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Novel polymeric sorbents based on imprinted Hg(II)-diphenylcarbazone complex for mercury removal from drinking water

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Abstract This study describes the preparation of ion-imprinted polymers for the selective removal of Hg(II) ions from aqueous media. Polymeric sorbents were prepared using different synthesis approaches in order to understand the influence of diphenylcarbazone, used as non polymerizable ligand, on absorption performance. In particular a bulk polymerization was firstly used to prepare two polymers, IIP1 and IIP2, in absence and in presence of diphenylcarbazone. The trapping of the ligand in IIP2, demonstrated by Fourier Transform Infrared Spectroscopy, promotes the formation of ternary complexes with mercury ions and 4-vinylpyridine inducing an increase of binding performance, as proved from IIP1 and IIP2 K_a values of high affinity binding sites ($1.7 \times 10^3 \pm 0.4 \text{ M}^{-1}$, $12.1 \times 10^3 \pm 0.5 \text{ M}^{-1}$). A third polymer (IIP3) was also synthesized using a precipitation polymerization to evaluate the contribution of morphological characteristics on absorption performance compared to the addition of diphenylcarbazone. Competitive studies revealed a stronger incidence of IIP3 morphology on selectivity performance. Indeed, monodisperse microbeads were obtained only in this case. Finally, the applicability of polymers to real-world samples was demonstrated through batch experiments using drinking water spiked with $1 \mu\text{g ml}^{-1}$ of Hg(II) ions confirming the best removal efficiency near to 80% of IIP2.

Keyword diphenylcarbazone/drinking water/ion imprinted polymers/mercury removal

INTRODUCTION

The release of various harmful heavy metal ions owing to industrial and agricultural processes, represent today one of the main cause of pollution.¹ Mercury is one of the most hazardous elements for human health for its relative solubility in water and living tissues² and its tendency to bioaccumulate in the human body causing weakness, neurological damages, chromosomal mutations, etc.³ The World Health Organization recommends a limit of $1 \mu\text{g L}^{-1}$ of mercury in drinking water⁴ which require a very accurate, selective and sensitive method of measurement. Common methods used for mercury extraction from water samples include, liquid-liquid extraction^{5,6}, solid-liquid extraction,⁷ flotation⁸ and membrane filtration.⁹ Immobilization of organic ligands on the surface of an inorganic or organic solid support is usually aimed to modify the surface with certain target functional groups that can enhance the affinity towards metal ions. Different chelating sorbents for preconcentration of mercury were obtained using dithiocarbamate resin,¹⁰ N-(2-pyridyl methyl) chitison,¹¹ 2,3-dimercapto propane-1-sulfonate,¹² dithizone derivative.¹³ According to these data, 1,5- diphenylcarbazone (DPC), a well known classical chelating ligand for mercury extraction, can be considered a potential chelating agent available to enhance the absorption performance of solid supports. Starting from the experience of our research group in the field of molecularly imprinted polymers,¹⁴⁻²² imprinted technology was used to prepare a new class of sorbent materials for mercury extraction prepared in the presence and in absence of DPC with the aim to evaluate the influence of this compound on absorption behavior of polymers. The general procedure of Ion Imprinted Polymers (IIPs) preparation consist in the formation of a ligand-metal complex followed by a copolymerization in the presence of an excess of cross-linking agent. After polymerization the template ion is removed by washing procedures leaving within the polymer network three-dimensional recognition cavities with a predetermined orientation, according to their stereochemical interaction with the template metal ion.^{23,24} Only few works using mercury as target ion are reported in literature. For its simplicity, the trapping approach using a non polymerizable ligand, was the most commonly used.²⁵⁻²⁷ Sing and coworkers prepared a Hg(II) imprinted polymer by the formation of a binary complex of mercury with 4-(2-thiazolylazo) resorcinol and thermally copolymerizing with methacrylic acid and ethylene glycol dimethacrylate.³ Recently, a voltammetric sensor for mercury detection using a new porphyrin derivatives as non polymerizable ligand was prepared.²⁶ Diazoaminobenzene was also chosen as complexing agent by Liu to prepare a Hg imprinted copolymers in presence of 4-vinylpyridine and ethylene glycol dimethacrylate.²⁵

In this work three Hg(II)-imprinted polymers were prepared using different synthesis approaches in order to understand the influence of DPC, used as non polymerizable ligand, on absorption performance of polymers The

choice to test this compound arises from the well known high affinity of DPC for mercury ions able to form a stable blue-violet Hg(II)-DPC complex. The use of DPC in IIP technology was recently demonstrated for lead(II) ions extraction.²⁸ All polymers were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) Dynamic Light Scattering (DLS) and Electrophoretic Light Scattering (ELS). Comparative selectivity studies were performed using typical heavy metals for water pollution such as Co(II), Pb(II), Cu(II). Finally, to confirm the applicability of polymers prepared to real-world samples, drinking water was selected and analyzed before and after incubation with polymer particles and the extraction recovery was calculated.

EXPERIMENTAL PROCEDURE

Reagents

DPC, mercury(II) chloride (HgCl₂), 4-vinylpyridine (4VP) and ethylene glycol dimethacrylate (EGDMA) were supplied from Sigma-Aldrich (Steinheim, Germany). Hydrochloric acid (HCl) and α - α' -azoisobutyronitrile (AIBN) was purchased from Fluka (Steinheim, Germany). Analytical grade acetonitrile and ethanol were obtained from J.T. Baker (Deventer, Holland). Elemental standard solution of Pb(II) and Hg(II) were prepared by appropriate dilution of 1000 mg L⁻¹ stocks purchased from Fluka (Steinheim, Germany). Nitric Acid (67-69%) for trace metal analysis and Cu(II) and Co(II) standard solutions (1000 mg L⁻¹) were supplied from Romil-SpA. Buffer solutions were prepared with deionized water provided by a water purification system (Human Corporation, Korea).

Instrumentation

FT-IR analysis was recorded on a JASCO 660 plus infrared spectrometer. SEM observations were carried out on a JEOL JSM 6500 F microscope, equipped with a field emission source. Measurements of DLS and ELS were made using a Malvern Zetasizer Nano ZS 90 on diluted samples. Sonication was carried out using a Sonorex RK 102H ultrasonic water bath (Bandelin Electronic, Berlin, Germany, Europe, www.bandelin.com). Centrifugation was achieved with a PK121 multispeed centrifuge (Thermo Electron Corporation, Waltham, Massachusetts, USA, www.thermoscientific.com). Batch rebinding experiments were carried out using a Cary 100 Scan UV-visible spectrophotometer (Varian, Palo Alto, CA, USA). For pH measurements, pHmeter Basic 20, (Crison, Alella, Barcelona, Spain, Europe, www.crisoninstruments.com) was used. Ions quantification was achieved by Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) iCAP 6000 Series (Thermo Scientific,

<http://www.thermoscientific.com>). UV-vis spectra were obtained with a Cary 100 Scan UV/vis spectrophotometer.

Synthesis of Hg(II)-imprinted polymers

In order to prepare a Hg(II)-imprinted polymer, a bulk polymerization was firstly used to obtain IIP1. In particular, HgCl₂ (0.0468 mmol), 4-VP (0.1872 mmol), EGDMA (0.936 mmol) and AIBN (0.037 mmol) were dissolved in 3 ml of acetonitrile and water mixture (4:1). The polymerization was carried out at 65°C for 24 hours under magnetic stirring (400 rpm). A second polymer, IIP2 was synthesized similarly to the above procedure with slight variation. In a first step DPC was dissolved in 3 ml of porogen solution containing 4-VP. After HgCl₂ addition, the resulting mixture was stirred for 5 h in order to form a stable complex between Hg(II) ions, 4VP and DPC. Finally, a third polymer, IIP3, was prepared by precipitation polymerization similarly to IIP1 but with a higher amount of porogen (13 ml). All polymers were washed several times with ethanol to remove the unreacted materials and successively with HCl 2M to extract Hg(II) ions until Hg(II) in solution was not detected by ICP-AES analysis. Finally, polymeric particles were washed with double distilled water to reach a neutral pH. The resulting fine powders were dried under vacuum in a desiccator before absorption studies. The corresponding non imprinted polymers were prepared using the same procedures but without the target ion.

Morphological studies

FT-IR analysis was performed using dry polymers dispersed in a matrix of KBr, followed by a compression at 10 tons to form pellets. Measurements of DLS and ELS were both carried out on diluted samples, to establish the size and zeta potential of polymer particles. The hydrodynamic diameter of beads dispersion has been determined at 25°C measuring the autocorrelation function at 90° scattering angle. Three separate measurements have been made to derive average. The polydispersity index (PDI) to measure the distribution of molecular mass in a given polymer sample, was evaluated for all polymers prepared and the results were compared. The surface morphology, size and shape of polymer particles was examined by SEM.

Batch adsorption studies

The binding capacity of all polymers was evaluated by batch rebinding experiments dissolving 5 mg of polymer particles in 1 ml of HgCl₂ phosphate buffer solution (pH 8), spanning the concentration range from 0 to 600 mg L⁻¹. The suspension was shaken for 18 h at room temperature. Then, the polymer was removed by filtration and the resulting solution was analysed by ICP-AES. The amount of analyte adsorbed on the polymer (mg g⁻¹) was calculated by:

$$Q = (C_i - C_e) V/m \quad (1)$$

where C_i and C_e represent the initial and the equilibrium concentration (mg L^{-1}), respectively, V the volume of water solution (L) and m the mass of polymer (g).

Scatchard analysis was provided by the following equation:

$$Q_e/C_e = (B_{\max} - Q_e) K_a \quad (2)$$

where Q_e represent the equilibrium concentration of Hg(II) bound per gram of polymer (mg g^{-1}), K_a (M^{-1}) is the association constant and B_{\max} ($\mu\text{M g}^{-1}$) is the apparent maximum number of binding sites. Therefore, K_a and B_{\max} of the polymer were determined from the slope and the intercept, respectively, by plotting of Q_e/C_e versus Q_e .

A simple Langmuir absorption isotherm was also used to evaluate the maximum absorption capacity Q_{\max} ($\mu\text{mol g}^{-1}$) of polymers:

$$1/Q_e = (1/Q_{\max} C_e K_L) + (1/Q_{\max}) \quad (3)$$

where Q_e and K_L correspond to the amount of analyte ion adsorbed at equilibrium ($\mu\text{mol g}^{-1}$) and the Langmuir constant ($\text{L } \mu\text{mol}^{-1}$), respectively. Q_{\max} will be determined from the linear plot of $1/Q_e$ against $1/C_e$.

Comparative selectivity studies

Ion recognition capacity of Hg-IIP materials are well reflected by Hg(II) selectivity in the presence of other competing ions. In particular a mixture solution (100 mg L^{-1}) of Hg(II), Co(II), Cu(II) and Pb(II) was used for bath experiments. The following equations were employed to evaluate the selectivity of different polymers prepared.

$$K_d = (C_i - C_f)/C_f V/m \quad (4)$$

where K_d , C_i e C_f represent the distribution coefficient ($L\ mg^{-1}$) of an ion on the polymer, the initial and final concentration of solutions ($mg\ L^{-1}$) respectively. The selectivity coefficient k of Hg(II) relative to the competing ion was calculated using the following equation:

$$k = K_d(Hg) / K_d(\text{foreign ion}) \quad (5)$$

In order to evaluate an imprinting effect, a relative selectivity coefficient k' was defined as follows:

$$k' = K_{\text{imprinted}} / K_{\text{non-imprinted}} \quad (6)$$

Removal of Hg(II) ions from drinking water

Batch experiments were done to explore the application of prepared polymers to real-world samples. In particular, the extraction capability of IIP2 and IIP3 in drinking water was evaluated. 50 mg of dried polymer was suspended in 100 ml of drinking water solution containing $1\ \mu\text{g}\ \text{ml}^{-1}$ of Hg(II) ions and stirred for 1 h. After batch experiments, unextracted and extracted concentrations of Hg(II) ions were determined.

RESULTS AND DISCUSSION

Polymers preparation

In this work different synthesis approaches for Hg(II)-imprinted polymers preparation were employed and the influence of DPC, used as non polymerizable ligand on absorption performance, was evaluated. A bulk polymerization was firstly employed to prepare IIP1 and IIP2 in absence and in presence of DPC. This technique was chosen for its simplicity, however irregular particles in size and shape are produced and some interaction sites are destroyed during grinding, influencing the IIPs loading capacity.¹⁷ For this reason a third polymer, IIP3, was prepared using a precipitation polymerization increasing the amount of porogen, in order to obtain monodisperse spherical beads and to evaluate the contribution of morphological characteristics on absorption performance, compared to the addition of DPC. The presence of DPC in prepolymerization step probably promoted a stable complex formation between 4VP, DPC and Hg(II) ions influencing the subsequent synthesis process. 4VP was chosen as functional monomer due to its high capacity to interact with mercury ions through its nitrogen atom.²⁵⁻³⁰ The soft conditions used in the washing steps to remove mercury ions, allowed the trapping of DPC in IIP2 matrix through π - π interactions with molecules present in the polymeric structure, as

stated in a recent paper.²⁸ The trapping of DPC in meshes of polymer was further demonstrated through FT-IR analysis overlying the corresponding IR spectra of all polymers prepared. To remark the substantial differences in each spectrum, an enlargement in the range of 1750-700 cm^{-1} was considered. IR spectrum of IIP2 (Figure 1b) showed the presence of two additional peaks (1295.9, 1320.9 cm^{-1}) attributable to the stretching of nitrogen bonded to the aromatic carbon of DPC, not found in IIP1 (Figure 1a, black circle).

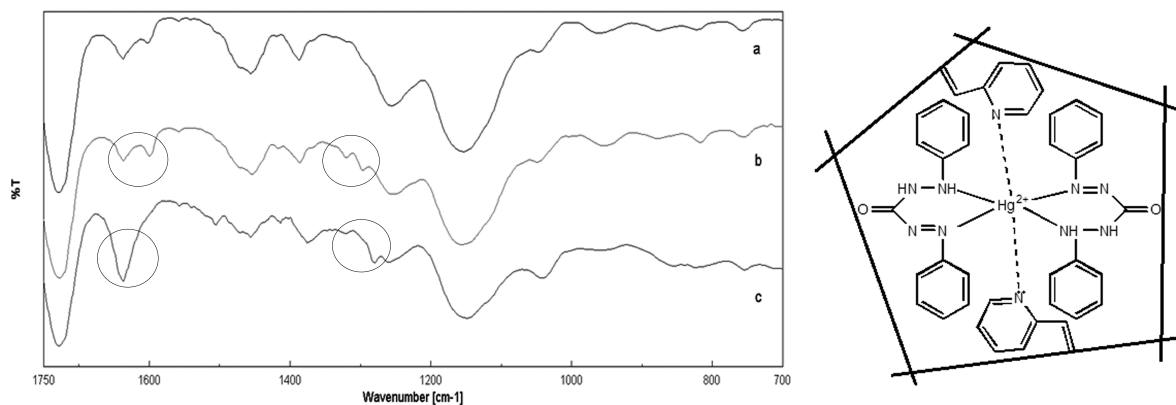


Figure 1 FT-IR spectra of IIP1 (a), IIP2 (b) and unleached IIP2(c). The black circles underline the presence of DPC in IIP2 (b) compared to IIP1 (a) and their changes of peaks between unleached (b) and leached IIP2 (c)

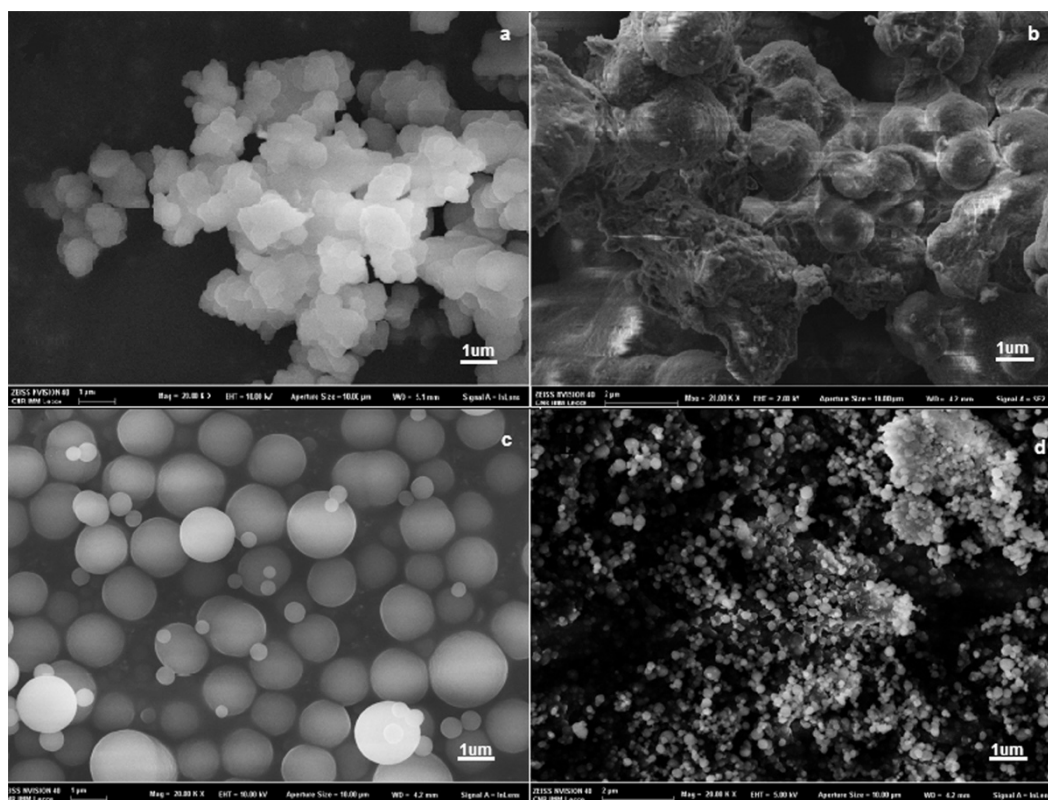


Figure 2 SEM images (20000x magnification) related to IIP1 (a), IIP2 (b), IIP3 (c) and NIP3 (d)

These peaks were slightly shifted compared to DPC spectrum (1289, 1309 cm^{-1}) due to the different chemical environment and to the interactions established with the polymer matrix. Moreover, the IR spectrum of leached and unleached IIP2 was also evaluated. A substantial difference between leached (b) and unleached (c) IIP2 spectra was obtained. The peak shape of C=N (1636.3 cm^{-1} , black circle) of leached IIP2 (b) changed drastically in unleached IIP2 spectra (c) emphasizing the possible interaction of mercury ions with nitrogen of 4VP.

Moreover, c spectrum showed a slight shift of the additional peaks (1280.5, 1322.0 cm^{-1} , black circle) observed in IIP2, attributable to the C-N stretching of DPC. These results show the possible interaction of mercury ions both with the nitrogen bonded to the aromatic carbon of DPC and the nitrogen of pyridine monomer. IIP1, IIP2 and IIP3 and the corresponding non imprinted polymers, were further characterized by DLS, ELS and SEM analysis. DLS measurements of IIP1, IIP2 and corresponding non imprinted polymers, showed high PDI values (IIP1=0.872; NIP1=0.790; IIP2=0.571; NIP2=0.504) that suggested the presence of many aggregates very polydisperse, as confirmed from SEM images (Figure 2a-2b). Indeed, irregularly shaped particles were obtained, as expected using a bulk polymerization. Instead, as it can be seen in Figure 2c, IIP3, prepared by precipitation polymerization, revealed the presence of monodisperse spherical beads with an average diameter in the very low micrometer size, as confirmed from DLS measurements (1183 ± 200 nm). Moreover, Z-potential value described a good stability of IIP3 particles suspended in water (39.6 ± 5.7 mV).

An interesting result showed a drastic reduction in the average particles size between IIP3 and the corresponding non imprinted polymer (Figure 2c). This variation, also noted between IIP1 and NIP1, was due to the nucleation stage of the reaction influenced by the presence of the template.³¹ Indeed, when the number of nucleated particles increase, the average particle diameter decreases for a given degree of a monomer conversion. These data confirmed that DLS analysis was suitable only for monodisperse spherical beads with a lower PDI value, whereas in other cases the SEM technique was considered the most reliable to obtain right morphological information.

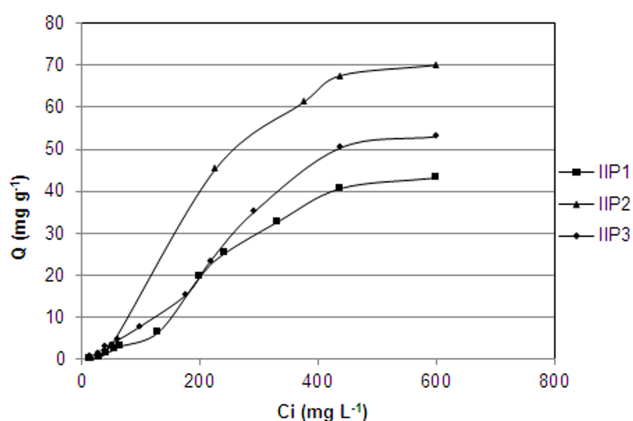


Figure 3 Batch rebinding experiments for IIP1, IIP2 and IIP3

Effect of pH value on the adsorption properties

Since it is well known that Hg(II) ions can form insoluble complexes in alkaline aqueous solutions,³² it has been verified the complete solubility at our concentrations, before all binding experiments.

To evaluate the effect of pH on adsorption performance, 5 mg of polymeric particles were dissolved in 1 ml of HgCl₂ buffer solution (100 mg L⁻¹) at pH 3, 8 and 11. The results obtained showed an adsorption efficiency highly pH dependent for all polymers with the highest adsorption capacity at pH 8. In particular, IIPs exhibited low affinities for Hg(II) ions extraction in acidic and very alkaline conditions, as showed by the low adsorption performance obtained. Acidic solutions have a greater affinity for metal ions, thus, Hg(II) ions were distributed more in the acidic solution than on polymeric particles. At very alkaline conditions, mercury ions form complexes with hydroxide ions producing soluble amphoteric hydroxides instead of being adsorbed on polymeric particles.³³ As a result, a low adsorption capacity of all polymers tested were recorder. For this reason, it was decided to use a phosphate buffer solution pH 8 to study the adsorption performance of polymers.

Absorption studies

The binding behavior of all polymers was tested by batch rebinding experiments and the binding data were processed by Scatchard and Langmuir analysis in order to evaluate binding characteristics of polymers prepared.

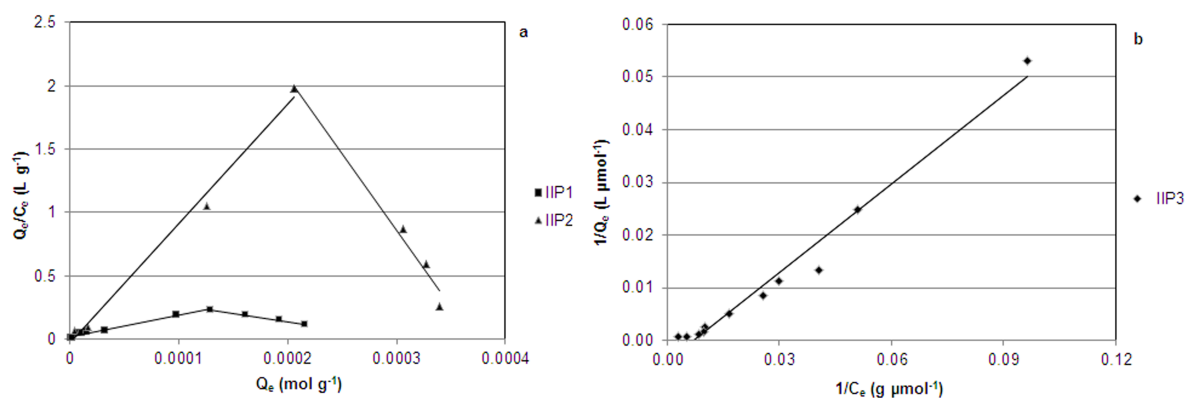


Figure 4 Scatchard plot of IIP1(■) with equations $y = 1657.2x + 0.0231$ for high affinity sites (left line), $y = 1349.2x + 0.4092$ for low affinity sites (right line), and IIP2 (▲) with equations $y = -12138x + 4.4955$ for high affinity sites (right line), $y = 9433.5x - 0.0328$ for low affinity sites (left line) (a); Langmuir isotherm of IIP3(b) with equation $y = 0.562x - 0.004$

Table 1 Scatchard and Langmuir isotherm constants for IIP1, IIP2 and IIP3

Scatchard model							Langmuir model		
Sorbents	High affinity sites			Low affinity sites			Q_{max} ($\mu\text{mol g}^{-1}$)	K_L (L mol^{-1})	R^2
	K_a (10^3 M^{-1})	B_{max} ($\mu\text{M g}^{-1}$)	R^2	K_a (10^3 M^{-1})	B_{max} ($\mu\text{M g}^{-1}$)	R^2			
IIP1	1.66	0.14	0.98	1.34	0.03	0.98	25.5	0.011	0.92
IIP2	12.14	0.03	0.98	9.43	3.47	0.99	54.6	0.029	0.89
IIP3	1.20	0.04	0.58	1.24	0.66	0.96	250.0	0.007	0.98

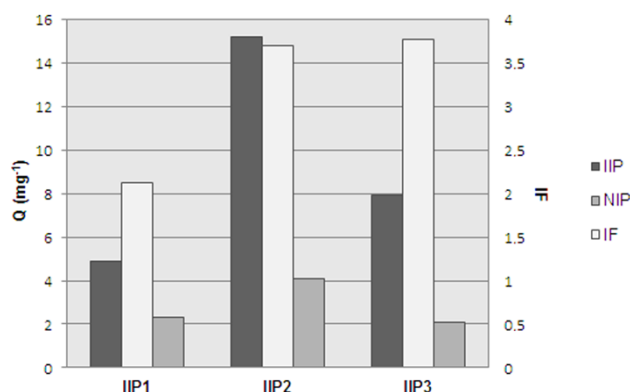


Figure 5 Comparison of IIPs absorption performance with the corresponding non imprinted polymers and Imprinting Factors (IF) evaluation. $[\text{Hg(II)}] = 100 \text{ mg L}^{-1}$

As it can be seen in Figure 3, the absorption capacity increase with analyte concentration until a saturation point was reached for all polymers prepared. IIP1 showed an experimental maximum adsorption capacity near to 40 mg g⁻¹, that was very lower than the maximum adsorption capacity of IIP2 (70 mg g⁻¹) prepared in the presence of DPC. This behavior suggests that the complexation between metal ions and DPC plays a substantial role in the adsorption of Hg(II) ions. Moreover, also using a precipitation polymerization, the performance of IIP3, compared to IIP1, increased (53 mg g⁻¹). This is due to the morphological characteristics of the sorbents that affect adsorption capacity significantly. Indeed, morphological differences observed between IIP1 and IIP3, due to the different polymerization techniques used, were the main reason of the higher absorption of IIP3 compared to IIP1. Probably, the low aggregation of microbeads obtained (Figure 2c), leaves a greater number of binding sites available for Hg(II) binding, enhancing the absorption of Hg(II) ions. Even if IIP2 showed morphological characteristics similar to IIP1 with irregular shaped particles (Figure 2b), the presence of DPC modified the chemical environment of IIP2 promoting the formation of ternary complexes with mercury ions and 4VP and improving its binding capacity that was better than IIP3.

In order to describe Hg(II) ion distribution between the liquid and adsorbent phases and to understand the nature of binding sites, Scatchard and Langmuir models were used to fit the adsorption processes of all ion imprinted polymers. According to the correlation coefficients (R²), Scatchard model was more suitable than Langmuir model to describe the binding behavior of polymers prepared by bulk polymerization (IIP1 and IIP2). Scatchard plots obtained for these polymers showed the presence of heterogeneous binding sites (Figure 4a) with a significant difference between K_a values of high affinity binding sites of IIP1 and IIP2, remarking the important contribution of DPC in Hg(II) ions extraction (Table 1). Otherwise, correlation coefficients obtained for IIP3 revealed the presence of homogeneous binding sites well described from a Langmuir isotherm. This results can be justified from morphological characteristics of this polymer (Figure 4b). In Figure 5 the adsorbed Hg(II) ions on each IIP and the corresponding NIP as well as the Imprinting Factor IF (ratio of the adsorbed Hg(II) amount by IIP and NIP) were reported. As it can be noted, IIP2 and IIP3 showed better specificity for Hg(II) ions than IIP1. Therefore, both trapping approach and precipitation polymerization technique have enhanced the absorption performances of polymers. In order to test the regeneration capacity of polymers, after incubation of IIP2 with HgCl₂ phosphate buffer solution pH 8 (100 mg L⁻¹), the polymer was centrifuged at 8000 rpm for 15 minutes with HCl solution 2M until Hg(II) ions were no detected by ICP-AES in the supernatant. The regenerated polymer showed uptake efficiency comparable to that of the fresh one over three cycles.

Selectivity evaluation

Typical heavy metals for water pollution such as Co(II), Pb(II), Cu(II) ions were chosen as competitors to evaluate selectivity performance. As shown in Figure 6, the interference ions did not cause significant reduction of Hg(II) absorption capacity.

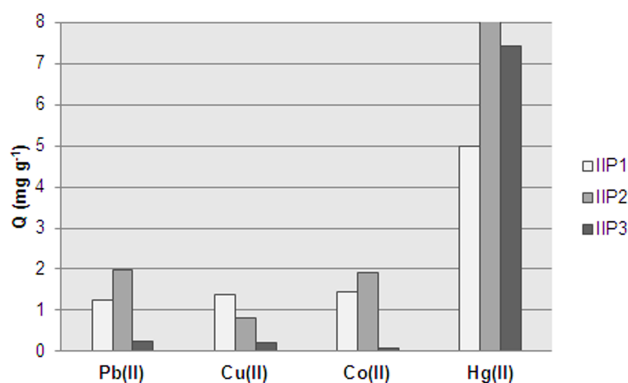


Figure 6 Selectivity studies of IIP1, IIP2 and IIP3 using a mixture solution of Pb(II), Cu(II), Co(II) and Hg(II): [M(II)]=100 mg L⁻¹

Table 2 Selectivity data on IIP1, IIP2 and IIP3

Metal ions	IIP1			IIP2			IIP3		
	K _d (ml g ⁻¹)	k	k'	K _d (ml g ⁻¹)	k	k'	K _d (ml g ⁻¹)	k	k'
Hg(II)	56.4			159.2			131.6		
Cu(II)	14.3	4.7	4.0	9.4	16.7	18.7	2.16	56.7	93.6
Co(II)	15.7	4.3	7.1	23.5	6.7	6.9	0.60	203.7	335.0
Pb(II)	13.3	5.1	5.6	23.8	6.6	6.2	2.4	50.8	25.3

As it can be seen in table 2, IIP2 prepared using DPC, showed better Hg(II) retention than IIP1 and IIP3 and a discrete selectivity. However, IIP3 exhibited higher binding ability for Hg(II) ions with respect to the competitors than IIP1 and IIP2, as it can be seen from selectivity coefficients that in all case are higher than 50.8. The relative selectivity coefficients of imprinted particles for Hg(II)/Cu(II), Hg(II)/Co(II) and Hg(II)/Pb(II), confirmed a clear selectivity effect especially for IIP3 with values that were almost 93.3, 335.0 and 25.3 times greater than that of NIP3 respectively. This means that, with this polymer, Hg(II) ions can be selectively removed from aqueous medium even in the presence of Cu(II), Co(II) and Pb(II). From these results, it can be hypothesized that the presence of aggregates in IIP1 and IIP2, can cause unspecific ions retentions. Thus, IIP3

monodisperse spherical beads have morphological characteristics that suggest the presence of imprinted cavities and specific binding sites in a predetermined orientation, free from aggregates, that allow to better discriminate between the competitors ions, resulting in a high selectivity of IIP3 for Hg(II) ions. It can be concluded that morphological characteristics were more effective than the inclusion of the ligand to obtain highly selective polymers

Application to real samples

To verify the feasibility of polymers, drinking water was tested. IIP2 and IIP3 that showed the best absorption performance, were incubated with drinking water samples spiked with $1 \mu\text{g ml}^{-1}$ of Hg(II) ions. Despite the high selectivity performance showed by IIP3, in drinking water a greater incidence of ligand on mercury ions extraction was observed. Thus, the best removal efficiency of IIP2 (78,8 %, RSD 0.9%) compared to IIP3 (61.6%, RSD 1.0%) was found that suggest a good anti-interference ability in real environmental water samples.

CONCLUSION

In this work selective Hg(II) imprinted polymers were prepared using different synthesis approaches and the influence of DPC, used as non polymerizable ligand on absorption performance was demonstrated. Absorption studies on IIP1 and IIP2 in absence and in presence of DPC, confirmed a strong incidence of this compound on the binding behavior of polymer against Hg(II) ions with a significant difference between K_a values of high affinity binding sites of IIP1 ($1.7 \pm 0.4 \text{ M}^{-1}$) and IIP2 ($12.1 \pm 0.5 \text{ M}^{-1}$). Moreover, an increase of absorption capacity compared to IIP1, was also observed for IIP3 that showed the presence of homogenous binding site, probably for the morphological characteristics of this polymer. Indeed, SEM images of IIP3 showed the presence of monodisperse spherical microbeads with a low propensity to aggregate, while the presence of some aggregate was observed for other polymers. Selectivity studies revealed that morphological characteristics of polymers were more effective than the ligand inclusion for the selectivity of Hg(II) imprinted polymers. However, batch experiments conducted using drinking water spiked with $1 \mu\text{g ml}^{-1}$ of Hg(II) ions showed a greater incidence of ligand on mercury ions extraction with a removal efficiency near to 80% of IIP2 after 1 h of treatment.

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