Use of the dummy approach for the synthesis of ion imprinted polymers with Ni(II) or Zn(II) as template ion for the solid- phase extraction of Cu(II)

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Abstract :

There is a strong interest in monitoring copper in environmental waters, but its direct analysis suffers from strong matrix interferences. This is why, a sample pretreatment based on solid-phase extraction (SPE) is often used but conventional sorbents usually lack specificity. It is overcome with ion-imprinted polymers (IIPs). This work evaluates for the first time the use of the dummy approach for the synthesis of Cu(II)-targeting IIPs. Two analog ions Ni(II) and Zn(II) were tested as templates and the resulting IIPs were packed in SPE cartridges. The SPE procedure was designed by optimizing a washing step following the sample percolation, to eliminate the interfering ions retained on the IIP by non-specific interactions. To optimize the washing step, solutions at different pH or containing tris(hydroxymethyl)aminomethane as a complexing agent at different concentrations were tested and combined. Zn-IIP appeared more promising than Ni-IIP, showing excellent specificity and a high selectivity. Its retention capacity was determined to be 100 µg/g, and different isotherm models were evaluated to fit with the adsorption data. Finally, applications to mineral and sea waters were successfully completed and led to high and repeatable extraction recoveries for Cu(II) (88 ± 1% and 83 ± 3%, respectively).

Keywords : copper, environmental waters, ICP-MS, ion-imprinted polymer, solid-phase extraction

Abbreviations

AIBN: 2, 2′-azobisisobutyronitrile; dSPE: dispersive solid phase extraction; EGDMA: Ethylene glycol dimethacrylate; EU: European Union; ICP-MS: Inductively coupled plasma mass spectrometry; IIP: Ion-imprinted polymer; MAA: Methacrylic acid; NIP: Non-imprinted polymer; Tris: tris(hydroxymethyl)aminomethane; WHO: World Health Organization.

1 Introduction

Environmental pollution of heavy metals has been a major concern for many years. With the growing economy and rapid industrialization, the source of heavy metals today is mainly anthropogenic activity including mining wastes, landfill leachates, municipal wastewater, urban runoff and industrial wastewaters [1]. Although an essential trace element for humans, copper is known as one of the most common heavy metal pollutants in water, mainly sourced from the electroplating, electronic and metal-finishing industries [2]. Excessive intake of copper or its long-term accumulation in the human body has been reported to cause serious diseases, including Indian childhood cirrhosis and Wilson's disease [3]. As suggested by the World Health Organization (WHO) as well as the Directive 98/83/CE of the European Union (EU), the health-based guideline value of copper in drinking waters is 2 mg L^{-1} [4,5]. In addition to the harmful effects on human health, the copper may also pollute the marine environment and impact the functioning of ecosystems, due to, for example, its use as a biocide in marine antifouling paints [6,7]. In this context, the interest in the monitoring of copper in environmental waters has immensely increased during the last few decades.

Nowadays, various techniques have been employed to quantify the copper in trace amounts, whereas the direct analysis of real samples suffers from strong matrix interferences, especially with the most highly sensible techniques such as inductively coupled plasma mass spectrometry (ICP-MS) and electrothermal atomic absorption spectrometry [8]. To solve this problem, a sample pretreatment is commonly used for eliminating abundant matrix components and/or enriching the target analytes [9]. Among various sample pretreatment methods, solid phase extraction (SPE) is the most frequently used one and its performance relies substantially on the nature of the sorbents. Nevertheless, conventional sorbents usually lack specificity, such as the ones based on metal-complexing agents or the functionalized resins for ion-exchange. For this reason, ion-imprinted polymers (IIPs) possessing specific ion recognition properties, and first introduced by Nishide et al. in 1976 [10], are currently undergoing significant development.

On the basis of a lock-and-key mechanism, IIPs result from the copolymerization of functional monomers and cross-linking agents in the presence of a template ion [11-12]. After leaching the template ions from the polymer, specific cavities have the memory of the size and coordination geometry, leading to a high specificity toward the target ion. As a control polymer, a non-imprinted polymer (NIP) is conventionally synthesized by using the same synthesis conditions but in the absence of template ions, so that no specific cavity is created in this polymer. Indeed, the template ion plays a crucial role in the formation of the cavity. This ion can be the target ion directly, or an analogue ion with the similar physicochemical properties, the so-called dummy approach [13]. The simplest method is to use the target ion as template, which in theory allows for a maximum imprinting effect. However, in practice, traces of target ions potentially remaining despite the drastic leaching step may escape from the polymer during its use. That poses an important risk of contamination and of false positive, particularly when determining the target ion at trace level. By contrast, using an analogue ion as a template easily gets around the problem. However, while this so-called dummy approach seems to be relatively common in the field of molecularly imprinted polymers [14], it is little explored in the field of IIPs.

During the last two decades, more than 40 Cu(II)-targeting IIPs have been prepared for SPE applications by different polymerization techniques and using various reagents, particularly functional monomers and porogen solvents [15-17]. However, it must be pointed out that the dummy approach has never been employed since the used template ion was always Cu(II). After synthesis, a vast majority of those IIPs were used in dispersive SPE (dSPE, also called solid phase extraction in batch) on the basis of an adsorption equilibrium between IIP particles and analytes. In general, this approach necessitates a sufficiently long incubation time for achieving the adsorption equilibrium, and then an operation of filtration, centrifugation, or decantation to recover the particles before proceeding to the final desorption step, which makes it time consuming approach and labor-intensive. In contrast with dSPE, SPE is performed by packing a cartridge or a column with IIP particles thus allowing the direct and rapid percolation of samples and elution of the concentrated copper. In particular, a washing step can be easily implemented and optimized to eliminate potential interfering ions prior to the final elution of target ions, which contributes to a better extraction specificity. However, to the best of our knowledge, there are only five studies demonstrating the specificity of Cu-targeting IIPs in SPE cartridges [18-22], two of which did not involve application to real samples [18,19], and none of which implemented an optimized washing step to remove interfering ions.

In our recently reported work [23], several IIPs were synthesized using Cu(II) as the template ion. After optimization of the synthesis conditions and the SPE procedure, especially the washing step, the best IIP exhibited a high specificity (recovery of Cu(II) *vs.* interfering ions) as well as a good selectivity (retention on IIP *vs.* NIP) and allows successful applications to mineral and sea waters. Nevertheless, a problem occasionally encountered was that the residual template ions Cu(II) leaked from IIP causing measurement biases, even though a time-consuming template leaching step was beforehand implemented using 3 M HCl. To overcome this problem, the approach of using an analogue ion as template was investigated in this work. Here, two Cu-targeting IIPs were synthesized via bulk polymerization using Zn(II) and Ni(II) as template ions. Methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), acetonitrile (ACN), and 2, 2'-azobisisobutyronitrile (AIBN) were used as functional monomer, crosslinking agent, porogen solvent, and initiator, respectively, as they led to the best IIP as observed in our previous study [23]. After grounding and sieving, the template ions were leached and the resultant particles were packed in SPE cartridges to be used. In order to promote specificity and selectivity, the washing step was optimized by using both an acid and a metal-complexing agent. The most promising IIP was further characterized by determining its capacity, breakthrough volume, and enrichment factor under its optimum SPE conditions, and used for applications with mineral and sea waters.

2 Material and methods

2.1 Reagents

$Ni(NO_3)_2$ (99.999%), $Zn(NO_3)_2$ (99.999%), EGDMA (98%), MAA (99%), NaOH (98%), and Tris (99.0%) were purchased from Sigma-Aldrich (St Quentin Fallavier, France). AIBN was obtained from Acros Organics (Noisy-le-Grand, France). ACN of HPLC grade was purchased from Carlo Erba-Réactifs-SDS (Val De Reuil, France). Ultra-pure grade water was obtained using a Milli-Q purification system from Millipore (Molsheim, France). Solution of 3 M HCl was obtained from dilution of 37% (wt.%) HCl (Emsure, Merck). EGDMA and MAA were distilled in order to remove inhibitors according to a protocol reported in our previous study [24]. All other reagents were used as received.

Standard mono-elemental ICP solutions of Co(II), Ni(II), Cu(II), and Zn(II) at 1 g L^{-1} were purchased from Sigma-Aldrich. Calibration solutions were prepared through serial dilutions of the standard solutions with 2% (wt.%) HNO_3 which is obtained diluting 65% (wt.%) HNO_3 from Merck (Darmstadt, Germany). A tuning solution for ICP-MS containing Ce, Co, Li, Mg, Tl, and Y at 1 mg L^{-1} in 2% (wt.%) HNO_3 was from Agilent Technologies (Les Ulis, France).

Multi-elemental solution for SPE experiments at 30 µg L^{-1} containing Co(II), Ni(II), Cu(II), and Zn(II), as well as mono-elemental solution of Cu(II) at different concentrations, were prepared through appropriate dilutions of the standard solutions with water. The pH was adjusted with HNO$_3$ or NaOH.

2.2 Synthesis of the IIPs

Firstly, 1 mmol of Ni(NO$_3$)$_2$ or Zn(NO$_3$)$_2$ was dissolved in 6 mL of ACN. 4 mmol of MAA as a functional monomer was immediately added. Then, the mixture was placed under continuous magnetic stirring for 2 h. Thereafter, 20 mmol of EGDMA as crosslinking agent and 0.24 mmol of AIBN as initiator were sequentially added. In order to remove oxygen prior to polymerization, the vial containing the solution was purged with N$_2$ for 15 min in an ice bath. Finally, the polymerization was performed by placing the sealed vial in a water bath at 60 °C for 24 h. A NIP was synthesized in parallel with each IIP under identical conditions but in the absence of template ion.

After polymerization, the solidified IIPs and NIPs were grounded and sieved with a grinder MM 301 and a vibratory sieve shaker AS 200 both from Retsch (Eragny sur Oise, France) in order to collect the particles between 25 and 36 µm. The IIP particles were placed in 3 M HCl under stirring for 5 cycles of 20 h. The related NIP particles as control polymers were subjected to the same acid treatment. After each cycle, the supernatant was collected through filtration for its analysis by ICP-MS in order to quantify the leached template ions. Afterwards, the IIP/NIP particles were rinsed with water until the medium was neutralized. Then, a sedimentation step was carried out using a mixture of MeOH/water (4/1, v/v) to eliminate the residual fine particles despite the sieving. After being dried at 50 °C, 30 mg of accurately weighted IIPs and NIPs were packed between two polyethylene frits (20 µm porosity, Merck) into a 1 mL polypropylene cartridge (Merck).

2.3 ICP-MS conditions

An Agilent 7850 ICP-MS was used for the quantification of elements. It was equipped with a quartz concentric nebulizer, a quartz Scott spray chamber, a quadrupole analyzer, and an Agilent ASX-500 autosampler. Prior to each set of measurements, an Agilent tuning solution was utilized for performance check in terms of sensitivity, stability (RSD < 3%), oxide less than 0.65%, and double-charged ion less than 1.5%. The solutions based on 2% HNO$_3$ were analyzed using "low matrix" mode, while mineral and sea water samples were analyzed using respectively "general purpose" and "high matrix introduction-4" modes after being diluted 20 times in 2% HNO$_3$ (conditions recommended by the supplier). The calibration curves were

given in Figure S1 in Supplementary Data. The LOQs as well as more precise analytical conditions are provided in Table S1 in Supplementary Data.

2.4 SPE procedure and its optimization

First, IIP/NIP particles were conditioned with 3 mL of HNO_3 solution (pH 5.5). A HNO_3 solution (pH 5.5) containing a certain amount of Cu(II) with or without interfering ions was next percolated. Then, the washing step was optimized by testing a series of HNO_3 solutions at decreasing pH from 5.0 to 1.0, then a series of Tris solutions at increasing concentrations (i.e. 0.02 mM, 0.2 mM, and 2 mM). The optimum washing conditions were 1 mL of Tris at 0.2 mM and 1.5 mL of HNO_3 (pH 3.6). Elution was achieved with 1 mL of 5% HNO_3. Each solution (sample, washing, elution) was percolated through the SPE cartridges at a flow rate of 1 mL min^{-1} and collected in metal-free tubes for its analysis in ICP-MS. After each use, the cartridges were rinsed with water for their storage. The enrichment factor was calculated as the ratio between the volume of percolated sample and that of eluent (1 mL) multiplied by the recovery of the analyte.

2.5 Adsorption isotherms modeling

Two parameters are usually required in adsorption isotherm models: C_e as equilibrium concentration and Q_e as adsorption capacity at equilibrium. In the present work, these two parameters were defined using the following equations:

$$C_e = (m_i - m_E) / V \qquad \text{Eq. (1)}$$
$$Q_e = m_E / m_s \qquad \text{Eq. (2)}$$

where m_i is the initial amount of analyte before the percolation (mg), m_E is the recovered amount of analyte in the elution fraction (mg), V is the volume of the percolated sample (L), and m_s is the quantity of sorbent (g). The applicability of those definitions was already demonstrated in our previous works [13].

Seven isotherm models were investigated, i.e. Langmuir, Freundlich, Redlich–Peterson, Sips, Dubinin-Radushkevich, single-site Scatchard, and dual-site Scatchard model. All fittings were performed via Origin (OriginLab Corporation) with the equations in non-linear form.

2.6 Real sample pretreatment

Two commercial mineral waters of Mont Roucous® and Evian® were selected and stored at room temperature. Natural seawater was collected at Sainte Anne du Portzic (48°21'N, 4°33'W;

Brittany, France) in high-density polyethylene bottles and stored at -20 °C. The salinity of the seawater was measured on site using Marel Iroise buoy [25]. Each non-spiked water was subjected to ICP-MS analysis under appropriate conditions (see section 2.3). For SPE experiments, the two mineral waters were accurately spiked with Cu(II) at 4 µg L^{-1}, while the seawater at 2 and 6 µg L^{-1}. All samples were adjusted at pH 5.5 with HNO$_3$. For mineral waters, 50 mL of the non-spiked or spiked samples were percolated through IIP and NIP cartridges, followed by a washing step with 1 mL of Tris at 0.2 mM at pH 5.5 and 1.5 mL of HNO$_3$ at pH 3.6. For seawater, 1 mL of the non-spiked or spiked samples were percolated, followed by a washing step with 1.5 mL of HNO$_3$ at pH 3.6. In both cases, the elution was performed with 1 mL of 5% HNO$_3$.

3 Results and discussion

3.1 Synthesis of the IIPs

Above all, it is worth mentioning that the synthesis conditions adopted in the present work have already been assessed using Cu(II) as the template ion in our previous work [23]: MAA as monomer, EGDMA as cross-linker, AIBN as initiator and ACN as porogen. Here, Ni(II) and Zn(II), two elements adjacent to Cu(II) in the periodic table, were selected as template ions since they have the most similar physico-chemical properties to Cu(II). In addition to the same charge (II), their coordination number as well as ionic radii are very close. As an example, for a configuration of octahedron in aqueous solution, their hydrated ionic radii are 0.69 Å for Ni(II), 0.73 Å for Cu(II), and 0.74 Å for Zn(II) [26,27]. This is why, the cavities created inside IIPs using Ni(II) or Zn(II) as template ion are supposed to be complementary to Cu(II) to a very large extent. More importantly, Cu(II) should be preferentially retained by the sorbent according to Irving-Williams order pertaining to the stability of transition-metal complexes [28]. Indeed, Cu(II) was found to possess the highest metal complex stability over several transition metals including Ni(II) and Zn(II) irrespective of the nature of the coordinated ligand. According to the above-mentioned synthesis conditions, two Cu(II)-targeting IIPs were obtained, i.e. Ni-IIP with Ni(II) as template ion and Zn-IIP with Zn(II) as template ion. After polymerization, the template ions were removed by submitting the IIP particles to 5 cycles of stirring in 3 M HCl. Percentages of leached Ni(II) and Zn(II) in each cycle were calculated relative to their respective amounts initially added during the synthesis. As presented in Table *1*, the sums of percentages were close to 100%, confirming for Ni-IIP and Zn-IIP, the effective removal of templates in both cases. Nevertheless, Zn(II) seemed to be less easily removed than Ni(II), implying that Zn(II) may be more strongly complexed by the MAA functional monomer.

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Besides, two NIPs were prepared for being the control polymer for each of both IIPs while applying the same synthesis conditions in the absence of template ions. They were subjected to the same acid treatment as the IIPs for the template removal. As expected, no Ni(II) nor Zn(II) was detected in any cycle.

Table 1 Percentage of leached template ions during the template removal from Ni-IIP and Zn-IIP in each cycle (stirring in 3 M HCl, 20 h each cycle).

Cycle	Ni-IIP	Zn-IIP
1	86.05%	58.19%
2	11.71%	24.30%
3	1.53%	10.98%
4	0.20%	2.80%
5	0.01%	0.93%
Sum	99.50%	97.22%

3.2 Optimization of the SPE procedure

After removal of the template ions, the IIP particles were introduced into a cartridge and an SPE procedure was developed with the aim of achieving optimal selectivity (i.e. high retention of Cu(II) on IIP and low retention on NIP) and specificity (lower retention of potentially interfering ions compared to Cu(II)). This protocol includes the three conventional steps, i.e. the sample percolation where targeted ions are expected to be retained on the sorbent, then washing to eliminate interfering ions that could be retained by non-specific interactions, and finally elution of the targeted ions. Co(II), Ni(II), and Zn(II) were selected as interfering ions to evaluate the specificity of IIPs towards Cu(II), since they are adjacent to each other in the transition metals group of the periodic table, but especially two of them have been used as template ions. It was found that the percolation in HNO_3 at pH 5.5 allowed the entire retention of Cu(II) ions on both Ni-IIP and Zn-IIP, and that 1 ml of 5% HNO_3 allowed its elution. However, without applying a washing step, the interfering ions led to the same SPE profiles as the target Cu(II) ions, indicating a lack of specificity of the procedure. This is why a washing step is required to get specificity as well as selectivity. Indeed, the washing step aims to disrupt the retention of ions retained by non-specific interactions at the surface of the polymer while maintaining the retention of target ions by specific interactions into the cavities. To achieve this, the washing step must be optimized, and it was performed in this work by testing two

different ways, by playing either on pH or on the concentration of Tris known for its ability to complex transition metal ions [29].

3.2.1 Optimization of the washing step using HNO$_3$ solutions

The pH value of the solution in contact with the IIP is known to impact significantly the adsorption/desorption of ions by affecting deprotonation/protonation of the polymerized functional monomer on the polymer surface and into the cavities (i.e. MAA, pK$_a$ 6.4 - 6.5 when incorporated in a polymer matrix [30]). Zn-IIP and its NIP were studied at first. A washing step was first implemented with successive fractions having a large range of pH using 0.5 mL of HNO$_3$ solutions at pH 5, 4, 3, 2, and 1. As illustrated in **Figure 1**a, all the ions were retained on both Zn-IIP and its NIP during the percolation as expected. For washing, a solution at pH 4 appeared too weak to remove interfering ions, whereas a solution at pH 3 appeared too strong to retain the target Cu(II) ions. This is why a second SPE procedure was performed using a range of pH values from 4 to 3 (i.e. 3.8, 3.6, 3.4, 3.2, and 3.0). In these conditions, almost all the ions were removed from NIP at pH 3.6 while they were retained on Zn-IIP (**Figure 1**b), thus highlighting the stronger retention of ions on Zn-IIP than on the NIP. After washing with a solution at pH 3.4, most of the interfering ions were removed from Zn-IIP, but these conditions also led to a significant loss of Cu(II) (i.e. 41%). Therefore, a new SPE procedure implementing 4 x 0.5 mL of a pH 3.6 solution was applied for washing, in triplicate showing low RSD (i.e. ≤ 7%). Results are reported in **Figure 1**c. As expected, the Cu(II) ions retained during the percolation were eliminated from NIP prior to Zn-IIP, confirming the high selectivity. Moreover, the interfering ions retained on Zn-IIP were progressively eliminated during the washing steps, which led to a strong improvement in the specificity of the IIP towards the Cu(II) predominantly present in the elution fraction. As previously assumed, despite using Zn(II) as template ion, this specificity must arise from the highly similar physiochemistry properties between Zn(II) and Cu(II), as well as the stronger affinity towards Cu(II) related to the Irving-Williams order.

Besides, it is noteworthy that the NIP presented a slight affinity towards Cu(II) despite the absence of specific cavities, as shown in **Figure 1**b and c. These results confirmed the fact that the functional monomer MAA possesses a stronger affinity towards Cu(II) over Co(II), Ni(II), and Zn(II), which showed a good accordance with the Irving-Williams order too. In fact, it was reported in the literature that quite many NIPs showed results consistent with the Irving-Williams order despite extremely distinct functional monomers used for their synthesis, but their intrinsic affinity towards Cu(II) is usually not discussed [20, 31-34].

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Ni-IIP and its NIP were next studied. According to the same methodology, the best results were obtained using 3 x 0.5 mL HNO$_3$ at pH 3.6 for the washing step. Similarly, Ni-IIP presented a high selectivity relative to its NIP as well as a high specificity towards Cu(II) with respect to the interfering ions (see Figure S2 in Supplementary Data). Although the specificity shown on Ni-IIP seemed a little better than on Zn-IIP, it is worth noting that the retention of ions on Zn-IIP must be stronger than on Ni-IIP as one more fraction of washing step was implemented on Zn-IIP. Hence, further optimization of SPE conditions was needed to continue the comparison between them.
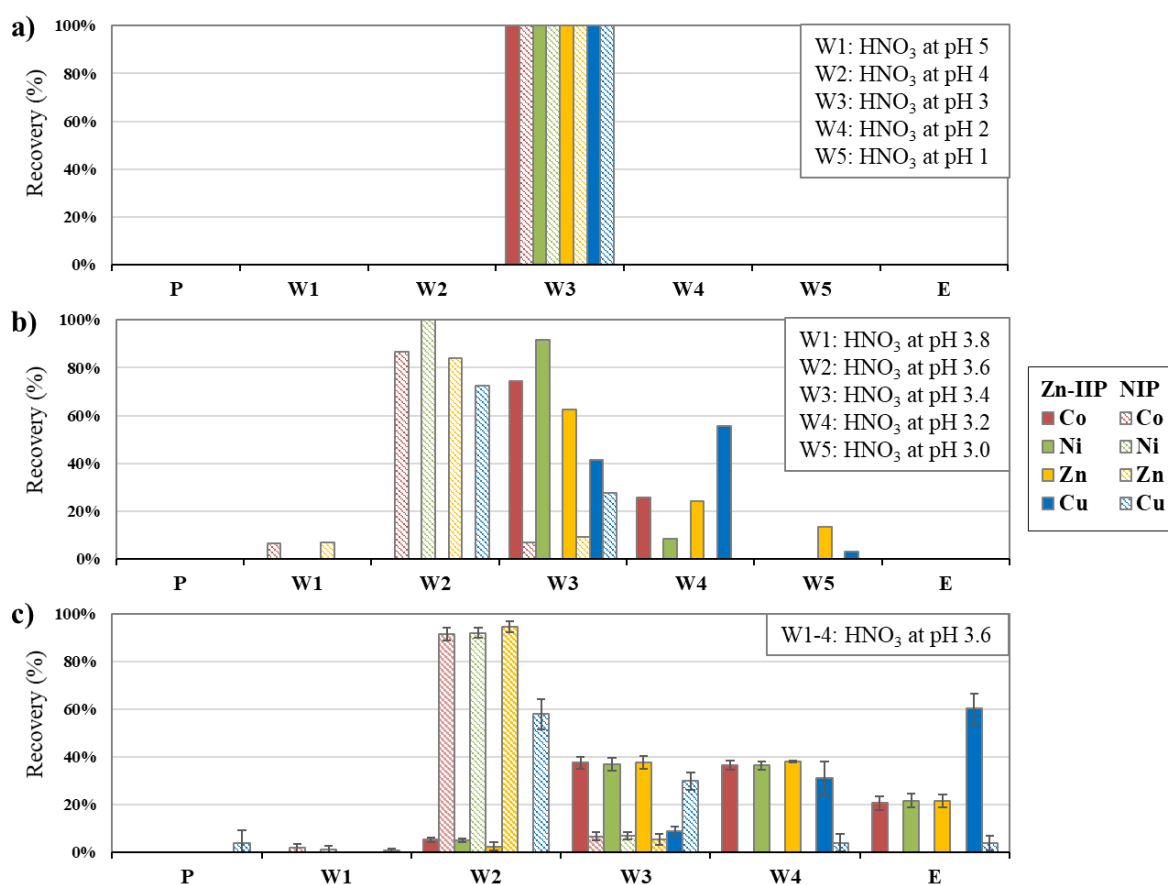
Figure 1 SPE profiles of Co(II), Ni(II), Zn(II), and Cu(II)on Zn-IIP and its NIP obtained by measuring the fractions in ICP-MS. Percolation (P): 1 mL of HNO$_3$ at pH 5.5 spiked with Co(II), Ni(II), Cu(II) and Zn(II) at 30 µg L^{-1} for each; Washing (W1-5): a) 5 x 0.5 mL of HNO$_3$ at pH 5, 4, 3, 2, and 1. b) 5 x 0.5 mL of HNO$_3$ at pH 3.8, 3.6, 3.4, 3.2 and 3.0. c) 4 x 0.5 mL of HNO$_3$ at pH 3.6; Elution (E): 1 mL of 5% HNO$_3$. (n=3)

3.2.2 Optimization of the washing step using Tris solutions

After studying the effect of the pH for washing on the selectivity and specificity of the retention process on the IIPs, a second approach based on the use of a complexing agent was next investigated using Tris at different concentration levels. The SPE procedure was first implemented with a large range of concentrations of Tris solutions at 0.02, 0.2, and 2 mM, all adjusted at pH 5.5. Besides, percolation and elution steps were conducted under the predetermined conditions.

Zn-IIP and its NIP were studied at first. As expected, an entire retention of the ions can be observed during percolation
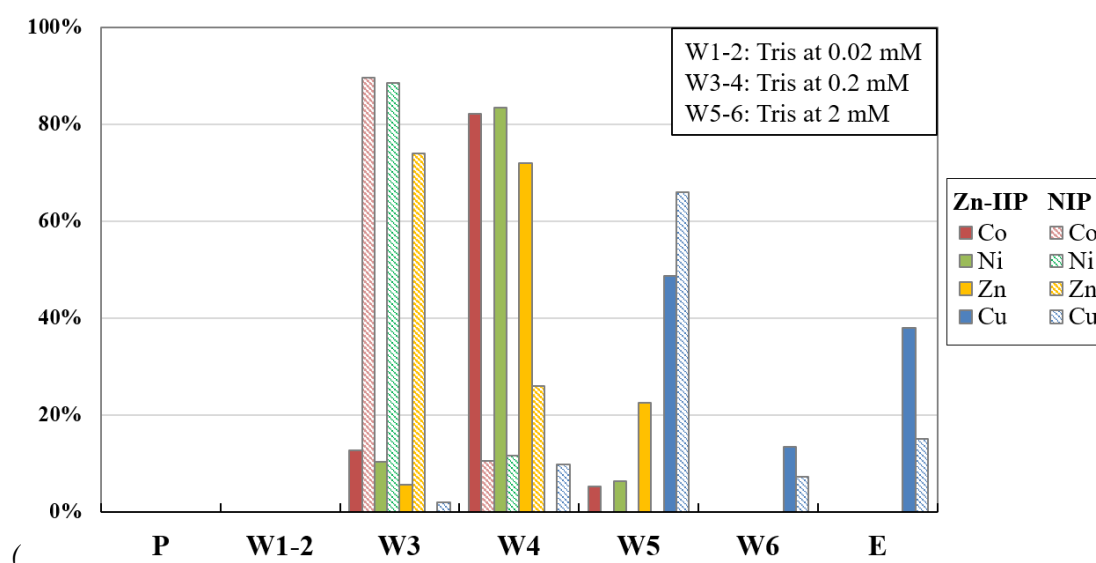

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Figure 2*). Regarding the washing step, Tris at 0.02 mM did not allow the desorption of any ion from the polymers, whereas, at 0.2 mM, a large majority of the interfering ions (i.e. Co(II), Ni(II), and Zn(II)) was removed from NIP, and from Zn-IIP thereafter. Thus, an excellent specificity towards Cu(II) can be observed again. Afterwards, 2 mM Tris gave rise to the elution of Cu(II) ions, but with a higher*
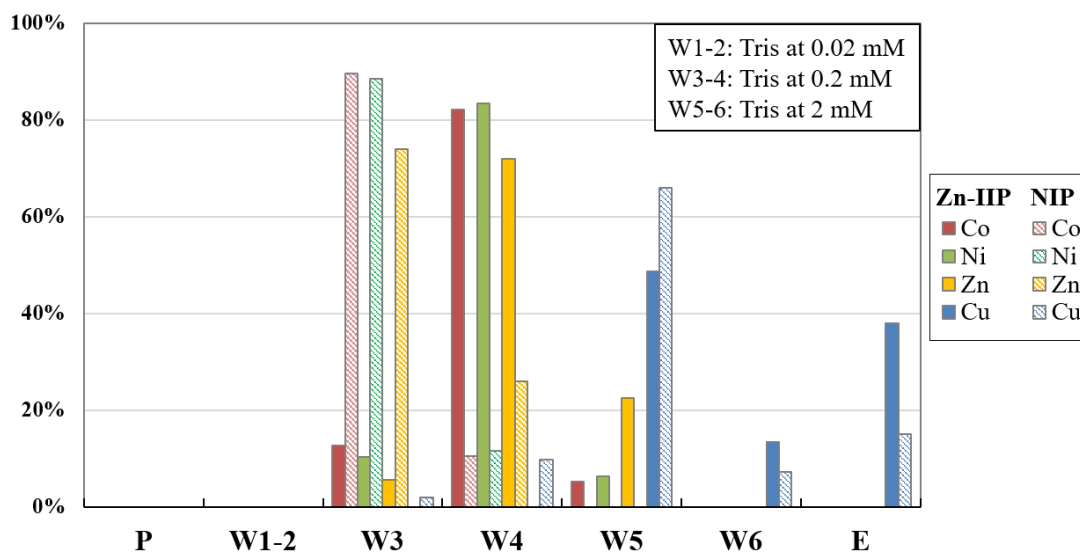
Figure *2*). In consequence, a higher recovery in the elution fraction was obtained for Cu(II) with Zn-IIP than using the NIP (38% *vs.* 15%), confirming the selectivity of Zn-IIP.
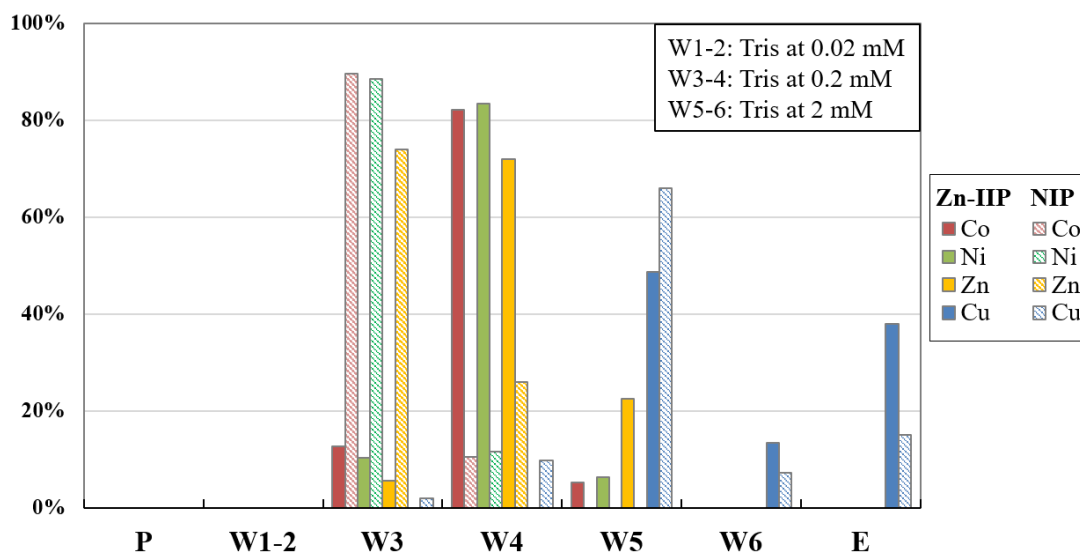

Figure 2 SPE profiles of Co(II), Ni(II), Zn(II), and Cu(II) on Zn-IIP and its NIP obtained by measuring the fractions in ICP-MS. Percolation (P): 1 mL of HNO_3 at pH 5.5 spiked with Co(II), Ni(II), Cu(II) and Zn(II) at 30 μg L^{-1} for each; Washing (W1-6): 2 x 0.5 mL of Tris at 0.02 mM at pH 5.5, 2 x 0.5 mL of Tris at 0.2 mM at pH 5.5, and 2 x 0.5 mL of Tris at 2 mM at pH 5.5; Elution (E): 1 mL of 5% HNO_3.

Unfortunately, this selectivity seemed not as good as the one obtained using HNO_3 at pH 3.6 (**Figure *1*c), and the recovery was not satisfactory neither, even though those results could be

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slightly improved by using only one fraction of 0.5 mL of Tris at 2 mM rather than two. Nevertheless, in terms of removal of the interfering ions, Tris at 0.2 mM seemed more efficient than HNO_3 at pH 3.6. Considering these advantages and limitations, a combination of Tris and HNO_3 was studied by using a new washing procedure with 1 mL of Tris at 0.2 mM followed by 1.5 mL of HNO_3 at pH 3.6. As shown in **Figure *3***, almost all interfering ions were eliminated from Zn-IIP thanks to the Tris, leading to an excellent specificity towards Cu(II). In addition, a majority of Cu(II) was removed from its NIP thanks to the HNO_3, leading to a high selectivity since the Cu(II) ions remained strongly retained on the Zn-IIP, resulting in a satisfactory and repeatable recovery of Cu(II) (i.e. $81 \pm 5\%$, n = 3) (Figure 3). The benefits of Tris and HNO_3 were successfully preserved and combined under these washing conditions, which were therefore set as the optimum conditions for Zn-IIP.

Ni-IIP and its NIP were next studied by employing directly the above-mentioned washing conditions, i.e. 1 mL of Tris at 0.2 mM followed by 1.5 mL of HNO_3 at pH 3.6. As expected, the resultant SPE profiles were significantly similar to those on Zn-IIP (see Figure 3 in supplementary data), showing an excellent specificity towards Cu(II) as well as a high selectivity relative to its NIP. Nevertheless, the recovery of Cu(II) appeared slightly reduced, i.e. $71 \pm 5\%$ on Ni-IIP *vs.* $81 \pm 5\%$ on Zn-IIP (see Figure S3 in supplementary data), confirming that the retention of Cu(II) by Zn-IIP was somewhat stronger than by Ni-IIP. This behavior may be ascribed to the fact that Zn(II) has an ionic radius closer to Cu(II) than to Ni(II). Moreover, during the template removal, Zn(II) seemed to be less easily removed than Ni(II) (see section 3.1), which could be explained by the formation of better structured specific cavities. Hence, Zn-IIP was selected as the most promising sorbent in this work, and was preferentially studied hereafter.
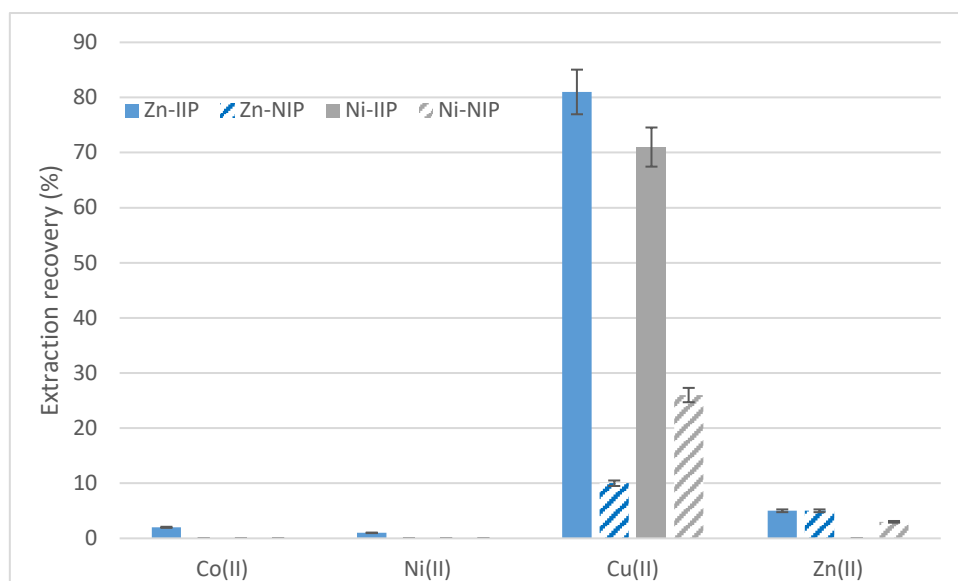
Figure 3 Extraction recoveries with the optimized SPE protocol of Co(II), Ni(II), Zn(II), and Cu(II) on Zn-IIP and Ni-IIP and their corresponding NIP. Percolation: 1 mL of HNO_3 at pH 5.5 spiked with Co(II), Ni(II), Cu(II) and Zn(II) at 30 µg L^{-1} for each; Washing: 1 mL of Tris at 0.2 mM at pH 5.5 and 1.5 mL of HNO_3 at pH 3.6; Elution: 1 mL of 5% HNO_3. (n=3)

The specificity and selectivity of Zn-IIP were next compared with the ones previously published in the literature of Cu-targeting IIPs. To the best of our knowledge, fives studies apart from our previous work evaluated the specificity and selectivity in SPE cartridges [18-22] but only two of them provided the extraction recovery of Cu(II) as well as that of interfering ions [20, 22], like the present work. As shown in Table *2*, Zn-IIP showed a superior selectivity (retention of Cu(II) on IIP *vs.* NIP) as compared to all other IIPs. In terms of specificity toward Cu(II), Zn-IIP appeared better than both the IIP developed by Cui et al. [22] and the one developed in our previous work [23], although they were all synthesized using MAA as monomer. The one developed by Yilmaz et al. showed a comparable specificity, whereas it was synthesized by using a non-commercial monomer, which did not allow an easy production and valorization [20].

Overall, these results substantiated for the first time the feasibility of using an analogue ion (i.e. Ni(II) or Zn(II)) as template for the synthesis of a Cu-targeting IIP. Even if not limited to IIPs targeting Cu(II), only a few studies were found in literature with the use of this dummy approach. To the best of our knowledge, only the studies performed in our lab by Boudias et al. were relevant, where IIPs targeting Ra(II) were synthesized using Ba(II) as template because Ra(II) with its radioactive properties was not safe to use [13,35]. In fact, a relatively frequent case is that an ion was used as template to synthesize IIPs next used to extract simultaneously several ions including the template ion, which should not be referred to the dummy approach

in a strict sense. For example, Otero-Romaní et al. synthesized an IIP using Ni(II) as template ion to extract Ni(II), Cu(II), Pb(II) and Zn(II) [36] and Moussa et al. synthesized an IIP using Nd(III) as template ion to extract all the lanthanide ions including Nd(III) [37].

Table 2 Comparison of selectivity and specificity between the Zn-IIP developed in the present work and other Cu-targeting IIPs in literature based on the extraction recovery obtained in SPE cartridges.

	Cui et al. [22]		Yilmaz et al. [20]		Our previous work [23]		Present work (Zn-IIP)	
	IIP	NIP	IIP	NIP	IIP	NIP	IIP	NIP
Cu(II)	91-99%	87-100%	97%	49%	70%	13%	81%	10%
Co(II)	52%	66%	8%	47%	20%	2%	1%	< 1%
Ni(II)	66%	82%	24%	50%	18%	< 1%	1%	< 1%
Zn(II)	83%	86%	28%	51%	23%	< 1%	4%	< 1%

Furthermore, in our case, the washing step was exceptionally finely optimized by testing numerous solutions with different natures and conditions. Tris and HNO_3 solutions resulted in very different SPE profiles, revealing the importance of the washing step as well as its optimization for an SPE procedure. In this sense, SPE cartridge seems more advantageous than batch since it allows easy and rapid percolation and collection of different solutions, particularly in the cases like the present work where numerous washing solutions with different natures and volumes were tested and combined to achieve the best extraction performance.

3.3 Capacity study

Retention capacity is another essential feature of SPE sorbents and it is expressed as the maximum amount of analyte that can be selectively retained per gram of sorbent. As the more promising sorbent is Zn-IIP, its capacity was determined by assessing the amount of Cu(II) recovered in the elution fraction by percolating increasing amounts of Cu(II) and using the optimized washing step (i.e. 1 mL of Tris at 0.2 mM followed by 1.5 mL of HNO_3 at pH 3.6) to ensure a strong contribution of the specific cavities in the retention process. The curve reported in **Figure *4*** is composed of two slopes: the highest one (solid) obtained for the lowest percolated amounts corresponds to the constant recovery of extraction of Cu(II) by specific interactions, while the lowest one (dotted) results from the non-specific interactions that are developed for higher percolated amounts after the saturation of the specific cavities. Regarding the NIP, only one single low slope can be observed as expected since it offers only non-specific

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interactions. Thus, the slope of its NIP curve was used to draw the dotted line of the Zn-IIP at higher concentrations, as it was already done in literature [35]. The capacity of Zn-IIP was estimated to be 100 µg g^{-1} as the recovered Cu(II) was no longer lied on the solid curve starting from a percolation of 3 µg of Cu(II) on 30 mg of the Zn-IIP.

The capacity value of Zn-IIP seems low, but it is more than sufficient to extract the trace-level amount of Cu(II) present in environmental water samples. In fact, many IIPs showing capacities of the same order of magnitude as µg g^{-1} have already been reported in the literature [33, 38-48]. Moreover, a great majority of IIPs were characterized in batch without implementing an optimized washing step, unlike the present work. Thus, non-specific interactions may contribute largely to analyte uptakes, resulting in some overestimation of the capacity. To further investigate this hypothesis, Zn-IIP and its NIP were subjected to the same experiment as above but without the washing step (see Figure S4 in Supplementary Data). Consequently, the maximum amount of Cu(II) retained on Zn-IIP was strongly promoted, and its NIP showed a retention of Cu(II) even better, which is likely due to the contribution of more numerous non-specific sites in this retention process. Therefore, these data appeared not reliable for the determination of capacity, revealing again the importance of the washing step.
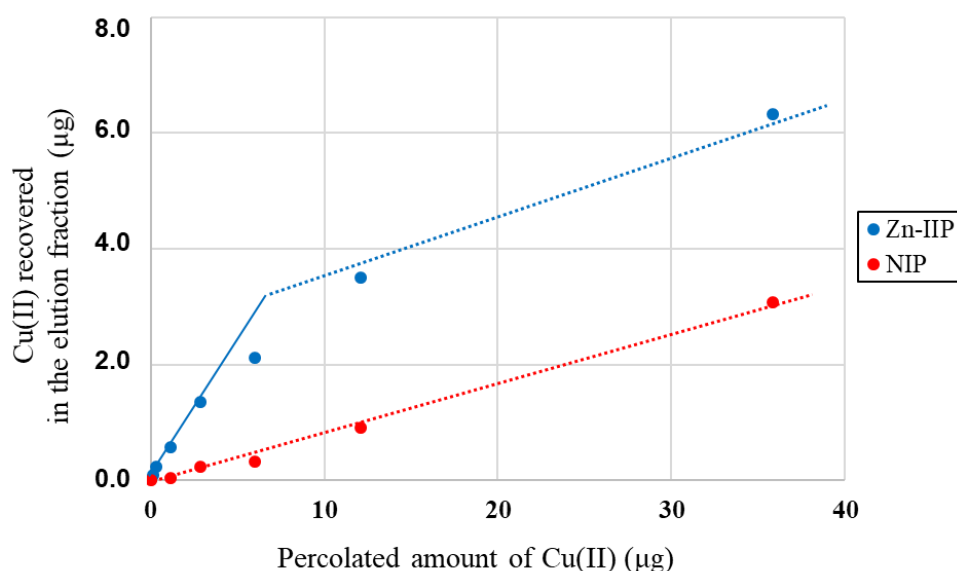

Figure 4 Adsorption capacity curves obtained by percolating an increasing amount of Cu(II) in 1 mL of HNO$_3$ at pH 5.5 on Zn-IIP and its NIP (30 mg for each). Amounts of Cu(II) were recovered in the elution fraction (1 mL of 5% HNO$_3$) after a washing step with 1 mL of Tris at 0.2 mM followed by 1.5 mL of HNO$_3$ at pH 3.6 and determined with ICP-MS.

3.4 Isotherm modeling

To further elucidate the adsorption behavior, seven different isotherm models were employed to fit the experimental data obtained during the capacity determination (**Figure 4**): Langmuir [49], Freundlich [50], Redlich–Peterson [51], Sips [52], Toth [53], single-site Scatchard [54], and dual-site Scatchard model [55]. Parameters deduced with each model and resultant regression coefficients R^2 were listed in Table *3*, and their plots were provided in Figure S5 in the Supplementary Data.

Langmuir and Freundlich isotherms were firstly studied. The former assumes a monolayer adsorption that occurs on an energetically uniform surface while the latter assumes a multilayer adsorption on a heterogeneous surface. Given those assumptions, the adsorption on Zn-IIP seems to be related to a multilayer adsorption as Freundlich isotherm gave a R^2 better than Langmuir (0.9968 *vs.* 0.9918). This statement was next supported by Redlich–Peterson and Toth isotherms. Redlich–Peterson isotherm is a hybrid model with the combination of elements from Langmuir and Freundlich equations. It reduces to Henry's law when the exponent in the equation $\beta = 0$, and to Langmuir isotherm when $\beta = 1$. Toth isotherm is a three-parameter isotherm with an exponent n in the equation related to surface heterogeneity, and it reduces to Langmuir isotherm when n = 1. They both fitted well showing high R^2, but the exponents β and n were both far from 1 (0.583 and 0.239, respectively). Thus, this confirms that the adsorption by Zn-IIP did not occur on an ideal monolayer. Sips isotherm is another hybrid isotherm that can be applied to both monolayer and multilayer adsorption. It approximates the Freundlich model at low concentrations and Langmuir model at high concentrations. Sip isotherm was found to describe best the adsorption behavior of Zn-IIP since it presented the best R^2 as compared to the four above-mentioned isotherms.

Table 3 Equations and parameters of the isotherm models for Zn-IIP as well as the parameters of Single-site Scatchard model for its NIP. C_e (mg L^{-1}): equilibrium concentration of Cu(II); Q_e (mg g^{-1}): adsorption capacity at equilibrium; Q_m (mg g^{-1}): maximum predicted adsorption capacity; K or E refers to the constant related to each model; n or β refers to the exponent related to each model.

Model	Equation	Parameters			R^2
		Q_m (mg g^{-1})	Constant (K or E)	Exponent (n or β)	
Langmuir	$Q_e = Q_m K C_e / (1 + K C_e)$	0.291	0.086	/	0.9918
Freundlich	$Q_e = K C_e^{1/n}$	/	0.035	1.876	0.9968

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			$L^{1/n}\ mg^{1-1/n}\ g^{-1}$		
Redlich–Peterson	$Q_e = K_1C_e/(1+K_2C_e^{\beta})$	/	K_1: 0.074 L g^{-1} K_2: 1.296 L mg^{-1}	0.583	0.9983
Toth	$Q_e = Q_mKC_e/(1+KC_e^n)^{1/n}$	0.360	0.532	0.239	0.9985
Sips	$Q_e = Q_mKC_e^{1/n}/(1+KC_e^{1/n})$	0.572	0.059 L mg^{-1}	1.477	0.9987
Single-site Scatchard	$Q_e = \dfrac{Q_mKC_e}{1+KC_e}$	0.015	1.895	/	0.8165
		0.006 (NIP)	1.824 (NIP)	/	0.9891 (NIP)
Dual-site Scatchard	$Q_e = \dfrac{Q_{m,1}K_1C_e}{1+K_1C_e} + \dfrac{Q_{m,2}K_2C_e}{1+K_2C_e}$	$Q_{m,1}$: 0.013 $Q_{m,2}$: 0.322	K_1: 1.602 K_2: 0.043	/	0.9981

Single-site Scatchard isotherm was usually used to identify if a sorbent possesses more than one kind of binding sites [56] as it assumes that the binding sites are homogeneous. With this isotherm, Zn-IIP exhibited a R^2 much lower than its NIP, i.e. 0.8165 *vs.* 0.9891. Indeed, Zn-IIP possesses the specific cavities in addition to the non-specific sites whereas its NIP possesses only non-specific sites. To overcome the limitation of single-site Scatchard isotherm, dual-site Scatchard was used to fit the adsorption data of Zn-IIP. As expected, a quite high R^2 was obtained (i.e. 0.9981) confirming the presence of two sets of binding sites inside Zn-IIP.

3.5 Application of Zn-IIP to real samples

The preconcentration performance of Zn-IIP was first assessed in pure media before the test with real samples. First, the percolation was conducted using 50 mL of HNO$_3$ at pH 5.5 spiked with Cu(II) at 1 μg L^{-1}, hence a quantity of Cu(II) largely below the previously determined capacity, i.e. 3.0 μg of Cu(II) for 30 mg of Zn-IIP. After applying the optimum washing step, recoveries of Cu(II) were found to be 88% on the Zn-IIP and 23% on its NIP in the elution fraction (i.e. 1 mL of 5% HNO$_3$). Next, the percolated volume was augmented to 70 mL, still leading to an acceptable recovery of Cu(II) of 76% on the Zn-IIP. Nevertheless, 50 mL was chosen for the further tests with real samples, given the higher recovery and also a satisfactory enrichment factor of 44 (calculated by multiplying the ratio of the initial sample volume to that of the final extract by the extraction yield).

Mineral waters of Mont Roucous® and Evian® and sea water were next tested to evaluate the potential of Zn-IIP for the determination of Cu(II) in complex aqueous samples. They were first diluted by a factor 20 to be directly analyzed by ICP-MS, as it is the approach usually performed to reduce matrix effect. However, the concentration of Cu(II) after dilution was inferior to the

LOQ (see Table S1 in Supplementary Data). The initial content of Cu(II) was thus estimated to be inferior to 1.70, 1.19, and 3.75 µg L^{-1} in the Mont Roucous®, Evian®, and sea water, respectively.

Next, those waters were subjected to the SPE procedure with Zn-IIP prior to the analysis in ICP-MS. The initial content of Cu(II) was determined by means of standard addition method. For each mineral water, 50 mL of non-spiked sample and of that spiked with Cu(II) at 2 µg L^{-1} were analyzed in triplicate, leading to 4 degrees of freedom (see Figure S6 in Supplementary Data). According to the contents of main ions provided in Table S2 in Supplementary Data, the concentration ratio between interfering ions and the spiking level of Cu(II) can be as high as 40,000 (Ca(II) *vs.* Cu(II) in the Evian® sample, for example). Despite this huge difference in concentration levels, a recovery of 88 ± 1% was obtained for both Mont Roucous® and Evian® waters, which was in a good accordance with the one obtained previously in pure media (88%). An enrichment factor of 44 was thus achieved in mineral waters. This means that not only the SPE process with the IIP allowed the specific purification of the extract, since it was previously demonstrated, but also its preconcentration, leading to a strong improvement in the sensibility of the analytical method compared to the conventional analysis of the same sample after its dilution with HNO$_3$. At a 95% confidential interval, the content of Cu(II) in Mont Roucous® water was determined at 0.20 µg L^{-1} in a range of 0.14 – 0.28 µg L^{-1}, while that in Evian® water at 0.09 µg L^{-1} in a range of 0.06 – 0.11 µg L^{-1} (see Figure S6 in Supplementary Data).

In the case of seawater, a volume of 50 mL was first tested whereas the obtained recovery of Cu(II) was very low, i.e. < 5% (n = 3). This result is likely due to a strong matrix effect caused by the fact that the seawater had an extremely high salinity around 32 g kg^{-1} (Figure S7 in Supplementary Data) and that it contained potentially some natural organic matters capable of complexing Cu(II). A second SPE procedure was then performed with a percolation volume reduced to 1 mL. The obtained recovery of Cu(II) was slightly enhanced to around 30%, but still not acceptable. Finally, a third SPE procedure was implemented by percolating 1 mL of sample and using only 1.5 mL of HNO$_3$ at pH 3.6 without 1 mL of Tris at 0.2 mM for the washing step, to favor the retention of Cu(II). Indeed, as previously illustrated in Figure 1c, this SPE procedure also allowed a good specificity and an extraction recovery of 91% by combining the fraction of the 4th washing and elution. Besides, the contribution of Tris was actually under question in this case, where the interfering ions in the seawater must far exceed the complexation capacity of Tris at only 0.2 mM. With the third SPE procedure, the non-spiked seawater as well as those spiked with Cu(II) at 2 and 6 µg L^{-1} were tested in triplicate, resulting finally in an acceptable and repeatable recovery of 83 ± 3% with 7 degrees of freedom (**Figure**

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5). This recovery was not significantly different to the one obtained in pure media (91%), indicating that the matrix effect was effectively reduced with the SPE procedure. The concentration of Cu(II) was successfully determined at 1.84 µg L^{-1} in a range of 1.45 – 2.29 µg L^{-1} at the 95% confidential interval.

Furthermore, for each water sample, the matrix effect implementing an SPE step with the Zn-IIP before the ICP-MS analysis was evaluated according to the method proposed in literature [57]. The interference of matrix effect was only 3%, 5%, and 5% for Mont Roucous®, Evian® and seawater, respectively. This confirms the efficient ability of Zn-IIP to eliminate abundant matrix components, and thus its high potential for the determination of Cu(II) in complex environmental samples.

Thanks to the easy reuse of sorbents allowed by the SPE cartridge, more than 50 SPE extractions were carried out on Zn-IIP with the same cartridge throughout the present work with ultra-pure spiked water, but also mineral or sea water. No significant loss of affinity towards Cu(II) (i.e. extraction yield) was observed, showing an excellent reusability as well as a high stability. It can therefore be said that there is no drop in performance after at least 50 uses, but the maximum number of uses has not yet been studied further. That should arise from the highly cross-linked and rigid structure produced by the synthesis conditions, in particular the template/monomer/cross-linker ratio and bulk polymerization technique.
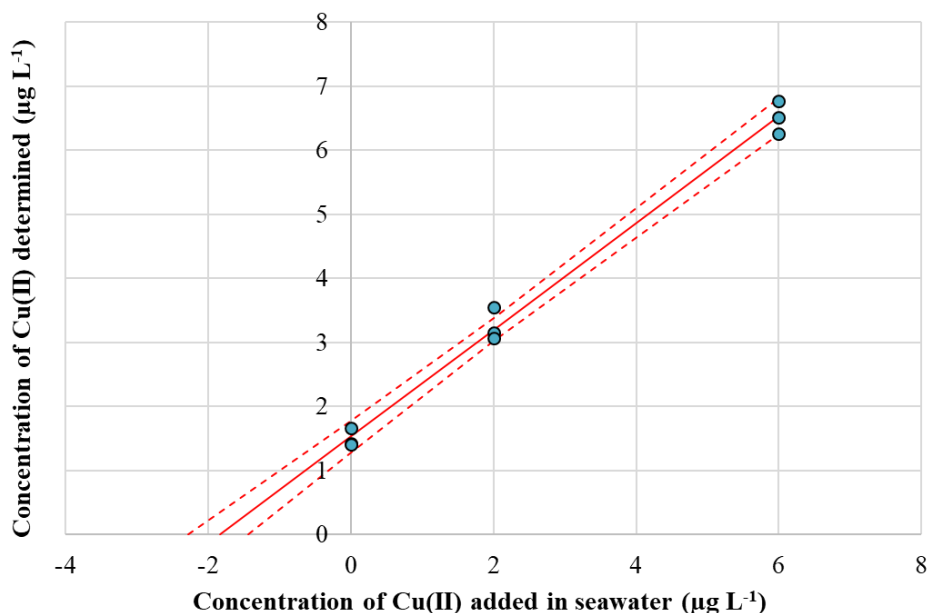
Figure 5 Determination of Cu(II) concentration in seawater by means of standard addition method. The dotted hyperbolic curves were obtained with a confidence interval of 95%. The experiments were conducted in triplicate for each concentration level.

4 Conclusions

For the first time, Ni(II) and Zn(II) were used as template ions for the synthesis of Cu-targeting IIPs. The two resultant IIPs were used in SPE with cartridges. A washing procedure was carefully optimized to remove the interfering ions before the final elution of Cu(II), by testing appropriate volumes of HNO_3 solutions at different pH, then Tris solutions at different concentrations, and finally by a combination of both. Under the optimum SPE conditions, Ni-IIP and Zn-IIP exhibited both an excellent specificity towards Cu(II) and a high selectivity. As compared to Ni-IIP, Zn-IIP seemed to present a stronger imprinting effect. Its capacity was determined to be 100 $\mu g\ g^{-1}$, the adsorption behavior was well elucidated using several different isotherm models. An enrichment factor of 44 was achieved by percolating 50 mL of sample on 30 mg of sorbent. Finally, applications to real samples (mineral waters and seawater) were successfully performed, demonstrating the high potential of Zn-IIP and of the developed SPE procedure. More importantly, these results supported a high feasibility of using an analogue ion as template for the synthesis of an IIP. Indeed, this so-called dummy approach may open up new possibilities in many problematic cases, for example when a target ion used as template is difficult to be completely removed from the polymer after its synthesis and when a target ion is too toxic. It is worthwhile devoting much effort to this approach given that most of the IIPs in the literature were still synthesized directly from the target ion.

Conflict of interest statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table S4 ICP-MS parameters and analytical conditions. Limits of quantification (LOQ) were calculated using the equation: $LOQ = 10 \times \sigma/k$, where σ is the standard deviation of counts per second (cps) of 10 blank solutions, and k is the sensitivity of the instrument (cps/(ng L^{-1})) for an element.

	RF power	1550 W
	Sampling depth	10.0 mm
Acquisition parameters	Plasma gas flow rate	15.0 L min^{-1}
	Auxiliary flow rate	0.90 L min^{-1}
	Carrier gas flow rate	1.05 L min^{-1}
	Isotopes monitored	^{59}Co, ^{60}Ni, ^{63}Cu, and ^{66}Zn
	Mode	Collision (Helium)
Analysis parameters	Peak pattern	1
	Integration time	0.3 s
	Number of replicates	5
	Number of sweeps	100
LOQ (μg L^{-1}) in 2% HNO$_3$ using "low matrix" mode	Co	0.002
	Ni	0.047
	Cu	0.051
	Zn	0.216
LOQ (μg L^{-1}) in Mont Roucous mineral water diluted 20 times in 2% HNO$_3$ using "general purpose" mode	Cu	0.085
LOQ (μg L^{-1}) in Evian mineral water diluted 20 times in 2% HNO$_3$ using "general purpose" mode	Cu	0.059
LOQ (μg L^{-1}) in sea water diluted 20 times in 2% HNO$_3$ using "High matrix introduction-4" mode	Cu	0.187

Table S5 Contents (mg L^{-1}) of main ions in the mineral waters of Evian® and Mont Roucous® as well as the calculated quantity ratio to the added Cu(II) at 2.0 μg L^{-1}. The data were obtained from the labels of their bottles.

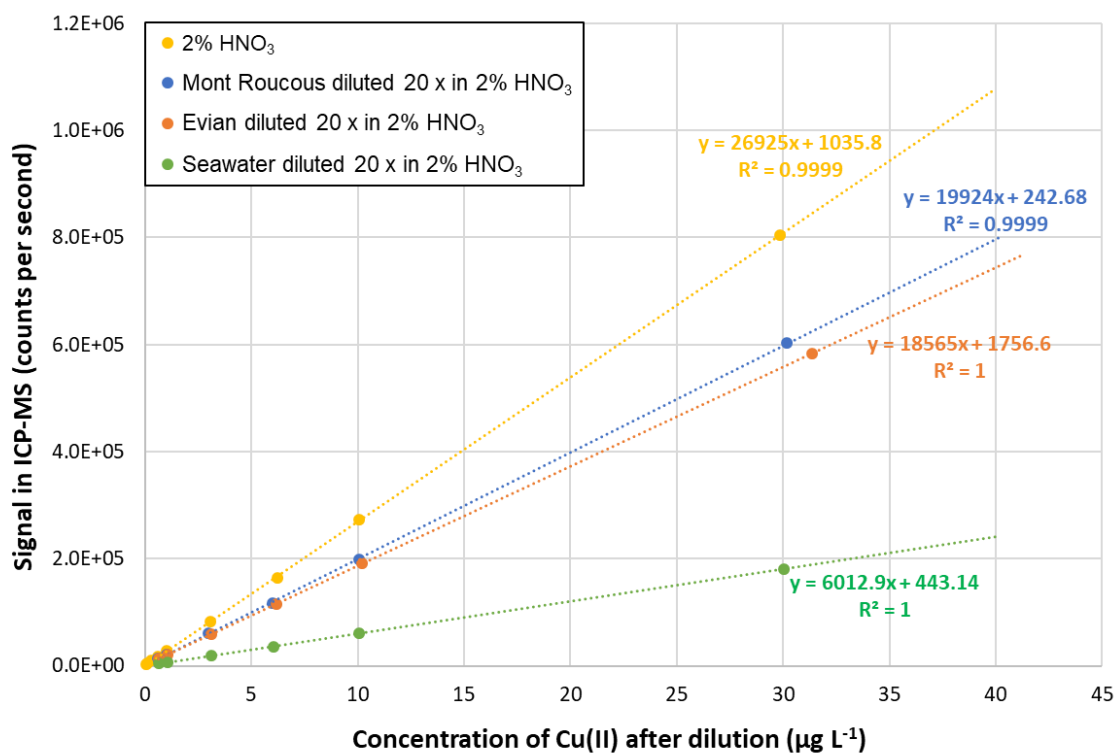| Mineral water	Main ion	Content (mg L^{-1})	Quantity ratio to the added Cu(II) (2 μg L^{-1})
Evian®	Ca^{2+}	80	40,000
	Na$^+$	6.5	3,250
	Mg^{2+}	26	13,000
	K$^+$	1	500
	HCO$_3^-$	360	180,000
	SO$_4^{2-}$	14	7,000
	Cl$^-$	10	5,000
	NO$_3^-$	3.8	1,900
Mont Roucous®	Ca^{2+}	2.9	1,450
	Na$^+$	3.0	1,500
	Mg^{2+}	0.5	250
	SO$_4^{2-}$	3.0	1,500
	NO$_3^-$	2.0	1,000
	F$^-$	< 0.1	< 50

Figure S6 Calibration curves of Cu(II) in 2% HNO₃ (Low matrix mode), in Mont Roucous and Evian mineral waters diluted 20 times in 2% HNO₃ (General purpose mode), and in seawater diluted 20 times in 2% HNO₃ (High matrix introduction – 4 mode) in ICP-MS.
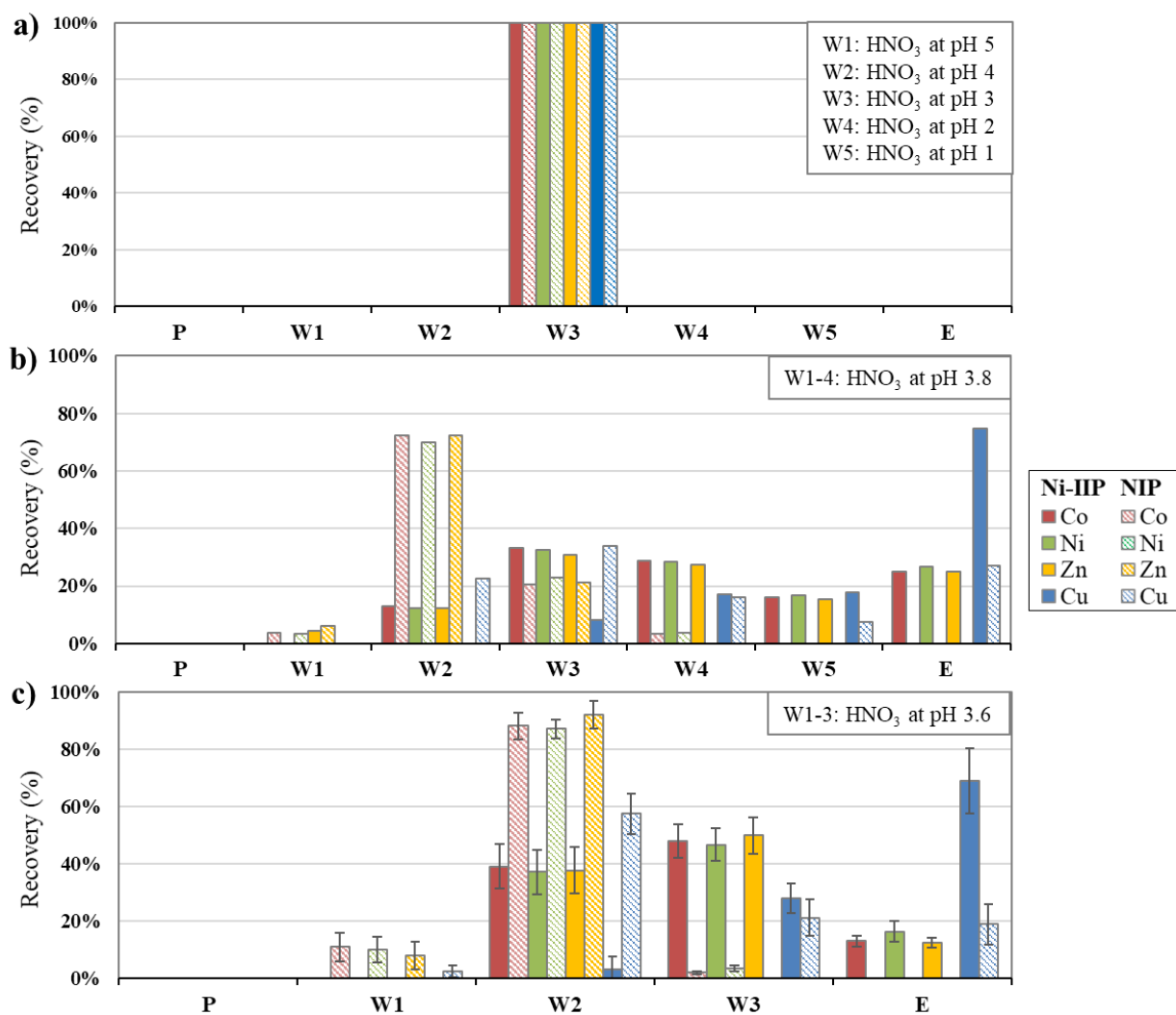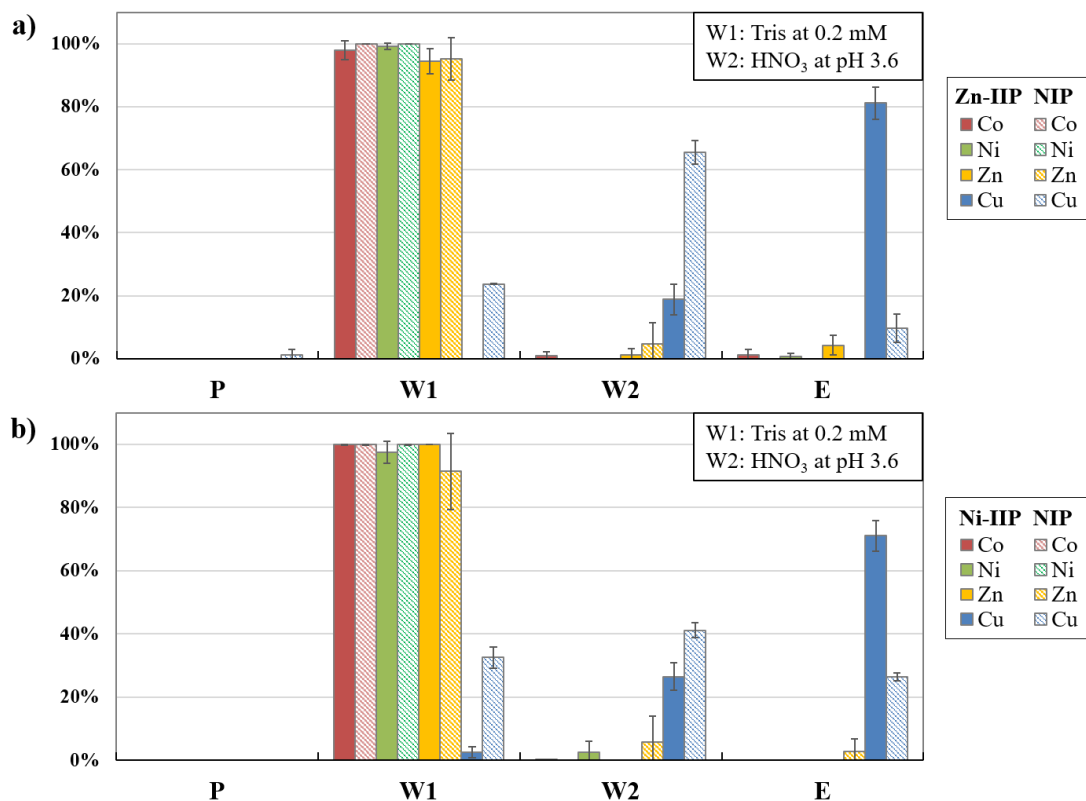
Figure S7 SPE profiles of Co(II), Ni(II), Zn(II), and Cu(II) on Ni-IIP and its NIP. Percolation (P): 1 mL of HNO₃ at pH 5.5 spiked with Co(II), Ni(II), Zn(II) and Cu(II) at 30 µg L⁻¹ for each; Washing (W1-5): a) 5 x 0.5 mL of HNO₃ at pH 5, 4, 3, 2, and 1. b) 4 x 0.5 mL of HNO₃ at pH 3.8. c) 3 x 0.5 mL of HNO₃ at pH 3.6; Elution (E): 1 mL of 5% HNO₃. The SPE protocol (c) was conducted in triplicate and the results were averaged.

Figure S3 SPE profiles of Co(II), Ni(II), Zn(II), and Cu(II) on a) Zn-IIP and its NIP; b) Ni-IIP and its NIP. Percolation (P): 1 mL of HNO₃ at pH 5.5 spiked with Co(II), Ni(II), Cu(II) and Zn(II) at 30 µg L⁻¹ for each; Washing (W1-2): 1 mL of Tris at 0.2 mM at pH 5.5 and 1.5 mL of HNO₃ at pH 3.6; Elution (E): 1 mL of 5% HNO₃. The experiments were conducted in triplicate and the results were averaged.
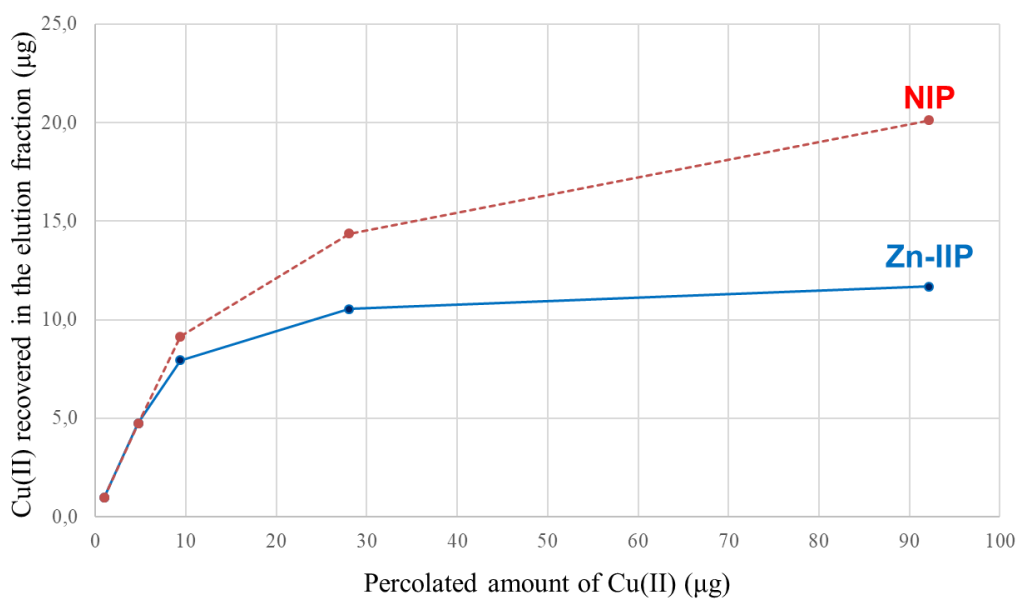
Figure S4 Adsorption capacity curves obtained by percolating an increasing amount of Cu(II) in 1 mL of HNO₃ at pH 5.5 on Zn-IIP and its NIP (30 mg of each). Amounts of Cu(II) were recovered in the elution fraction (1 mL of 5% HNO₃) without performing a washing step.
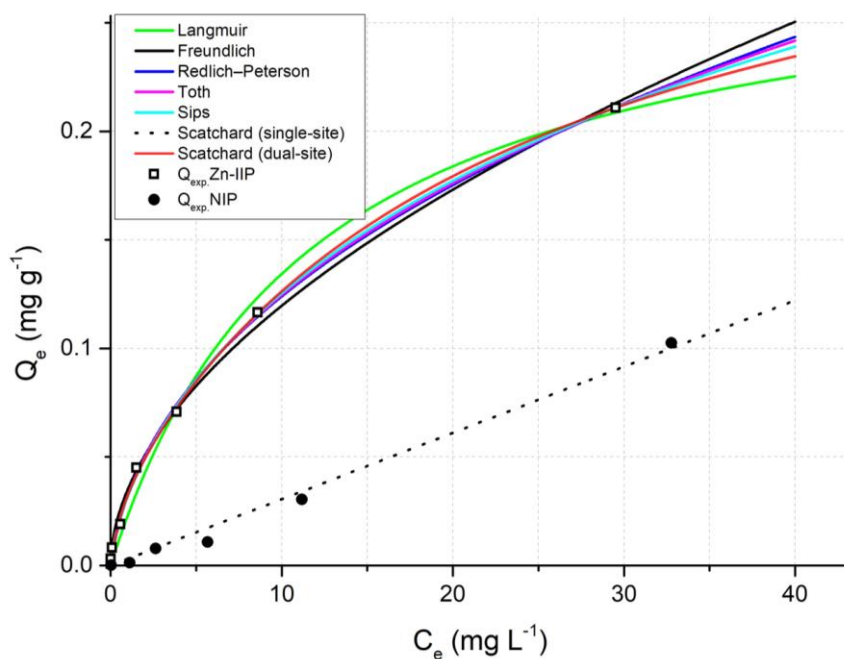

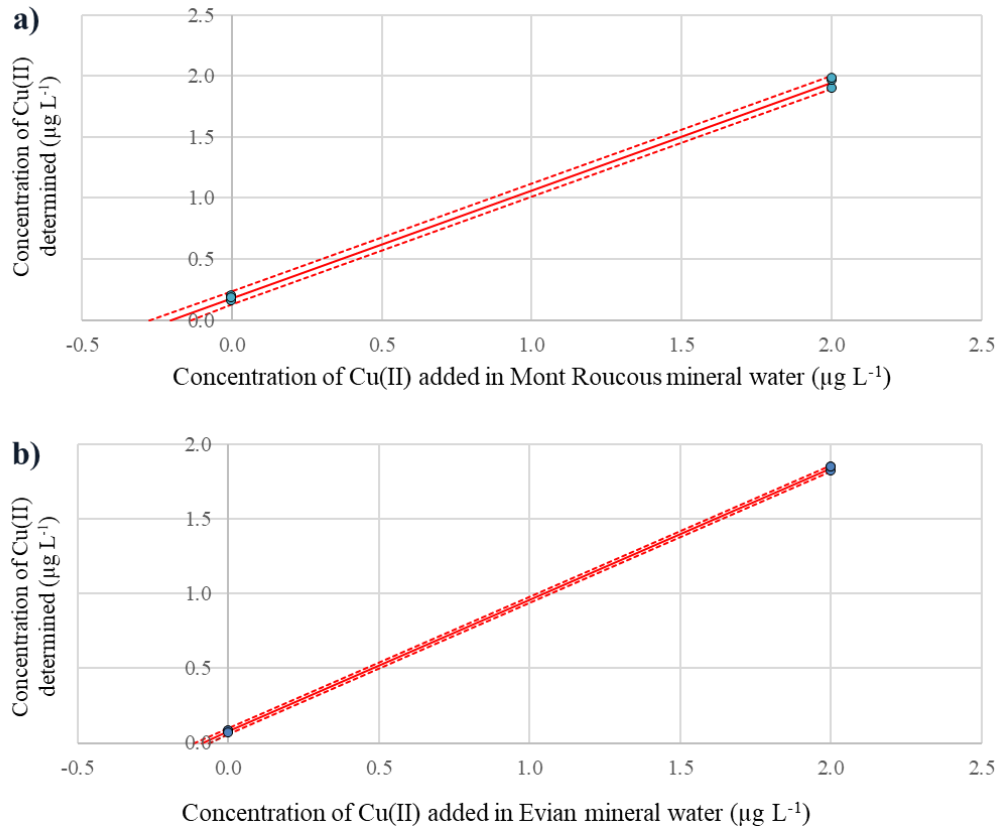*Figure S5 Plots of the isotherm models with the experimental data of Zn-IIP and its NIP.*

a)

b)

Figure S6 Determination of Cu(II) concentration in mineral water of a) Mont Roucous and of b)Evian by means of standard addition method. The experiments were conducted in triplicate for each concentration level.
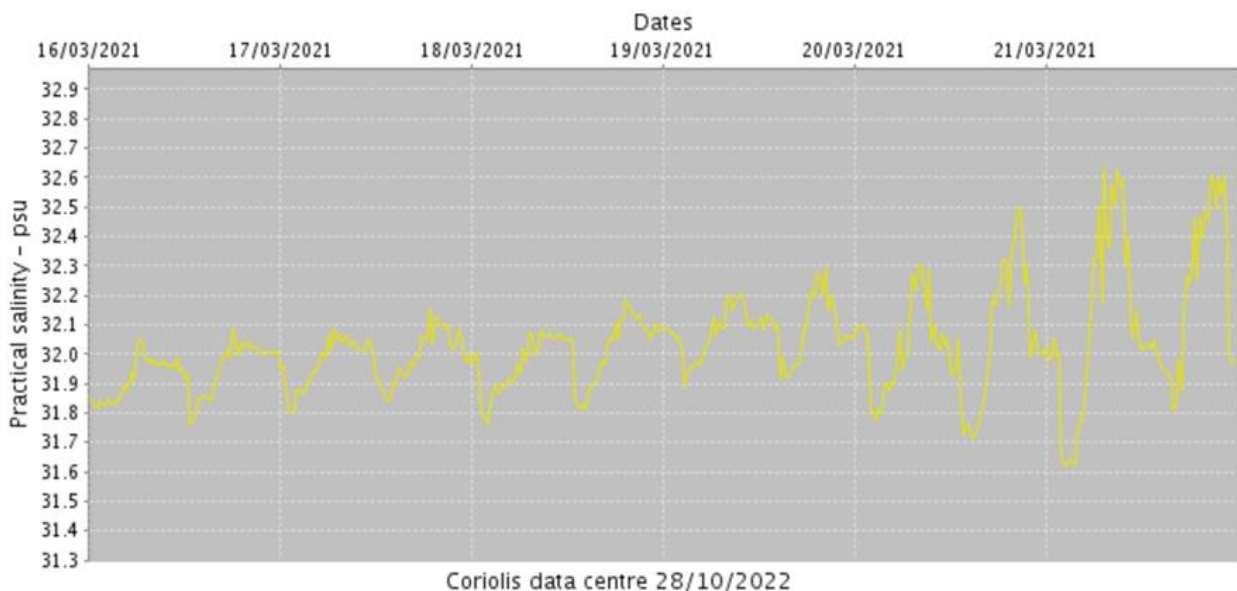

Figure S7 Measurement of the sea water salinity using Marel Iroise buoy (1 psu = 1 g of salt per kg of sea water) [1].

[1] S. Blain, J. Guillou, P. Treguer, P. Woerther, L. Delauney, E. Follenfant, O. Gontier, M. Hamon, B. Leilde, A. Masson, C. Tartu, R. Vuillemin, High frequency monitoring of the coastal marine environment using the MAREL buoy, Environ. Monit. Assess. 6(6) (2004) 569-75. https://doi.org/10.1039/b314073c