An ion-imprinted polymer for the selective extraction of mercury(II) ions in aqueous media

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Abstract
A double-imprinted polymer exhibiting high sensitivity for mercury(II) in aqueous solution is presented. Polymer particles imprinted with mercury(II) were synthesised by copolymerising the functional and cross-linking monomers, N’-[3-(Trimethoxysilyl)-propyl]diethylenetriamine (TPET) and tetraethylorthosilicate (TEOS). A double-imprinting procedure employing hexadechloroethylnmmonium bromide (CTAB), as a second template to improve the efficiency of the polymer, was adopted. The imprinted polymer was characterised by FTIR, scanning electron microscopy (SEM) and the average size determined by screen analysis using standard test sieves. Relative selective coefficients (k) of the imprinted polymer evaluated from selective binding studies between Hg2+ and Cu2+ or Hg2+ and Cd2+ were 10 588 and 3 147, respectively. These values indicated highly-favoured Hg2+ extractions over the 2 competing ions. The results of spiked and real water samples showed high extraction efficiencies of Hg2+ ions, (over 84%) as evaluated from the detected unextracted Hg2+ ions by ICP-OES. The method exhibited a dynamic response concentration range for Hg2+ between 0.01 and 20 µg/ml, with a detection limit (LOD, 3σ) of 0.000036 µg/ml (36 ng/l) that meets the monitoring requirements for the USA EPA of 2 000 ng/l for Hg2+ in drinking water. Generally, the data (n=10) had percentage relative standard deviations (%RSD) of less than 4%. Satisfactory results were also obtained when the prepared sorbent was applied for the pre-concentration of Hg2+ from an aqueous confirmed reference material. These findings indicate that the double-imprinted polymer has potential to be used as an efficient extraction material for the selective pre–concentration of mercury(II) ions in aqueous environments.

Keywords: Ion-imprinted polymer, selective extraction, mercury(II) ion, pre-concentration

Introduction
In recent years the release of various harmful heavy metal ions into the environment has attracted great attention worldwide because of their toxicity and widespread use. Mercury(II) is among those which are of great concern (Büyüktiryaki et al., 2007). It is a widely-distributed environmental pollutant in aqueous environments and its toxicity to humans and animals even at low concentrations is well known. Mercury(II) is included in all lists of priority pollutants as a result, and different regulations and guidelines have been developed for monitoring its levels in water and sediments (Hayes, 1997). Considering the extreme toxicity of mercury, the United States Environmental Protection Agency (EPA) has mandated an upper limit of 10 nM (2 000 ng/l) for Hg2+ in drinking water. Generally, the data (n=10) had percentage relative standard deviations (%RSD) of less than 4%.

Therefore a sample preparation/pre-concentration step prior to analysis is usually necessary. The step must rely on inexpensive, intelligent and robust functional materials with high sensitivity, selectivity and specificity for the targeted analytes. Solid phase extraction (SPE) has been used for pre-concentration of mercury and other heavy metals due to its flexibility, environmental-friendliness, speed, simplicity, safety and ease of automation (Thurman et al., 1998). The choice of sorbent is a key point in SPE because it can control the analytical parameters such as selectivity, affinity and capacity (Dean, 1998). The main challenge of the available SPE sorbents has always been selectivity of the analyte of interest in the presence of closely-related analogues.

Several solid supports, such as chelating resins (Nastasovic et al., 2004), modified silica (Tzvetkova et al., 2010), modified clay (Guerra et al., 2009), alumina (Duan et al., 2003) and ion exchange resins have also been used for the pre-concentration of mercury or its other forms. For example, Duolite GT-73 resin has been used for the pre-concentration of mercury(II) and gold from hydrochloric acid media in the presence of co-existing metal ions. Due to the high affinity of the resin to the transition metal ions, the mercury was adsorbed alongside other metals. The competing metals were released by leaching with mineral acids, leaving behind the mercury which was then desorbed by digestion of the resin with peroxide and the acid (Pohl et al., 2005). The extraction selectivity of these materials was found to be inadequate, and as such the development of highly-selective materials for mercury species extraction continues to be of great interest (Wu et al., 2007). More recently, ion-imprinted polymers (IIPs) or molecular-imprinted polymers (MIPs) have been identified as suitable materials and are increasingly used in contaminant or trace analysis, as they are suitable for applications where analyte selectivity is essential.

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IIPs are nano-porous polymeric materials, which upon leaching the imprint ion can thereafter selectively rebind the ion in the presence of closely-related ions. Ion-imprinting procedures are similar to those of molecular imprinting, except that metal ions rather than molecules are the ones used for imprinting. Unlike the MIPs, the IIP field is still in its infancy (Rao et al., 2006). The preparation of IIPs involves the complication of the target ion (known as template or print ion) with the functional monomer (known as the ligand or the substrate) (Sudee et al., 1999). This is followed by a polymerisation reaction with an excess cross-linking agent that fixes the pre-assembled binding groups around the print ion (Vlatakis et al., 1993). Eventually the print ion is leached out with a suitable solvent, leaving behind specific recognition sites with a memory for the original print ion (Sellersgren et al., 2001; Bartsch et al., 1998). Consequently, the recognition vacancies left behind, when the print ion is leached out from the formed polymer, will be selective and complementary to it in shape, size and functionality (Rao et al., 2006). Therefore, IIPs show higher selectivities and affinities in rebinding the print ion than its analogues (Ferrer et al., 1999; Masque et al., 2001). A particularly promising application of ion-imprinting polymers is the selective (i) SPE pre-concentration of analytes present in trace amounts (Martin-esteban et al., 2001; Sellersgren, 1999) or (ii) separation from other coexisting species (Tsukagoshi et al., 2001) or complex matrix, which may lead to selective environmental clean-up of analytes, not achievable by the conventional methods (Li et al., 2007).

In this paper, a mercury(II) IIP that was synthesised and applied to water samples collected in the vicinity of Grahamstown, Eastern Cape Province, South Africa, will be discussed. The synthesis procedure employed was the hierarchical double-imprinting approach proposed by Wu et al. (2007). Our group used a monomer with more nitrogen (N) donor atoms (3 in the triamine as opposed to 2 in the diamine which Wu et al. used) to improve coordination during the pre-assembly step in the imprinting process. In order to improve selectivity and competitive binding, a more rigorous method was used to leach out the template ion thus resulting in more available cavities for rebinding. This was carried out to improve on the relative selectivity coefficients (k’), (300 – 500), that were reported by Wu et al. (Wu et al., 2007). A large k’ value means selectivity of the prepared polymer material relative to the competing ions is high.

**Experimental**

**Chemicals**

N'-[3-(trimethoxysilyl)-propyl] diethylenetriamine (TPET) and tetraethylorthosilicate (TEOS), hexadecyltrimethylammonium bromide (CTAB), sodium hydroxide, nitric acid, sodium acetate and acetic acid were supplied by Sigma-Aldrich (Saint Louis, MO, USA), and mercury(II) nitrate monohydrate and Hg(NO₃)₂ · H₂O by BDH AnalR (London, England). Reagents used were at least of analytical grade. All water used was obtained from Direct Q 3UV millipore system (Billericia, MA, USA). NIST traceable mercury(II) certified reference material of water, lot number D2-MEB33811MCA was obtained from Inorganic Ventures (Christiansburg, VA, USA).

**Instrumentation and apparatus**

ICP-OES, ICAP 6000 series, Thermo Electron Corporation, (Waltham, MA, USA) was used to measure the concentration of the unextracted Hg²⁺ as well as that of Cd²⁺ and Cu²⁺ in aqueous media (at 194.4, 214.38, 324.754 nm respectively). To ensure that Hg²⁺ as the imprint ion was thoroughly washed off the imprint polymer, an XRF EDX 900 spectrometer, Pan Analytical, Shimadzu, (Kyoto, Japan), was used to detect the concentration of mercury from the washings of the polymer as well as in the dried polymer itself.

For morphology and characterisation, scanning electron microscope (SEM) micrographs for the imprinted (washed and unwashed) and the non-imprinted polymer powders were obtained at 20 kV on a JSM 840 field emission scanning electron microscope JEOL, (Tokyo, Japan). FTIR spectra (4000 - 400 cm⁻¹) were recorded by a Bruker Tensor 27 FTIR spectrophotometer (Ettlingen, Germany).

The polymer particles were obtained by centrifuging with MSE Misral 1000 centrifuge, Sanyo Gallenkamp, (Loughborough, England), at 45,000 r/min for 10 min. A Jenway 3510 pH meter, (Dunmow, England) was used to measure the pH values. Standard Test sieves Retsch GmbH & Co., (Haan, Germany), were used to obtain the average size of the polymer particles by screen analysis.

**Preparation of the mercury(II) ion-imprinted polymer and removal of the print species (templates)**

The mercury(II) ion-imprinted polymer was prepared by following a literature procedure (Wu et al., 2007) with some modifications. Hg(NO₃)₂ · H₂O (print ion), CTAB (surfactant micelle as second print species), TPET (monomer), TEOX (cross linking agent), 1 M NaOH (pH modulator) and ultrapure water (porogen) were mixed according to the following optimal molar ratios: 1:2:2:5:10:4:1500, respectively. The mixture was magnetically stirred at 900 r/min for 4 h. Off-white gels were yielded. The gels were mixed with more water, refluxed at 90°C for 1 h and recovered by centrifugation.

The gels that resulted were washed with 3 M NaOH until the pH of the washings was at 7.5. The gels were further washed several times with water, before drying in the oven at 60°C for about 4 h. The resultant granules were ground and sieved to a homogenous off-white powder to yield the mercury(II) ion-imprinted polymer of 25-30 µm particle size as measured by the standard test sieves. The particles still contained the mercury(II) ions and CTAB templates and were referred to as the unwashed ion-imprinted polymer (IIP) particles.

The mercury(II) ions and CTAB templates were exhaustively removed from the unwashed IIP particles by refluxing with 3 M HNO₃, and 99.99% ethanol in the ratio 1:1 v/v, respectively, for a total of 7 h of 1 h cycles. At the end of every 1 h cycle the solid IIP particles were recovered by centrifugation. The procedure was repeated 7 times, which resulted in a total of 7 h, for optimal template removal. A fresh solvent of the nitric acid and ethanol was added at the beginning of every cycle. The concentration of mercury(II) ions in both the supernatant and the IIP, on the other hand, were determined at the end of every 1 h removal cycle. The concentration of mercury in the supernatant liquids and corresponding IIP particles for each of the 1 h removal cycles were analysed by XRF spectrophotometer.

Optimal template removal at the 7th cycle was marked by no further change in the quantity of mercury(II) ions detected in the supernatant liquid. The IIP particles that resulted after the template removal provided the washed IIP particles. A
Effect of pH on extraction of Hg\textsuperscript{2+}

A constant value was reached. This marked the optimum time for the adsorption-equilibrium, the mixtures were then filtered and the concentration of the unextracted Hg\textsuperscript{2+} ions was determined by ICP-OES. The experiment was performed in triplicate. Mean values and standard deviations were determined. From the values, the extraction efficiencies (EEs) were evaluated using Eq. (1):

\[
EE(\%) = \frac{\text{spiked concentration} - \text{unextracted concentration}}{\text{spiked concentration}} \times 100
\]  

Optimisation of IIP quantity needed for maximum extraction of Hg\textsuperscript{2+}

20 mℓ aliquots of 1 µg/mL Hg\textsuperscript{2+} spiked water, each containing increasing concentrations of the Hg\textsuperscript{2+} imprinted polymer (5, 10, 15, 20, 30, 35, 25 and 40 mg) as well as the sodium acetate/acetic acid buffer, were mechanically shaken and kept for 24 h. The mixture was then filtered and the concentration of the unextracted Hg\textsuperscript{2+} measured by ICP-OES. The experiment was performed in triplicate. Mean values and standard deviations were determined. From the values, the extraction efficiencies (EEs) were evaluated using Eq. (1):

\[
EE(\%) = \frac{\text{spiked concentration} - \text{unextracted concentration}}{\text{spiked concentration}} \times 100
\]  

Optimisation of time needed for maximum extraction of Hg\textsuperscript{2+}

Following the procedure for optimisation of quantity, unextracted Hg\textsuperscript{2+} ions (at 5 min intervals) were determined until a constant value was reached. This marked the optimum time needed for the polymer to bind.

Effect of pH on extraction of Hg\textsuperscript{2+}

The optimal time and quantity of the IIP were used in the evaluation of the effect of pH by performing binding experiments at different pH. The pH of the solutions was adjusted using sodium acetate/nitric acid for pH 1-3, sodium acetate/acetic acid for pH 4-7.5, ammonium hydroxide/ammonia for pH 8-10 and ammonium hydroxide/sodium hydroxide for pH 10-12.

Selectivity experiments

Using the optimised conditions, competitive and selectivity experiments were performed. Both the imprinted and non-imprinted polymers were used to obtain 2 sets of experimental data. Polymer material (25 mg) was added to 20 mℓ aqueous solutions containing 1 µg/mL Hg\textsuperscript{2+}/Cd\textsuperscript{2+} and 1 µg/mL Hg\textsuperscript{2+}/Cu\textsuperscript{2+}. The pH was then adjusted accordingly to pH 7.2. These were placed in sealed containers and stirred magnetically at 900 r/min for 15 min. After the adsorption-equilibrium, the mixtures were filtered and the concentration of each ion in the remaining solution was measured by ICP-OES. The measured values gave the concentrations of the unextracted ions, from which EEs were evaluated. The experiments were performed in triplicate and the results subjected to statistical analysis at the 95% confidence limit.

The effect of imprinting on selectivity was defined by:

\[
K_s = \frac{C_i - C_u}{C_i} \times \frac{V}{m}
\]  

where:

\[K_s\] the distribution coefficient
\[C_i\] and \[C_u\] the initial and final concentrations, respectively
\[V\] the volume of the solution used for the extraction
\[m\] the mass of the polymer used for extraction.

The selectivity coefficient (k), for the binding of a particular metal ion in the presence of a competing ion can be obtained by:

\[
k = \frac{K_{\text{imprinted}}}{K_{\text{non-imprinted}}}
\]  

The relative selectivity coefficient \(k'\):

\[
k' = \frac{k_{\text{imprinted}}}{k_{\text{non-imprinted}}}
\]  

The results allow an estimation of the effect of imprinting on selectivity.

Sample preparation and analysis

Real water samples (tap, sea, river, pulverised coal solution, treated and untreated sewage, from the vicinity of Grahamstown, South Africa) were filtered through the Millipore Millex-HV hydrophilic PVDF 0.45 µm filter and refluxed for 1 h with 1% H\textsubscript{2}O\textsubscript{2} to oxidise the organic matter. The pH of the resulting water samples was adjusted accordingly to pH 7.2. For each of the samples the concentration of Hg\textsuperscript{2+} was determined by ICP-OES in 100 mℓ aliquots, for background, spiked (1µg/mL) and spiked with IIP (1µg/mL + 75 mg IIP). The samples with the IIP were continually shaken for 1 h to allow for equilibration after which the unextracted concentration of the ions was determined. EEs were then evaluated. The imprinted polymer with rebound Hg\textsuperscript{2+} was then eluted with millipore water, 3M HNO\textsubscript{3}, millipore water in sequence, and the desorbed Hg\textsuperscript{2+} was subsequently determined with ICP-OES. This procedure was followed for the determination of Hg\textsuperscript{2+} in the certified reference material (CRM).

Results and discussion

Characterisation of the polymers

Spectroscopic and physical characteristics of the polymer material were in agreement with those reported in literature (Wu et al., 2007). The SEM micrograph of the imprinted polymer displayed a regular, spherical morphology with numerous pores on the spherical surface (figure not shown), which is a suitable geometrical and textural property for a potential adsorbent. This indicates that there are many well-defined binding sites on the imprinted polymer. The irregular, amorphous morphology exhibited in the non-imprinted SEM micrographs showed no well-defined binding sites, hence indicating its lack of suitability to act as an adsorbent.

Characterisation of the imprinted (unwashed and washed) and non-imprinted polymers by FTIR showed similar locations and appearances of major bands. Of particular interest was the peak at 1 472 cm\textsuperscript{-1} due to the existence of the N-Hg-N stretching vibrations. It was strong in the unwashed polymer, relatively weak in the washed polymer and absent in the non-imprinted polymer. The strong peak in the unwashed polymer spectrum indicated the abundant existence of a coordination complex, [Hg(TPET)]\textsuperscript{2+} in its polymer structure. The relatively weak peak in the washed polymer was due to the removal of most of the Hg\textsuperscript{2+} ions from the polymer, thus resulting in very little coordination remaining between Hg\textsuperscript{2+} and TPET after washing. The Hg\textsuperscript{2+} ions were not included during the synthesis.
Washing off the mercury(II) ions and CTAB

The very weak N-Hg-N stretch at 1,472 cm⁻¹ in the FTIR spectrum of the washed polymer, as well as the low concentration of mercury (0.111%) determined by XRF in the final washing of the IIP, suggested that Hg²⁺ ions were thoroughly washed out. By contrast, the direct determination of mercury concentration of the washed IIP by XRF was 13.158% (see Table 1). This was noted to be very high for a polymer which was thoroughly washed, and for a material to be used in trace analysis. A logical explanation to these discrepancies is that some of the mercury may have gotten bound to the structure of the polymer during synthesis, to the extent that it could not be removed by the methods that were used for washing in this study. Another assumption is that, since XRF is a very sensitive technique and measures total mercury, it could be that the mercury that was detected in the washed IIP, even after thorough washing, was not the one involved in the selective nano-pore formation of the IIP, and is therefore of little concern to our study as it would not affect the performance of the polymer if it was not involved in the initial binding of the template.

Extraction behaviours of the polymer

The percentage of Hg²⁺ extracted increased with the quantity of polymer from 5 mg up to 25 mg, after which further increase in the quantity of the polymer did not yield any increase, as shown in Fig. 1. This marked the optimum quantity of the polymer powder (25 mg) needed to bind maximally. The highest extraction efficiency (EE) of Hg²⁺ achieved was calculated as 88.8 ± 0.1%.

Figure 2 shows the time dependence of the adsorption capacities of Hg²⁺ ions on the polymer powder (25 mg) as a function of time. Hg²⁺ ion adsorption increases with time during the first 15 min, after which it levels off (Fig. 2), exhibiting fast kinetics for binding the Hg²⁺ ions. A good EE (%) of the bound ions was recorded (89.9 ± 0.1%), even at these short equilibration-adsorption times.

The effect of pH on Hg²⁺ ion adsorption by the polymer powder (25 mg) is shown in Fig. 3. The polymer exhibited low affinities for Hg²⁺ ion extraction in very acidic and alkaline conditions, as indicated by the low EEs, with the highest calculated being 87.3 ± 0.1% at pH 7.2 ± 0.2. Low pH (acidic) solutions have a greater affinity for metal ions such as the Hg²⁺ ion; hence the ion was distributed more in the acidic solution than on the IIP particles. Thus the low EEs were recorded at low pH. Under alkaline conditions (high pH), it is likely that the Hg²⁺ ion complexed with the hydroxide ions forming soluble amphoteric hydroxides instead of being adsorbed on the IIP particles. As a result, low EEs were recorded.

Table 1

| Number of washings | % of Hg remaining in each washing (±0.002) | % of Hg remaining in corresponding dried polymer (±0.002) |
|--------------------|------------------------------------------|----------------------------------------------------------|
| 1                  | 6.335                                    | 35.486                                                   |
| 2                  | 0.873                                    | 33.347                                                   |
| 3                  | 0.675                                    | 26.343                                                   |
| 4                  | 0.426                                    | 24.562                                                   |
| 5                  | 0.111                                    | 13.158                                                   |
| 6                  | 0.108                                    | 13.153                                                   |
| 7                  | 0.109                                    | 13.155                                                   |

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Selectivity studies of the imprinted polymer powder (25 mg) for Hg$^{2+}$ versus closely related ions, Cd$^{2+}$ and Cu$^{2+}$

Competitive adsorption of Hg$^{2+}$/Cd$^{2+}$ and Hg$^{2+}$/Cu$^{2+}$ couples were investigated in an equilibration-adsorption batch system (see Table 2).

Cd$^{2+}$ ion was chosen as a competing ion because, like Hg$^{2+}$, it binds well with amine ligands, while Cu$^{2+}$ has a higher affinity for the same type of ligand (Wu et al., 2007). Additionally, both of the competing ions have the same charge, have comparative ionic radii, and often coexist with Hg$^{2+}$ ions, exhibiting certain interference properties in aqueous environments. Table 3 summarises the distribution coefficient ($K_d$), the selectivity coefficient ($k$), and the relative selectivity coefficient ($k'$) values of the competing ions with respect to the target ions, i.e., Hg$^{2+}$ ions.

As indicated in Eq. (1) the $K_d$ values are the ratios of the concentration of a particular ion between the imprinted polymer and the aqueous environment. It signifies the extraction ability of a unit quantity of the polymer for a particular ion in a unit volume of solution. $K_d$ values for the imprinted polymer for all ions were higher than those for the non-imprinted polymer, indicating that even the non-imprinted polymer has non-selective sites which any ion may be bound to. The $K_d$ value for the imprinted polymer used to extract Hg$^{2+}$ ions in the spiked samples was significantly higher (3 965) and Hg$^{2+}$/Cu$^{2+}$ (10 588) indicate that the prepared polymer is highly selective to Hg$^{2+}$ even in the presence of its closely-related analogues.

### Table 2

| Spiked ultrapure water (1 µg/mℓ) | % of Hg$^{2+}$ extracted | % of Cd$^{2+}$ extracted | % of Cu$^{2+}$ extracted |
|----------------------------------|--------------------------|--------------------------|--------------------------|
|                                  | IIP          | NIP          | IIP          | NIP          | IIP          | NIP          |
| Hg$^{2+}$                        | 99.89 (1.33) | 27.48 (0.92) | -            | -            | -            | -            |
| Cd$^{2+}$                        | -            | -            | 36.41 (0.44) | 23.11 (0.26) | -            | -            |
| Cu$^{2+}$                        | -            | -            | -            | 13.81 (0.47) | 7.36 (0.16)  | 6.83 (0.47)  |
| Mixture of Hg$^{2+}$/Cd$^{2+}$   | 88.88 (0.65) | 11.79 (0.09) | 21.79 (0.37) | 13.06 (1.03) | -            | -            |
| Mixture of Hg$^{2+}$/Cu$^{2+}$   | 96.11 (1.02) | 14.64 (0.58) | -            | 7.36 (0.16)  | 6.83 (0.47)  | -            |

Note: Values in parentheses are ± RSD values.

### Table 3

| Ion                 | $K_d$ (mℓ/g) x 10$^3$ | $K$ | $k'$ |
|---------------------|-----------------------|-----|------|
|                     | IIP       | NIP  | IIP       | NIP  | IIP       | NIP  |
| Hg$^{2+}$           | 908       | 0.1516 | -       | -    | -        | -    |
| Cd$^{2+}$           | 0.2290    | 0.1202 | -       | -    | -        | -    |
| Cu$^{2+}$           | 0.0640    | 0.1131 | -       | -    | -        | -    |
| Mixture of Hg$^{2+}$/Cd$^{2+}$ | - | - | 3965 | 1.26 | 3147 | - |
| Mixture of Hg$^{2+}$/Cu$^{2+}$ | - | - | 14188 | 1.34 | 10589 | - |

Validation and application to water samples

Calibration was performed using Hg$^{2+}$ standards at different concentrations in the range of 0-20 µg/mℓ. The obtained linear range regression equation and correlation coefficient ($r$) for Hg$^{2+}$ were $C_{cal} = 0.995 C_{cw} + 0.004$ and 0.9997, respectively, where $C_{cal}$ and $C_{cw}$ were instrumental (ICP-OES) signal and calculated (prepared) concentrations of Hg$^{2+}$ for each standard, respectively. Results showed that the linear range was several orders of magnitude for the determination of Hg$^{2+}$ in aqueous environments. The limit of detection (LOD, 3σ) was calculated as 0.036 ng/mℓ (36 ng/ℓ) and meets the monitoring requirements for the USA EPA of 2 000 ng/ℓ for Hg$^{2+}$ in drinking water.

The accuracy of the method was validated by determining the Hg$^{2+}$ concentration of an aqueous NIST traceable CRM, with certified Hg$^{2+}$ concentration of 9.99 ± 0.03 µg/mℓ. After concentrating the CRM with the imprinted sorbent, mean Hg$^{2+}$ concentrations of 10.01 ± 0.01 µg/mℓ for the 9.99 µg/mℓ CRM and 0.004 and 0.9997, respectively, were instrumental (ICP-OES) signal and calculated (prepared) concentrations of Hg$^{2+}$ for one hundred-times diluted original CRM, were determined with ICP-OES for $n = 10$. The accuracy and precision of the method were found to be acceptable at 95% confidence limit for the concentration and analysis of Hg$^{2+}$ in aqueous solutions.

When the method was applied to real water samples, high extraction efficiencies, over 84% in all cases (see Table 4), were obtained. This demonstrated the suitability of the sorbent to selectively extract mercury(II) ions from complex aqueous matrices.
In this study, a mercury(II) ion-imprinted functionalised polymer with exceedingly high performance, as marked by the fast equilibration-adsorption kinetics, the very large relative selectivity coefficients, high extraction efficiency percentages of the targeted ion (Hg⁺), even in the presence of other closely-related ions, was successfully prepared. The polymer was simple and relatively easy to prepare. To the best of our knowledge, this is the first time such relative coefficients (k'), in the ranges of several thousands, have been reported. Experimental results obtained show that the polymer has high analytical potential for selective extraction and pre-concentration of mercury(II) ions in the presence of closely-related ions. Its use as a solid-phase extraction sorbent can be further evaluated in future.

**Conclusions**

In this study, a mercury(II) ion-imprinted functionalised polymer with exceedingly high performance, as marked by the fast equilibration-adsorption kinetics, the very large relative selectivity coefficients, high extraction efficiency percentages of the targeted ion (Hg⁺), even in the presence of other closely-related ions, was successfully prepared. The polymer was simple and relatively easy to prepare. To the best of our knowledge, this is the first time such relative coefficients (k'), in the ranges of several thousands, have been reported. Experimental results obtained show that the polymer has high analytical potential for selective extraction and pre-concentration of mercury(II) ions in the presence of closely-related ions. Its use as a solid-phase extraction sorbent can be further evaluated in future.

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### Table 4

| Water sample          | Tap       | Sea       | River      | Treated sewage | Untreated sewage | Pulverised coal solution |
|-----------------------|-----------|-----------|------------|---------------|-----------------|--------------------------|
| Background            | -         | -         | -          | -             | -               | ~0.0056                  |
| 1 µg/m³ Hg⁺² spiked   | 1.0002    | 0.9998    | 1.0009     | 1.0019        | 1.0017          | 1.0056                   |
|                       | (0.02)    | (0.02)    | (0.03)     | (0.02)        | (0.05)          | (0.03)                   |
| Calculated values     | 0.0002    | -0.0002   | 0.0009     | 0.0019        | 0.0017          | 0.0056                   |
| 1 µg/m³ Hg⁺²⁺+ IIP    | 0.1338    | 0.1403    | 0.1400     | 0.1479        | 0.1516          | 0.1459                   |
|                       | (0.0002)  | (0.0002)  | (0.0002)   | (0.001)       | (0.002)         | (0.002)                  |
| EE (%)                | 86.62     | 85.97     | 86.01      | 85.24         | 84.87           | 85.49                    |
|                       | (0.99)    | (0.47)    | (1.02)     | (0.68)        | (0.94)          | (1.06)                   |

Note: Values in parentheses are % RSD values