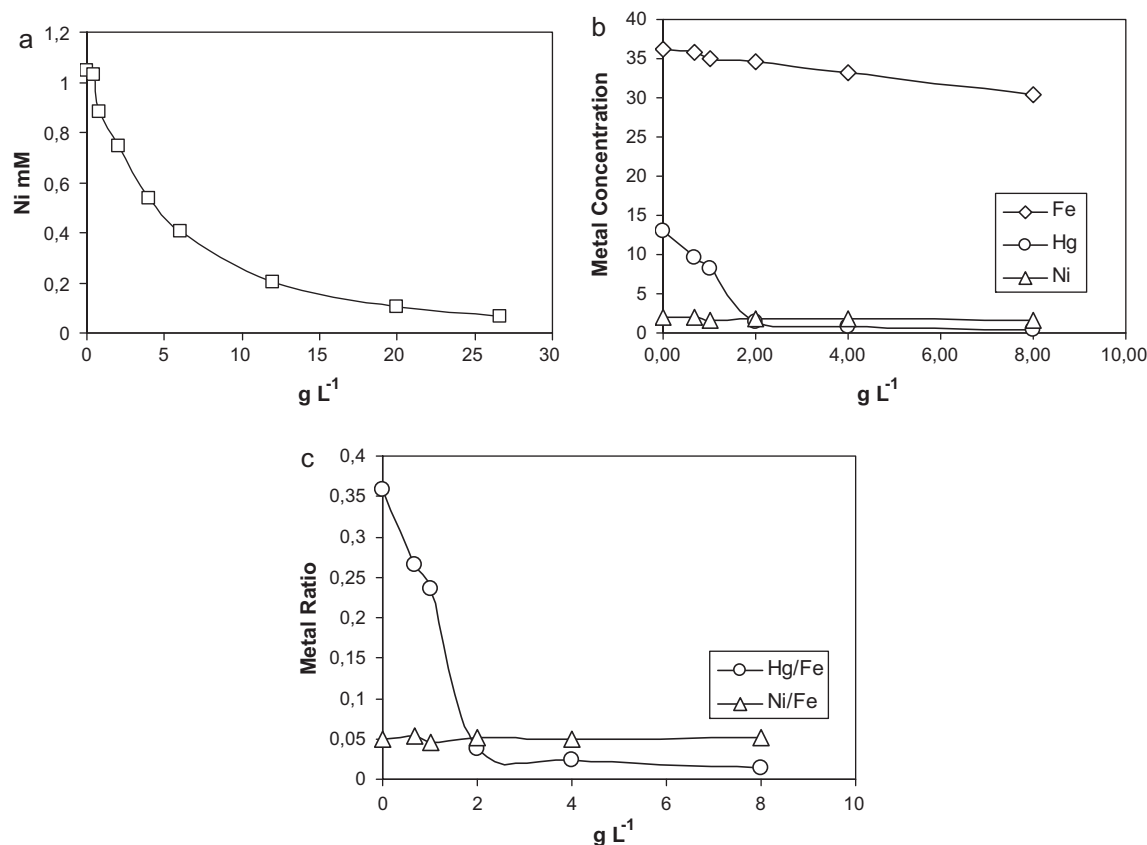
Fig. 5. (a) Ni^{2+} concentration in wastewater as a function of mass of adsorbent/volume of solution. (b) Fe (g L^{-1}), Ni (g L^{-1}) and Hg (μg L^{-1}) concentration in wastewater as a function of mass of adsorbent/volume of solution. (c) Selectivity on Hg adsorption referred to concentration ratio Hg/Fe and Ni/Fe.

Table 2
Concentrations of Fe(III) and Ni(II) in g L^{-1} and Hg(II) in μg L^{-1} from button cell recycling effluent.

Element	Raw effluent (pH = 0.1)	Neutralized effluent (pH = 5.1)	After adsorption with S$_5$-PPH
Fe(III)	111.5 (1.28)	36.2 (0.28)	30.5 (0.24)
Ni(II)	6.87 (0.32)	1.91 (0.02)	1.67 (0.01)
Hg(II)	23,270 (0.34)	13.6 (0.35)	0.42 (0.01)

formed. This solid can remove heavy metals [38], which explains the observed reduction in the concentration of Ni(II) and Hg(II) in the solution. The proposed adsorbents may be effective in cases where the concentration of Hg(II) is low but nonetheless above the legal limit [37]. Thus, different volumes of this solution were added to 0.1 g of S$_5$-PPH and the levels of Fe(III), Ni(II) and Hg(II) were analyzed after one day of stirring at room temperature. A drastic decrease of Hg(II) was obtained compared to Fe(III) and Ni(II), as shown in Fig. 5b, which demonstrated the expected selectivity of this sorbent for Hg(II), since Hg(II) is a soft acid and thiol groups are soft bases. This selectivity is shown in Fig. 5c, where the Hg/Fe concentration ratio decreased with the amount of sorbent added, whereas the Ni/Fe concentration ratio remained almost constant.

4. Conclusions

The functionalized porous phosphate heterostructure materials were successfully used for the adsorption of Ni(II) and Hg(II) heavy metals, as described by an adsorption process of the Langmuir type. This adsorption capacity depends on the type and amount of the organic groups incorporated in the silica galleries. Two mechanisms were involved in the adsorption process; a first one due

to a selective interaction of the cations with the functional group and a second one originated by a cationic exchange from PO$^-$ and SiO$^-$ groups. The adsorbent containing most organic groups was therefore used for the remediation of wastewater. The results indicate that hybrid N$_5$-PPH and S$_5$-PPH materials are good potential alternative materials for removing Ni(II) and Hg(II) from industrial wastewater.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.03.110.

References

[1] A. Kabata-Pendias, H. Pendias, Trace Elements in the Soil and Plants, CRC Press, Florida, 1989.
[2] D. Barceló, M. Petrovic, Emerging Contaminants From Industrial and Municipal Waste. The Handbook Of Environmental Chemistry, Vol. 5/S/1, Springer-Verlag, Berlin/Heidelberg, 2008.
[3] A.H.M. Veeken, S. de Vries, A. Van der Mark, W.H. Rulkens, Selective precipitation of heavy metals as controlled by a sulphide selective electrode, Sep. Sci. Technol. 39 (2003) 1–19.
[4] A. Möller, A. Grahn, U. Welander, Precipitation of heavy metals from landfill leachates by microbially produced sulphide, Environ. Technol. 25 (2004) 69–77.
[5] V.K. Verma, S. Tewari, J.P.N. Rai, Ion exchange during heavy metal biosorption from aqueous solution by dried biomass of macrophytes, Bioresour. Technol. 99 (2008) 1932–1938.

[6] V.J. Inglezakis, M.D. Loizidou, Ion exchange of some heavy metal ions from polar organic solvents into zeolite, Desalination 211 (2007) 238–248.

[7] R. Kiefer, W.H. Höll, Sorption of heavy metals onto selective ion-exchange resins with aminophosphonate functional groups, Ind. Eng. Chem. Res. 40 (2001) 4570–4580.

[8] G. Metcalf, H. Eddy (Eds.), Wastewater Engineering, Treatment, Disposal, and Reuse, 3rd ed., McGraw-Hill, New York, 1991.

[9] Z. Amjad, Reverse Osmosis: Membrane Technology, Water Chemistry and Industrial Applications, 1st ed., Springer-Verlag, Berlin/Heidelberg, 1993.

[10] X. Chai, G. Chen, P.L. Yue, Y. Mi, Pilot scale membrane separation of electroplating wastewater by reverse osmosis, J. Membr. Sci. 123 (1997) 235–240.

[11] A. Jusoh, L.S. Shiung, N. Ali, M.J.M.M. Noor, A simulation study of the removal efficiency of granular activated carbon on cadmium and lead, Desalination 206 (2007) 9–16.

[12] O.S. Amuda, A.A. Giwa, I.A. Bello, Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon, Biochem. Eng. J. 36 (2007) 174–181.

[13] M.J.S. Yabe, E. Oliveira, Heavy metals removal in industrial effluents by sequential adsorbent treatment, Adv. Environ. Res. 7 (2003) 263–272.

[14] K.M. Hong, M.S. Kim, J.G. Chung, Adsorption characteristics of Ni(II) on γ-type alumina particles and its determination of overall adsorption rate by a differential bed reactor, Chemosphere 54 (2004) 927–934.

[15] N.L.D. Filho, D. Ribeiro do Carmo, Selective adsorption of heavy metal ions and voltammetric determination of mercury, Talanta 68 (2006) 919–927.

[16] K.G. Bhattacharyya, S.S. Gupta, Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review, Adv. Colloid Interface Sci. 140 (2008) 114–131.

[17] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, J. Colloid Interface Sci. 280 (2004) 309–314.

[18] W.Y. Shi, H.B. Shao, H. Li, M.A. Shao, S. Du, Progress in the remediation of hazardous heavy metal-polluted soils by natural zeolite, J. Hazard. Mater. 170 (2009) 1–6.

[19] P. Miretzky, A.F. Cirelli, Hg(II) removal from water by chitosan and chitosan derivatives: a review, J. Hazard. Mater. 167 (2009) 10–23.

[20] W. Yantasee, C.L. Warner, T. Sangvanich, R.S. Addleman, T.G. Carter, R.J. Wiacek, G.E. Fryxell, C. Timchalk, M.G. Warner, Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles, Environ. Sci. Technol. 41 (2007) 5114–5119.

[21] J. Kostal, A. Mulchandani, W. Chen, Affinity purification of plasmid DNA by temperature-triggered precipitation, Macromolecules 34 (2001) 2257–2261.

[22] A. Amirbahman, A.L. Reid, T.L. Haines, J.S. Kahl, C. Arnold, Association of methylmercury with dissolved humic acids, Environ. Sci. Technol. 36 (2002) 690–695.

[23] D.E. Salt, M. Blaylock, N.P. Kumar, V. Dushenkov, B.D. Ensley, I. Chet, I. Raskin, Phytoremediation: a novel strategy for the removal of toxic metals from the environment using plants, Biotechnology 13 (1995) 468–474.

[24] M. Algarra, M.V. Jiménez, E. Rodríguez-Castellón, A. Jiménez-López, J. Jiménez-Jiménez, Heavy metal removal from electroplating wastewater by aminopropyl-Si MCM-41, Chemosphere 59 (2005) 779–786.

[25] M. Jaroniec, O. Olkhovyk, Surface Chemistry in Biomedical Environmental Science, Part 3, Springer, Netherlands, 2006, pp. 325–326.

[26] A. Benhamou, M. Baudu, Z. Derriche, J.P. Basly, Aqueous heavy metals removal on amine-functionalized Si-MCM-41 and Si-MCM-48, J. Hazard. Mater. 171 (2009) 1001–1008.

[27] J. Aguado, J.M. Arsuaga, A. Arencibia, M. Lindo, V. Gascón, Aqueous heavy metals removal by adsorption on amine-functionalized mesoporous silica, J. Hazard. Mater. 163 (2009) 213–221.

[28] D. Pérez-Quintanilla, A. Sánchez, I. del Hierro, M. Fajardo, I. Sierra, Functionalized HMS mesoporous silica as solid phase extractant for Pb(II) prior to its determination by flame atomic absorption spectrometry, J. Sep. Sci. 30 (2007) 1556–1567.

[29] L. Mercier, T.J. Pinnavaia, Heavy metal ion adsorbents formed by the grafting of thiol functionality to mesoporous silica molecular sieves: factors affecting Hg(II) uptake, Microporous Mesoporous Mater. 20 (1998) 101–106.

[30] R. Moreno-Tost, M.L. Oliveira, D.L. Eliche-Quesada, J. Jiménez-Jiménez, A. Jiménez-López, E. Rodríguez-Castellón, Evaluation of Cu-PPHs as active catalysts for the SCR process to control NOx emissions from heavy duty diesel vehicles, Chemosphere 72 (2008) 608–615.

[31] D. Eliche-Quesada, M.I. Macías-Ortiz, J. Jiménez-Jiménez, E. Rodríguez-Castellón, A. Jiménez-López, Catalysts based on Ru/mesoporous phosphate heterostructures (PPH) for hydrotreating of aromatic hydrocarbons, J. Mol. Catal. A 255 (2006) 41–48.

[32] M.D. Soriano, J. Jiménez-Jiménez, P. Concepción, A. Jiménez-López, E. Rodríguez-Castellón, J.M. López Nieto, Selective oxidation of H₂S to sulphur over vanadia supported on mesoporous zirconium phosphate heterostructures, Appl. Catal. B: Environ. 92 (2009) 271–279.

[33] G. Aguilar-Armenta, M.E. Patino-Iglesias, J. Jiménez-Jiménez, E. Rodríguez-Castellón, A. Jiménez-López, Application of phosphate heterostructure materials for gas separation, Langmuir 22 (2006) 1260–1267.

[34] R. Piazuelo, E. Rodríguez-Castellón, J. Jiménez-Jiménez, A. Jiménez-López, J. Benavente, Chemical surface and electrochemical characterization of zirconium phosphate heterostructures, Microporous Mesoporous Mater. 115 (2008) 23–32.

[35] J. Jiménez-Jiménez, M.R. Alonso, D. Eliche, E. Rodríguez-Castellón, A. Jiménez-López, Synthesis and characterization of acid mesoporous phosphate heterostructure (PPH) materials, J. Mater. Chem. 15 (2005) 3466–3472.

[36] A.J. Tchinda, E. Ngameni, I.T. Kenfack, A. Walcarius, One-step preparation of thiol-functionalized porous clay heterostructures: application to Hg(II) binding and characterization of mass transport issues, Chem. Mater. 21 (2009) 4111–4121.

[37] 2000/479/EC: Directive 96/61/EC, Concerning integrated pollution prevention and control (IPPC).

[38] H.Y. Hui, H.C. Li, C.H. Pin, S.L. Chih, C.C. Yung, Thermodynamics and kinetics of adsorption of Cu(II) onto waste iron oxide, J. Hazard. Mater. 144 (2007) 406–411.