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Selective recognition of arsenic by tailoring ion-imprinted polymer for ICP-MS quantification

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ABSTRACT

A novel arsenic-ion imprinted polymer (As-IIP) was firstly synthesized for the separation and recovery of trace elemental As from environmental water samples. Polymers prepared from bifunctional monomers with intrinsic metal-binding capability are a platform for tailoring ion-selectivity *via* imprinting moiety–template interaction, without complex formation and ligand immobilization. In the present study, As-IIPs based on 1-vinylimidazole, 4-vinylpyridine and styrene were designed to investigate the imprinting mechanism in relation to their structural and functional properties. In terms of selectivity as well as imprinting effects compared with the non-imprinted polymer (NIP), 1-vinylimidazole-based As-IIP exhibited superior analyte recognition for As ion among 23 competing elements, with a 25-fold enhancement in the practical dynamic and static adsorption capacity range (0.048–4.925 μmol g^{-1}). The robust As-IIP sorbent features good reusability up to 20 cycles and a wide working pH 5–7 for a firstly reported solid-phase extraction (SPE) application. As a result of selective sample clean-up, As-IIP-SPE offered limits of detection (LOD) and quantification (LOQ) down to 0.025 and 0.083 μmol L^{-1}, respectively, for environmental sample analysis using inductively coupled plasma-mass spectrometry.

1. Introduction

Among the wide array of metal(loid) pollutants, arsenic (As) is of paramount environmental significance due to its carcinogenicity and acute toxicity [1–3]. Its ubiquitous existence in the nature originates from natural processes such as weathering and volcanic emission, as well as anthropogenic activities including mining, use of pesticides and fossil fuel combustion [4]. The demand to routinely monitor the trace occurrence of As in natural water systems, with typical level less than 10 μg L^{-1}, consequently requires selective sample clean-up to afford a complexity of environmental water matrix.

Up to now, pretreatment methods of environmental water sample analysis primarily involve solid-phase extraction (SPE) techniques to replace the now obsolete liquid–liquid extraction (LLE), under the predictable trend in modern analytical chemistry toward procedural simplicity, minimal reagent consumption, expedient field sampling and automation [5]. SPE is especially favourable for metal ion extraction, considering its flexibility in principal sorbent design for complex formation between the analytes and a selected ligand, e.g. polyaniline and polypyrrole materials have been adopted for the extraction of As [6,7]. Similarly, high affinity reagents, such as ammonium pyrrolidine dithiocarbamate and dimercaptosuccinc acid, were also applied to aid As adsorption on carbon nano tubes and titanium oxide solid supports [8,9]. These specific complex-forming interactions, however, are also shared by a range of ions with similar properties [9–11]. While this chelation technique is being exhaustively exploited, scientists have been searching for a new generation sorbent system to re-define selectivity for elemental analysis in environmental matrices with ion-imprinting technology [12–14].

In recent years, ion-imprinted polymers (IIPs) have been investigated for their remarkable capability to recognize selective ions. The concept of ion-imprinting is understood as a process whereby cross-linking functional monomers align in a predetermined orientation according to their stereo-chemical interactions with the template metal ions. Upon removal of the template, well-defined recognition sites are formed with the memory effect programmed in a fixed polymeric structure. The selectivity is substantially enhanced depending on the coordination geometry, charge and size of the analyte ions [15].

Since monomer–template interaction has been identified as a major contributor to IIP selectivity, a number of research studies have attempted to manipulate functional moieties for imprinting the analytes of interest. “Trapping” a non-vinylated chelating ligand

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within the polymeric network is a popular approach to imprinting a metal complex derived from a variety of ligand choices [13,16]. However, without chemical immobilization, these functional ligands may interact with other elements, resulting in relatively unselective IIPs [14]. As polymerizable ligands are scarce, this problem has been partially addressed by laborious and complicated synthesis of vinylated ligands for metal binding, such as (4-ethenylphenyl)-4-formate-6-phenyl-2,2′-bipyridine [17], (2Z)-N,N′-bis(2-aminoethylic)but-2-enediamide [18], N-methacryloyl-(L)-cysteinemethylester [19] and 2-methyacryloylamidohistidine [20,21]. Alternatively, the direct preparation of the most fundamental linear polymer became a reliable strategy for fabricating IIP selectivity from bifunctional monomers. Carrying variable metal-binding moieties, simple monomers such as vinylimidazole and vinylpyridine can be customized for ion selectivity without special skills or equipment [22–24]. There is still no preference, among various choices, for a particular polymer accountable in delivering imprinting power.

Despite the fact that imprinting technology is still in its infancy, its application is widespread in eco-environmental industry including effluent water treatment for heavy metal and elemental pollutants. For instance, the recent development of imprinted chitosan beads has enabled the removal of arsenic [25,26]. However, the potential of turning it into an analytical sorbent has been overlooked during the preparation and application of these reported materials. Apart from the advertised selectivity, imprinting technology would confer considerable upgrade to modern sample preparation for As only if more creditable analytical properties were better explored. Therefore, we were prompted to pioneer an ideal As-IIP SPE sorbent with a capacity for reproducible recovery in elemental As analysis. Further, in an attempt to optimize analyte selectivity of the imprinted material, this work is also the first to elucidate the binding mechanism by comparing three analogues of functional monomer, namely 1-vinylimidazole, 4-vinylpyridine and styrene. Variable imprinting effect among the synthesized IIPs was evident based on evaluation on their analyte selectivity against concomitant species, in comparison to the performance of non-imprinted polymer (NIP) control. Herein, a selected As-IIP in this work highlights simple polymer preparation, outstanding analyte selectivity and analytical robustness, for a firstly reported SPE application in trace As environmental analysis using inductively coupled plasma-mass spectrometry (ICP-MS).

2. Experimental

2.1. Instruments

ELAN DRC II ICP-MS instrument (PerkinElmer, Waltman, MA, USA) with a Meinhard nebulizer and a cyclonic spray chamber was used in all elemental determinations with operation parameters summarized in Table 1. Measurement of pH was carried out using a Thermal Scientific (Waltham, MA, USA) ORION 3 STAR Benchtop pH meter. A Julabo (Seelbach, Germany) SW22 shaking water bath and Kubota (Bunkyo, Kyoto, Japan) 8420 centrifuge was utilized in the static adsorption capacity study. A mini-sieve set purchased from Sigma–Aldrich was used for screening polymer powder.

Table 1
Operation parameters of ICP-MS.

Parameter	Setting
ICP-DRC-MS	PerkinElmer ELAN DRC II
RF power	1175 W
Plasma gas flow	15 L min^{-1}
Auxiliary gas flow	1 L min^{-1}
Nebulizer gas flow	0.96 L min^{-1}
Cones	Pt and Ni
AutoLens	Engaged
Mass monitored	^{75}As
Dwell time	50 ms

Fourier-transformed infra-red spectra were obtained with a PerkinElmer Paragon 1000 PC instrument. Polymeric surface morphology was characterized by a LEO 1530 Field Emission Scanning Electron Microscope (SEM, JEOL, Akishima, Tokyo, Japan).

2.2. Chemicals and reagents

Sodium arsenate dibasic heptahydrate, 1-vinylimidazole, 4-vinylpyridine, ethylene glycol dimethacrylate (EGDMA) and 2,2′-azobis-isobutyronitrile (AIBN) were obtained from Sigma–Aldrich (St. Louis, MO, USA). Styrene was purchased from Riedel-de Haën (St. Louis, MO, USA). Methanol (HPLC grade, DUKSAN, Ansan, Gyeonggi-do, Korea) and acetic acid (99.8%, Riedel-de Haën) were used in the synthetic solvent system. Acidic solution was prepared from concentrated nitric acid (ARISTA, BDH, UK) for IIP leaching and SPE eluent.

MilliQ water (Millipore, Billerica, MA, USA) of 18.2 MΩ cm was used in preparation of all aqueous solutions. Elemental standard solutions of As, V, Mo, In, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Se, Ag, Cd, Sb, Ba, Au, Hg, Tl, Pb and Bi were prepared by appropriate dilution of 1000 mg L^{-1} stocks purchased from VHG Labs (Manchester, NH, USA).

Daily operation of ICP-MS used liquefied argon gas (Hong Kong Oxygen & Acetylene, Hong Kong) of 99.9995% purity.

2.3. Synthesis of As-ion-imprinted polymers

Three types of As-IIP were synthesized in this work, each using one of the monomers 1-vinylimidazole, 4-vinylpyridine or styrene. The procedures and reactant ratio of bulk polymerization, according to previous description [22], were as follows:

1.6 mmol of arsenate template ion and 6.5 mmol monomer were first dissolved in 10 mL 25% (v/v) HAc/MeOH in a reaction flask. Following 5 min of magnetic stirring, 32 mmol EGDMA cross-linker and 40 mg AIBN initiator were introduced into the mixture. After purging for another 5 min, the mixture was polymerized at 60 °C under N_2 atmosphere overnight, yielding a white rigid solid. The product was ground and screened through a 125-μm sieve to powder. After MeOH rinsing, the polymer was successively treated with 2 M HNO_3^- until the As template could no longer be detected by ICP-MS from the washings. The leached polymer was exhaustively washed with water until restored a neutral pH. Finally, oven-dried at 80 °C.

Non-imprinted versions of the respective monomers, denoted here as NIP, were also prepared for the control study of the imprinting effect. The same preparation procedures were followed but without the template ion.

2.4. SPE procedures

SPE cartridges were prepared by packing synthesized As-IIP or NIP of 80 mg in each 3-mL fritted tube (Sigma–Aldrich) for the studies of selectivity, dynamic adsorption capacity and sample recovery. The packed column was briefly conditioned with 2 mL MilliQ water. The amount of 5 mL sample was passed through the column with a flowrate of 1 mL min^{-1}. pH adjustment was unnecessary if the acidity of the sample fell within pH 5–7. The retained analytes were eluted with 5 mL 0.6 M HNO_3 and subsequently analysed by ICP-MS.

2.5. Batch experiments

The following procedures were used in the determination of static adsorption capacity and adsorption kinetics: As-IIP or NIP was suspended in a portion of standard solution with constant shaking for a fixed time. The suspension was then centrifuged, syringe-filtered before ICP-MS analysis.

2.6. Sample collection

Fresh water samples were collected from Shing Mun River of Hong Kong during the spring of 2011. Samples were collected in clean polypropylene bottles, then filtered through 0.45 μm membrane and subject to immediate analysis. Any pending samples were stored at 4 °C.

3. Results and discussion

The use of bifunctional vinylated compounds, acting simultaneously as a monomer and an interactive agent, is one of the most extensively adopted approaches in preparing IIPs. Although it has been previously proposed that the matrix–template interaction *via* N-functionalized moieties is a major contributor to the imprinting effect and recognition power of the imprinted material [18,19], this proposal has not been verified. Thus, our major objective here was to elucidate the binding mechanism of As-IIPs. In this regard, a systematic investigation was launched to compare the typical vinylated pyridine and imidazole, which are heterocyclic analogues comprising one and two nitrogen atoms, respectively. Considering the non-substituted homocyclic structure, styrene polymer was also incorporated along the analogous series in the experimental design of selectivity studies.

3.1. Comparative selectivity studies

The imprinting effect and the ion-recognition behaviors of As-IIP materials are well reflected by As selectivity in the presence of other competing ions, according to a series of distribution and comparative parameters:

$$K_\mathrm{d} = \frac{C_\mathrm{i} - C_\mathrm{f}}{C_\mathrm{f}} \times \left(\frac{\text{volume of solution, mL}}{\text{mass of polymer, g}}\right) \tag{1}$$

where K_d, C_i and C_f represent the distribution coefficient (mL g^{-1}) of an ion on the polymer, initial and final solution concentrations (μg L^{-1}), respectively. The selectivity coefficient, k, of As relative to the competing ion can then be calculated accordingly:

$$k = \frac{K_{\mathrm{d(As)}}}{K_{\mathrm{d(foreign\,ion)}}} \tag{2}$$

By comparing the ion selectivities between As-imprinted and non-imprinted polymer, the imprinting effect could be evaluated, giving rise to the term relative selectivity coefficient (k'):

$$k' = \frac{k_{\text{As-imprinted}}}{k_{\text{non-imprinted}}} \tag{3}$$

In order to systematically evaluate the performance of the enlisted polymeric materials, they were subject to a selectivity study by comparing the adsorption of 20 μg L^{-1} As against a list of elemental ions, namely, V, Mo, In, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Se, Ag, Cd, Sb, Ba, Au, Hg, Tl, Pb and Bi, at the same concentration. Comparing the k values among different imprinted sorbents (Table 2), imidazole-based As-IIP presented better As retention and selectivity than the vinylpyridine polymer under competition of 23 other elements. Although the adsorptivities of non-targeted ions V, Mo, In, Se, Ag, Sb, Au and Hg were found comparable to that of the As template, the process of ion-imprinting substantially improved the analyte specificity in terms of k' value. As expected, the overall ion recognition power of the styrene-based control

Table 2
Selectivity data on the As-imprinted and non-imprinted polymers.

Elements	1-Vinylimidazole			4-Vinylpyridine			Styrene		
	K_d[a]	k[b]	k'[c]	K_d	k	k'	K_d	k	k'
As-imprinted polymer (As-IIP)									
As	934	–	–	46.8	–	–	5.51	–	–
Sc	18	49.8	3.42	2.02	23.2	2.98	1.03	5.33	2.36
Ti	116	8.05	5.42	3.86	12.1	3.80	1.03	5.33	0.818
V	4495	0.208	1.08	221	0.212	0.441	1.07	5.13	1.91
Cr	9.91	94.2	2.03	3.49	13.4	0.731	1.03	5.33	1.34
Mn	0.040	23,337	17.9	0.015	3121	2.90	0.010	550	9.83
Fe	1.78	522	41.8	1.82	25.8	0.931	2.80	1.97	1.24
Co	4.47	208	0.367	0.347	135	3.50	0.441	12.5	2.55
Ni	4.90	190	0.397	0.731	64.1	0.402	0.728	7.57	1.12
Cu	2.05	455	48.0	3.55	13.2	0.146	1.12	4.93	1.38
Zn	2.82	331	6.38	2.82	16.6	0.178	0.682	8.08	2.27
Ge	7.09	132	6.29	1.66	28.2	1.05	0.543	10.1	3.37
Se	447	2.09	2.47	45.3	1.04	1.07	6.30	0.875	0.808
Mo	3640	0.257	6.64	11,061	0.004	0.092	6.97	0.791	0.875
Ag	5536	0.169	9.94	1974	0.024	0.307	3.14	1.76	0.879
Cd	3.97	235	0.542	0.661	70.9	1.82	1.60	3.44	1.34
In	7092	0.132	0.135	3.33	14.1	15.3	1.66	3.32	0.772
Sb	327	2.86	1.70	13.7	3.43	1.87	6.43	0.857	0.853
Ba	0.677	1380	1.67	0.391	120	0.178	1.21	4.57	0.265
Au	597	1.56	89.8	2212	0.021	0.123	176	0.031	0.522
Hg	2443	0.382	25.6	2016	0.023	0.568	144	0.031	0.734
Tl	65.6	14.2	35.6	64.4	0.727	0.268	35.0	0.157	0.734
Pb	0.677	1381	1.82	2.09	22.4	0.464	0.728	7.57	0.372
Bi	0.317	2947	3.23	1.59	29.5	0.543	2.85	1.93	0.458

[a] Distribution coefficient (mL g^{-1}).
[b] Selectivity coefficient.
[c] Relative selective coefficient.

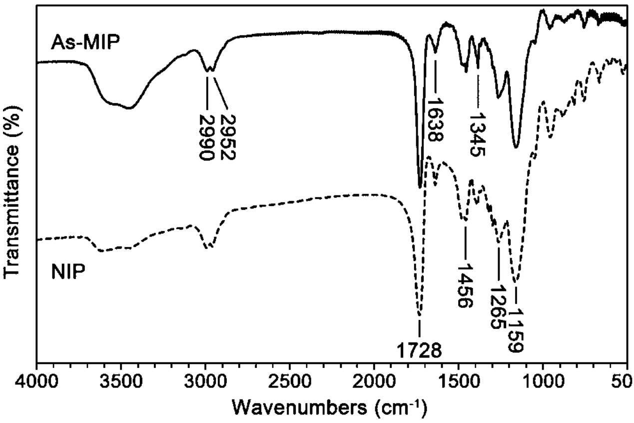

Fig. 1. IR spectra of imidazole-based As-MIP and NIP samples.

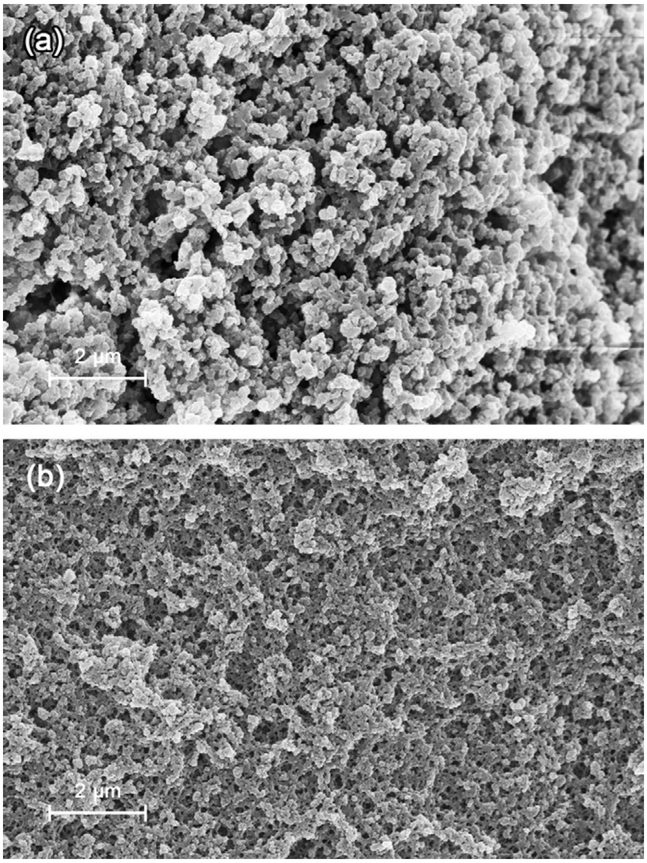

Fig. 2. Scanning electron microscopic images of (a) As-IIP and (b) NIP particles at 20,000× magnification.

was insignificant, due to the absence of coordinative functionality. These observations verify the hypothesis that the recognition ability of ion-imprinted polymer is in critical relationship to number of binding points in the solid matrix, hence, the density of ion-binding N-functionalities of the precursor monomer. In view of the best performance shown in all parameters, imidazole-based As-IIP was selected for downstream SPE application.

3.2. Characterization studies

In order to characterize the synthesized polymer, infra-red (IR) spectroscopy was performed to determine the molecular characteristics of the EGDMA/1-vinylimidazole matrix (Fig. 1). Absorption peaks at 2990 and 2952 cm^{-1} correspond to the stretching frequencies of methyl(ene) groups. The strong spike at 1728 cm^{-1} indicates the carbonyl vibration of the EGDMA, whereas the antisymmetric C–O stretching of the ester is represented by broad 1265 and 1159 cm^{-1} bands. The weak adsorptions at 1638 and 1456 cm^{-1} are assigned to the C=C and C=N structure of the aromatic imidazole ring. The frequency of antisymmetric CH_3 deformation is identified at 1345 cm^{-1}.

Scanning electron microscopic (SEM) images are presented in Fig. 2. SEM characterizes the surface morphologies of both imprinted and non-imprinted imidazole polymers. Due to the nature of bulk polymerization, particles of both polymers generally display a non-spherical appearance. The textural characteristics were closely examined at 20k× magnification, revealing a distinctive pattern on the imprinted surfaces. The porous quality of the As-IIP explicitly evidence the formation of As-imprinted cavities after template leaching, whereas the rough surface of NIP displays the lack of comparable porous structure that essentially activates uptake of the analytes.

3.3. Analytical parameters of As-IIP SPE

Various parameters affecting the SPE performance of As-IIP sorbent were investigated, in order to optimize the retention, elution and hence quantitative recovery of As analytes.

First of all, the pH of the sample solution affects the retention behavior by determining the degree of ionization of As analytes as well as the nature of the polymer matrix. In order to study the retention profile, the recovery of a series of 20 $\mu g L^{-1}$ standards was measured after SPE sampling at different pHs. Fig. 3 indicates an optimum range of pH within 5–7. At pH < 4, the analyte started stripping off from the sorbent as the As ions were protontated in an acidic environment (pK_{a1} for arsenate is 2.2) which eventually interrupted the binding interaction. On a contrary, lower recovery in extreme basic medium was due to keen competition between analytes and the hydroxyl anions. Therefore, the working pH 5–7, which is about the typical value of natural water, was adopted in the routine SPE analysis for procedural convenience.

The loading flowrate of the sample solution is a critical time-dependent parameter controlling analytes' adsorption onto the recognition site of the polymer matrix. Experimental result showed that the analyte recoveries were compromised beyond 1.5 mL min^{-1}. Thus, a flow of 1.0 mL min^{-1} was then chosen the optimum flowrate to secure analyte recovery during column procedures.

Acidic solutions were considered to be the ideal choice of AS-IIP eluent as they protonate As anions and release them from the binding sites without the need for specific complexing agents such as EDTA [27] and thiourea [28]. The use of hydrochloric acid was cautiously avoided as it is the primary source of isobaric interference $^{40}Ar^{35}Cl^{+}$ ($m/z = 75$) in $^{75}As^{+}$ detection by ICP-MS [29]. Instead,

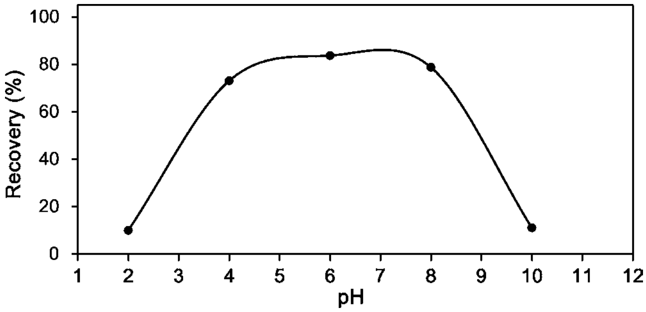

Fig. 3. Study of the recovery of 20 $\mu g L^{-1}$ As analyte in SPE using As-IIP sorbent at different loading pHs.

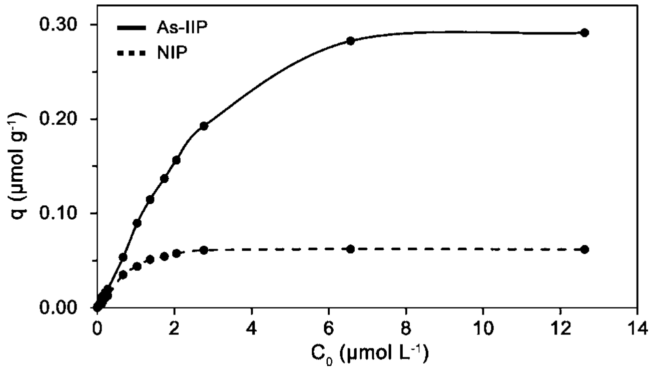

Fig. 4. Study of static adsorption capacity of template As on As-IIP and NIP carried out by suspending 10 mg polymer in a series of 5-mL standards.

nitric acid solution was used and a concentration of 0.6 M was found effective for completing analyte recovery in 5-mL portions without dilution.

3.4. *Adsorption characteristics of As-IIP*

3.4.1. *Static adsorption capacity*

To further evaluate the uptake behavior of the selected As-IIP, a series of the adsorption properties were characterized in terms of the analyte As ion. Static adsorption capacity was defined as the limit of uptake in equilibrium using batch procedures described in Section 2.5. 10 mg of polymeric sorbent was equilibrated overnight in a series of 5-mL standards over a concentration range from 0 to 1000 µg L^{-1}. The amount of analyte adsorbed on the polymer (µmol g^{-1}) was calculated as:

$$q = (C_0 - C_e) \times \frac{V}{m} \tag{4}$$

where C_0 and C_e represent the initial and equilibrium concentrations (µmol L^{-1}), respectively, V the volume of standard solution (L) and m the mass of sorbent used (g). As shown in Fig. 4, the amount of adsorption increased with analyte concentration until a saturation point was reached. The study of NIP has shown a similar pattern with saturation occurring at a much lower concentration level, which suggests a lower capacity than that of As-IIP.

According to a simple Langmuir adsorption isotherm:

$$\frac{1}{q_e} = \frac{1}{q_{max} b C_e} + \frac{1}{q_{max}} \tag{5}$$

where q_e and b correspond to the amount of analyte ion adsorbed at equilibrium (µmol g^{-1}), and the Langmuir constant (L µmol^{-1}), the values of maximum adsorption capacity q_{max} (µmol g^{-1}) could be determined from the linear plot of $1/q_e$ against $1/C_e$ (Fig. 5), which is a well-fitted Langmuir model implying monolayer ion adsorption [30]. The adsorption capacities of As-IIP and NIP were found to be 4.926 and 0.191 µmol g^{-1}, respectively, of which the significant difference indicates the role of ion-imprinting in determining the sorption property of the sorbent. Ion-binding cavities resultant from imprinting essentially activated the polymer surface for extensive ion uptake, whereas the interactions of NIP, lacking ion-recognition ability, remained unspecific. The superior adsorption capacity of As-IIP sorbent is as high as 6 mg L^{-1}, representing the material's robustness in SPE application.

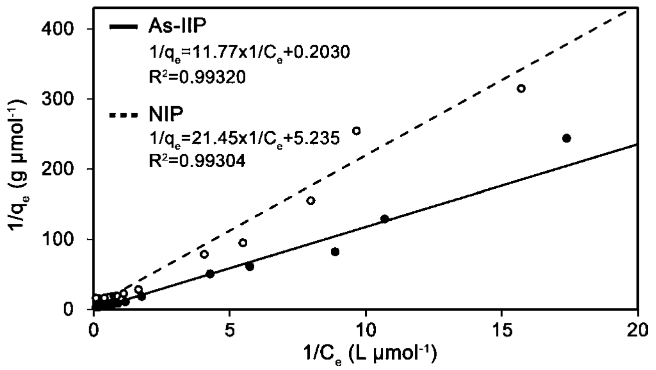

Fig. 5. Langmuir isotherms of template As adsorption on As-IIP and NIP.

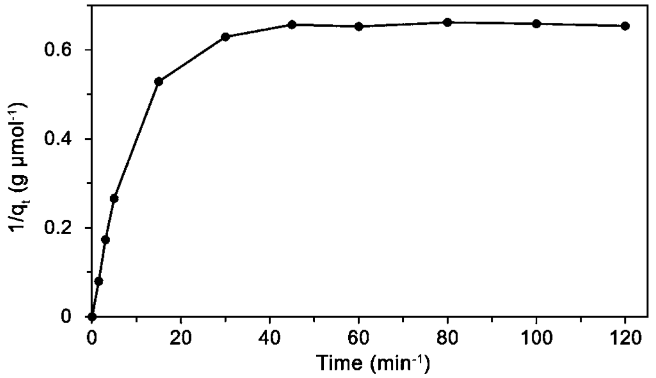

Fig. 6. Uptake of template As ion by As-IIP as a function of time. Analyte concentration was measured at time intervals from a suspension of 50 mg polymer in 20 µg L^{-1} standard.

3.4.2. *Adsorption kinetics*

In order to investigate the time-dependence of As-IIP ion adsorption, real-time As level was monitored in a batch experiment while 50 mg As-IIP was equilibrated in a 25 mL of 20 µg L^{-1} standard. Within 35 min, adsorption equilibrium was reached (Fig. 6). The linear plot of $-\ln(1-F)$ against t describes the adsorption kinetics according to the first-order equation of Lagergren [31]:

$$-\ln\left(1 - \frac{q_t}{q_e}\right) = K_{ad} t \tag{6}$$

where q_t and q_e were the amount of template ion adsorbed at time interval t and equilibrium, respectively. The adsorption rate, as represented by the slope in Fig. 7, was 0.102 min^{-1}.

3.4.3. *Dynamic adsorption capacity*

In SPE operation, dynamic capacity gives a more realistic evaluation to the working capacity of the sorbent, by considering the sole ion adsorption performance within the mass transfer zone (MTZ). In order to determine the breakthrough capacity of 200 mg

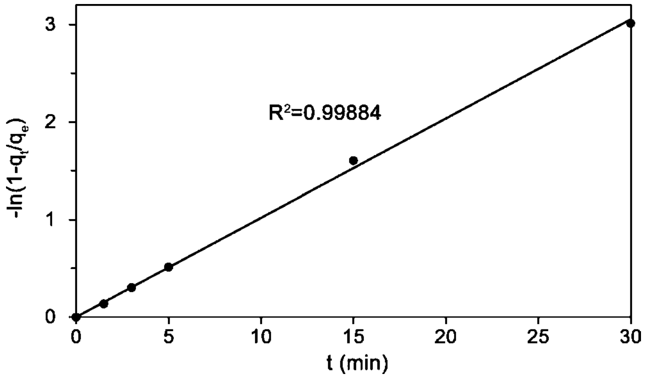

Fig. 7. A Lagergren first-order plot for the As adsorption rate of As-IIP.

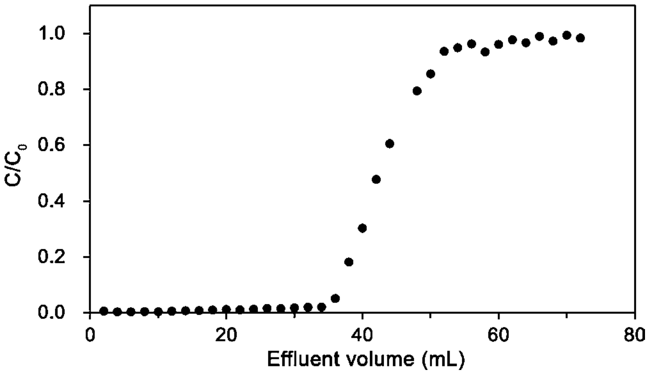

Fig. 8. A breakthrough curve of a 200-mg As-IIP for the template As ion. C/C_0 is the ratio between the concentrations measured in every 2-mL aliquot of effluent and the initial value 20 μg L^{-1}.

As-IIP sorbent, SPE experiment was conducted by analysing every 2-mL aliquot of 20 μg L^{-1} standard passing through the column. A breakthrough point defined as 2% exhaustion [32] was reached after percolating 34 mL standard (Fig. 8). As expected, the calculated breakthrough capacity of 0.048 μmol g^{-1} was lower than that of static adsorption. The value represents a total capacity of 0.29 μg As in 80 mg SPE sorbent to accommodate the natural analyte levels in real samples.

3.5. Analytical figures of merit and effect of interference

As a benefit from outstanding ion-selectivity, the As-IIP-SPE column eliminated potential interference for sensitive ICP-MS measurement which is prone to sample matrix effect. The limit of detection (LOD) of the target As analyte using the optimized As-IIP SPE, as summarized in Table 3, was comparable to other reports of solid-phase preconcentration [6,9,33–35]. The LOD and LOQ values were calculated according to the FDA guidelines as three and ten times, respectively, the standard deviations of five blank extractions divided by the slope of the calibration curve [36], which was prepared by the extraction of 0.5–20 μg L^{-1} standards. The good extraction precision at different concentration levels was also expressed in terms of relative standard deviations (R.S.D.), which were 1.9% at 0.5 μg L^{-1} and 4.2% at 20 μg L^{-1}.

The effect of interfering ions on the retention of As analyte was also assessed. The selection of the interferents for the study was based on the binding affinity of those elements which were comparable to that of the target analyte. Experiments were conducted to evaluate the retention of the target ion on the imprinted sorbent from a standard solution containing large excess of V, Se, Mo, Ag, In and Sb elements of which the selectivity coefficients k are smaller or close to 1 (Table 2). Result showed that the recovery of 0.1 μg As was reproduced within the range of 104.3–116.9% under 1000 μg L^{-1} challenge of each foreign species. In spite of high adsorptivity on the sorbent, up to 93.8% of the selected interferents were removed from the sample after SPE extraction, indicating a good tolerance and specificity of the As-IIP-SPE for sample clean-up.

Table 3
Analytical figures of merit of using As-IIP as SPE sorbent.

LOD, μg L^{-1}	0.025
LOQ, μg L^{-1}	0.083
Precision, R.S.D. (%)[a]	
0.5 μg L^{-1}	1.9
20 μg L^{-1}	4.2
Linearity, R^2	0.99988
Spike sample recovery (mean ± S.D., %)[a]	
0.5 μg L^{-1}	90.5 ± 3.58
20 μg L^{-1}	86.7 ± 7.03

[a] $n = 3$.

We then evaluated the applicability of the As-IIP in environmental water analysis. Water samples were collected from Shing Mun River of Hong Kong, and analysed. This water is known to have substantial levels of Na, Mg, Al, K, Ca, Mn, Fe, Sn and Ba. The high levels of non-metal N and Cl, regarded as interference for trace determination, indicate rich content of nutrients and organic matters. The target As analyte was quantitatively recovered within 86.7–90.5% from spiked river samples at 0.5 and 20 μg L^{-1} levels. Eventually, trace level of As was detected from the river sample with concentrations of 0.67 ± 0.03 μg L^{-1}, respectively. These data confidently reflect the specificity and robustness of the As-IIP in SPE application even in the presence of various foreign species.

To reassure the reusability of the As-IIP sorbent, life-cycles of sample loading and elution procedures were successively performed on a SPE column. It was shown that the stability of the polymeric sorbent enables at least 20 SPE cycles with no observable change in performance and the analyte recovery remained within 6.5% R.S.D. This is ideal for routine laboratory use.

4. Conclusions

The original development of As-IIP, focusing on SPE application of As, was hereby described. The use of a simple bifunctional monomer in the process of ion-imprinting eliminates the necessity for specific ligand synthesis and immobilization. Based on comparative study using vinylated imidazole, pyridine and styrene monomers, the relationship between imprinting effect and the metal-binding functionalities in terms of analyte selectivity relative to the NIPs has been proven. As a direct outcome of the ion-imprinting technique, the selectivity and adsorption capacity of the selected imidazole-based polymer was greatly enhanced. Finally, these advantages of As-IIP were adopted in SPE application to achieve robust environmental analysis at ppt levels.

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