Optimal synthesis of a Ni(II)-dimethylglyoxime ion-imprinted polymer for the enrichment of Ni(II) ions in water, soil and mine tailing samples

Modise Rammika[1]*, Godfred Darko[2] and Nelson Torto[2]
[1]*Department of Agricultural Research, Private Bag 0033, Gaborone, Botswana*
[2]*Department of Chemistry, Rhodes University, PO Box 94, Grahamstown 6140, South Africa*

Abstract

A Ni(II)-dimethylglyoxime ion-imprinted polymer {Ni(II)-DMG IIP} was optimised by the uniform design experimental method and used to adsorb Ni(II) ions from water, soil and mine tailing samples. This aimed to improve the performance of this ion-imprinted polymer in trapping Ni(II) ions from soil and mine tailing samples which are characterised by complex matrices. The optimisation was carried out by varying the molar ratios of monomer to crosslinker to porogen and template to ligands, as well as by keeping these parameters constant and varying the concentrations of initiator, 2,2'-azobisisobutyronitrile (AIBN). The optimal molar ratios of crosslinker to monomer, monomer to template and nickel(II) sulphate hexahydrate ($NiSO_4.6H_2O$) to 4-vinylpyridine to dimethylglyoxime were found to be 3.3:1.0, 0.6:1.0 and 1.0:0.6:3.6, respectively, with 30 mg and 8 mℓ as the optimum amounts of initiator and porogen, respectively. Through this optimisation, extraction efficiency for Ni(II) increased from 98 to 100% in aqueous samples. The extraction efficiencies for the soil and mine tailing samples were 98-99% and 99%, respectively, with an enrichment factor of 2 in mine tailing samples and ranging from 27 to 40 in soil samples. The method displayed good accuracy, as it was validated with certified reference materials (SEP-3 and BCR-142R) and the values obtained were close to the certified ones. The improved quality of results obtained from water, soil and mine tailing samples showed that the uniform design experimental method is effective and efficient for optimising imprinted polymers using a lower number of experiments performed.

Keywords: Ni(II)-dimethylglyoxime ion-imprinted polymer, optimised, uniform design experimental method, enrichment factors, monomer:template ratio, crosslinker:monomer ratio.

Introduction

Ion-imprinted polymers (IIPs) are highly selective cross-linked polymeric materials synthesised by complexing a template and a functional monomer in the presence of a crosslinker. The reaction proceeds via a free radical initiation in an appropriate solvent normally referred to as a porogen. The ion-imprinting effect is due to the 'memory' of the ion (template) that has previously been used and subsequent removed. The memory is a result of the effect of the size and charge of the ion that was present in the cavity during polymerisation. The bonds formed between the template and the functional monomers in ion-imprinted polymerisation reactions are weaker, non-covalent (Arshady and Mosbach, 1981; Wulff and Sarchan, 1972), as compared to stronger, covalent (Wulff and Sarchan, 1972; Yan and Ramström, 2005) bonds. There are several factors that influence the polymerisation, and hence the subsequent performance of the IIPs. These factors include the nature and masses of monomers (Zhu et al., 2007; Yu and Mosbach, 2000; Okutucu and Telefoncu, 2008; Piletska et al., 2009; Yilmaz et al., 1999; Zhang et al., 2005; Zhang and Li, 2006; Song et al., 2009; He et al., 2007; Kim and Spivak, 2003; Andersson et al., 1999), crosslinkers (Wulff and Sarchan, 1972; Yan and Ramström, 2005; Zhu et al., 2007; Yu and Mosbach, 2000;

Okutucu and Telefoncu, 2008; Piletska et al., 2009; Yilmaz et al., 1999; Zhang et al., 2005; Zhang and Li, 2006; Song et al., 2009; He et al., 2007; Kim and Spivak, 2003; Andersson et al., 1999; Holland et al., 2010; Mijangos et al., 2006), porogen (Arshady and Mosbach, 1981 and Wulff and Sarchan, 1972; Yan and Ramström, 2005; Zhu et al., 2007; Yu and Mosbach, 2000; Okutucu and Telefoncu, 2008; Holland et al., 2010; Mijangos et al., 2006; Yoshizako et al., 1998), template (Yilmaz et al., 1999; Zhang and Li, 2006; He et al., 2007; Kim and Spivak, 2003; Andersson et al., 1999; Holland et al., 2010), and initiator used (Mijangos et al., 2006; Chu et al., 2003), as well as the temperature (Piletska et al., 2009; Mijangos et al., 2006), pressure (Piletska et al., 2009), method of initiation (He et al., 2007) polymerisation time (Piletska et al., 2009; Mijangos et al., 2006), magnetic field (Piletska et al., 2009), and the dielectric constant (Piletska et al., 2009) of the components of the monomer mixture employed. It is therefore important to optimise the parameters in order to drive the equilibrium of the polymerisation reaction towards complex formation, so as to improve the formation and performance of the IIP. There are several approaches that can be used to optimise these parameters (Yu and Mosbach, 2000; Okutucu and Telefoncu, 2008; Piletska et al., 2009; Yilmaz et al., 1999; Zhang et al., 2005; Zhang and Li, 2006; Song et al., 2009; He et al., 2007; Kim and Spivak, 2003; Andersson et al., 1999; Holland et al., 2010; Mijangos et al., 2006; Yoshizako et al., 1998; Chu and Lin, 2003). Most have reported an approach where a single parameter was varied with others kept constant (Zhu et al., 2007; Zhang et al., 2005; Zhang and Li, 2006; Song et al., 2009; He et al., 2007; Kim and Spivak, 2003; Holland et al., 2010; Mijangos

et al., 2006; Yoshizako et al., 1998; Chu and Lin, 2003). However, other groups varied more than one parameter at a time (Zhu et al., 2007; Okutucu and Telefoncu, 2008; Piletska et al., 2009; Yilmaz et al., 1999; Andersson et al., 1999). The uniform design of experiments employed in this study (Zhu et al., 2007) is a statistical approach that uses a combination of experimental parameters.

The most important parameters that determine the performance of IIPs are the molar ratios of crosslinkers to monomers (Yan and Ramström, 2005; Zhu et al., 2007; Yu and Mosbach, 2000; He et al., 2007; Spivak, 2005), monomers to template (Yan and Ramström, 2005; Yu and Mosbach, 2000; Yilmaz et al., 1999; Zhang and Li, 2006; He et al., 2007; Kim and Spivak, 2003; Andersson et al., 1999; Spivak, 2005), the volume and type of porogen (Yan and Ramström, 2005; Yu and Mosbach, 2000; Song et al., 2009; He et al., 2007; Yoshizako et al., 1998; Spivak, 2003) and the initiator used (Piletska et al., 2009; Mijangos et al., 2006; Yanagihara et al., 1999). The volume/mass of template used ought to be optimised, because increasing the concentration of the components in the polymerisation mixture will favour an increase in the pre-polymer complex, according to Le Chatelier's principle. This drives the equilibrium of the reaction towards complex formation and thus improves the performance of the polymer formed. The monomer complexes with the template, and the process is dependent on the concentration of the monomer. Adsorption processes are usually modelled using the Langmuir, Freundlich and Temkin models (Zhang and Li, 2006). The Temkin model is generally accepted as the most suitable model for chemical adsorption.

Non-specific adsorption, however, occurs when the volume of the monomer is in excess and a very low concentration of monomer results in a polymer with fewer functional groups and therefore insufficient binding sites. A better fit between the binding sites and the template leads to an increase in the affinity and selectivity of the IIP in ion recognition. However, increasing the concentration of the monomer reduces the crosslinker to monomer ratio which affects the morphology and stability of the polymer matrix and, consequently, the imprinted binding sites. In this regard, the concentration of the crosslinker has to match that of the monomer.

The template, initiator, monomer and the crosslinker must be soluble in the porogen (Yoshizako et al., 1998). The nature and volume of the porogenic solvent determines the strength of non-covalent interactions and influences polymer morphology which directly affects the performance of an IIP (Song et al., 2009). Therefore the concentration of the porogen used is very important. The polymerisation reaction is started by an initiator which provides the free radicals. The free radicals are generated by thermal or photolytic cleavage of azobis (nitriles) or peroxides (Yanagihara et al., 1999). Reducing the mass of the initiator leads to the reduction in temperature during polymerisation to form polymers with good imprinting cavities (Piletska et al., 2009; Mijangos et al., 2006), and, at the same time, the polymerisation rate also increases with initiator amount (Chu and Lin, 2003). Therefore a balance has to be struck to ensure that all the double bonds are broken using a minimum amount of initiator.

In this paper, a Ni(II)-dimethylglyoxime ion-imprinted polymer {Ni(II)-DMG IIP} was optimised using the uniform design experimental method and then used to enrich Ni(II) ions from water, soil and mine tailing samples. This is the first ion-imprinting study which was able to selectively enrich Ni(II) ions from mine tailing samples. Current methods of separation such as chemical precipitation (Massoumi, and Hedrick, 1969), electrodeposition (Ruotolo and Gubulin, 2002), cementation (Chang et al., 2007), ultra-filtration (Hong et al., 1998), ion exchange (Shao et al., 1991), activated carbon adsorption (Wilson et al., 2006), liquid-liquid extraction (Sarma and Reddy, 2002; Maruyama et al., 2007) and solid-phase extraction (SPE) (Hennion, 1999) are less selective. Where Ni(II) ions occur at low concentrations, there is a problem of interference from closely-related ions (Pourreza et al., 2006; Kiptoo et al., 2007). However, it has been our observation that most ion-imprinting studies do not report optimisation studies, most likely because of their long, tedious and time-consuming nature. Our experience in this study suggests that the uniform design experimental method is a more convenient and reliable method for optimising the ion-imprinting polymerisation process. In this method, the polymerisation process parameters of interest were varied so as to evaluate their impact on the polymerisation process, while parameters with less impact were held constant (Zhu et al., 2007).

Experimental

Chemicals and reagents

Analytical grade ammonium acetate, 4-vinylpyridine (4-VP), 2,2'-azobisisobutyronitrile (AIBN), 2-methoxy ethanol, styrene, nickel(II) sulphate, hexahydrate ($NiSO_4 \cdot 6H_2O$), divinyl benzene (DVB), dimethylglyoxime (DMG), trace metal grade nitric acid, hydrochloric acid, hydrogen peroxide and the stock solution (1 000 mg/ℓ) of Ni(II) were obtained from Sigma-Aldrich (Steinheim, Germany). Filter paper was purchased from Whatman (Maidstone, UK). An A10 milli-Q system from Millipore RiOs (Bedford, USA) was used to generate ultrapure water. Light sandy soil certified reference material (CRM), (BCR-142R) was obtained from the European Commission Joint Research Centre (Brussels, Belgium). A custom solution of certified reference material (CRM), SEP-3, was obtained from Inorganic Ventures (Christiansburg, USA).

Instrumentation

Concentrations of metals were determined using an iCAP 6000 series inductively coupled plasma-optical emission spectrometer (ICP-OES) from Thermo Electron Corporation (Cheshire, United Kingdom). The solution pH was measured by the Jenway 3510 pH meter (Essex, UK).

Preparation of the different compositions of Ni(II)-DMG IIPs

Ni(II)-DMG IIP was prepared as outlined by Rammika et al. (2011). For the uniform design experiments, a series of Ni(II)-DMG IIPs were prepared through the process described but with varying concentrations of the reactants (Tables 1, 2 and 3 and Fig. 1). The amounts of template, monomer, crosslinker, crosslinking monomer, ligand and porogen were varied from 0.105 to 0.526 g, 0.05 to 0.41 mℓ, 0.36 to 3.21 mℓ, 0.23 to 2.07 mℓ, 0.093 to 0.836 g and 2.0 to 18.0 mℓ, respectively. The 'array' in the uniform design experimental method is as shown in Tables 1 and 2.

The choice of 4-VP as a monomer was based on the strong binding that occurs between nickel and nitrogen atoms on the ligand (Kopel et al., 1999). 4-VP is also known

Table 1 — The uniform design experiment showing how the variations of styrene, DVB and 2-methoxy ethanol affect recovery (n=3)					
Run	[a]Volume of Styrene (mℓ)	[b]Volume of DVB (mℓ)	Volume of 2-methoxy ethanol (mℓ)	Molar ratio (b:a)	%EE
1	0.688	2.493	18	2.3:1.0	95.96
2	1.376	1.424	16	0.7:1.0	98.89
3	2.065	0.356	14	0.1:1.0	-
4	0.459	2.849	12	4.0:1.0	94.63
5	1.147*	1.781*	10*	1.0:1.0	98.26
6	1.835	0.712	8	0.2:1.0	99.35
7	0.229	3.205	6	9.0:1.0	94.87
8	0.918	2.131	4	1.5:1.0	92.81
9	1.606	1.068	2	0.4:1.0	96.45

Amounts used in previous study: Rammika et al. (2011)

| Table 2 — Molar ratios of DVB to 4-VP and 4-VP to $NiSO_4 \cdot 6H_2O$ (n=3)				
[a]Moles of DVB	[b]Moles of 4-VP	[c]Moles of $NiSO_4 \cdot 6H_2O$ (g)	Crosslinker/ monomer molar ratio (a:b)	Monomer: template molar ratio (b:c)
0.003999	0.003603	0.000600	1.1:1.0	6.0:1.0
0.003999	0.003198	0.001200	1.3:1.0	2.7:1.0
0.003999	0.002802	0.001800	1.4:1.0	1.6:1.0
0.003999	0.002396	0.000400	1.7:1.0	6.0:1.0
0.003999	0.002000	0.001000	2.0:1.0	2.0:1.0
0.003999	0.001603	0.001600	2.5:1.0	1.0:1.0
0.003999	0.001198	0.002000	3.3:1.0	0.6:1.0
0.003999	0.000802	0.000800	5.0:1.0	1.0:1.0
0.003999	0.000396	0.001400	10.1:1.0	0.3:1.0
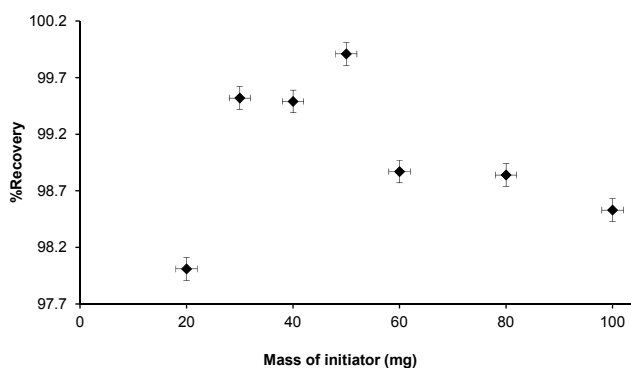
Figure 1
Effect of the mass of initiator on extraction efficiency of Ni(II)-DMG IIP

to be a good functional monomer for metals (Daniel et al., 2003; Nishide et al., 1976; Romaní et al., 2008; Saraji and Yousefi, 2009). The crosslinker, DVB, was used as it is less polar and hence interacts less with the template and the monomer. DVB has also been shown to have an increased loading capacity relative to EDMA, trimethylolpropane tria-crylate, 1,6-Hexanediol diacrylate and tripropylene glycol diacrylate (Wulff and Sarchan, 1972). Polymers prepared using DVB as a crosslinker were shown to have a better binding of the analyte and lower non-specific binding than EDGMA (Yilmaz et al., 1999).

2-methoxy ethanol was used because it is moderately polar (with polarity index of 5.5) and has been found to have a much higher selectivity coefficient (99%) than methanol (90.33%), tetrahydrofuran (37.66%), acetic acid (33.83%), dichloroeth-ane (10.57%), N,N-dimethyl formamide (4.59%) and toluene (1.50%) (Gladis and Rao, 2004). The polarity of the porogen determines the level of interaction between the template and the functional monomer. A highly polar porogen will interact with the template or functional monomer, or both, resulting in fewer opportunities for the template and functional monomer to interact. This leads to the creation of a lower number of imprinting sites and reduces the absorption efficiencies of the IIP. A less polar porogen will interact less with the template and the functional monomer. The interaction of the template and the functional monomer will be strong and the IIP formed will precipitate quickly (Arshady and Mosbach, 1981; Wulff and Sarchan, 1972; Yan and Ramström, 2005; Yoshizako et al., 1998; Spivak, 2005). A moderately polar porogen is there-fore desirable, because it results in the formation of uniform imprinting sites in the IIP.

Ligands keep the template in place. DMG was chosen as it binds with metal ions by donating electrons, as does 4-VP, and has been used for the determination of nickel in urea (Bickerdike and Willard, 1952), seawater (Forster and Zeitlin, 1966) and, most recently, cell phones (Thyssen et al., 2008). AIBN was used as it is soluble in 2-methoxy ethanol, the poro-gen used in this experiment, and has a temperature of initiation (65 °C) which is lower than the boiling point of the porogen (124-125 °C).

Sample collection and preparation

Sea, river, untreated sewage and treated sewage water samples were collected and treated as outlined by Rammika et al. (2011). Soil and mine tailing samples were collected in polyethylene bags from buildings around the Chemistry and Pharmaceutical Sciences Building (Rhodes University, Grahamstown) and Selibe Phikwe copper-nickel mine (Selibe Phikwe, Botswana), respectively. Soil samples were collected at any exposed ground surface, without following any particular scheme, as the environment is paved. For mine tailings, 1.0 kg of samples were taken at a depth of 15 cm using a soil auger. One composite sample represented 1 ha and each composite sample consisted of 15 subsamples. Three composite samples were taken to the laboratory where they were air-dried, passed through a 2.0 mm sieve and homogenised in a mortar. Each sample was divided into 3 subsamples and 0.5 g was acid digested using a standard protocol (Thompson, 2009) prior to ICP-OES analysis.

Analytical quality control procedure

BCR-142R and SEP-3 certified referenced materials were used to validate the analytical procedure. Analytical calibrations, based on the recommended concentration points and emission lines of each element, were carried out in aqueous standard solutions. Adsorption and desorption experiments were carried out using 50.0 mg of the Ni(II)-DMG IIP in 10.0 mℓ portions of the certified reference materials. Repeatability of the method was evaluated by comparing the signals obtained from 5 determinations of the reference materials. The limits of detection (LOD) and quantification (LOQ) were evaluated as 3 and 10 times the estimated regression standard deviation, respectively, based on 5 replicate determinations.

Results and discussion

Characterisation of the polymers

The morphology of the imprinted, non-imprinted and DMG polymers is discussed in Rammika et al. (2011); the polymers in this earlier study were also characterised using infrared spectra.

Optimisation of template, monomer, porogen, crosslinker, crosslinking monomer, ligand and initiator

The uniform design experimental approach reduced the number of experiments that were initially proposed from 162 (or 189 if the initiator is included) to 54 by varying the concentrations of template, monomer, porogen, crosslinker, crosslinking monomer and ligand at 9 levels with 3 replicates. Initially the concentrations of the parameters including the initiator were to be varied one at a time while keeping others constant.

By varying the concentrations of crosslinking monomer, crosslinker and porogen, extraction efficiencies ranging from 98.26 to 99.35% were achieved (Table 1). The percentage extraction efficiency was calculated as shown in Eq. (1):

$$\%EE = \left(\frac{Ci - Cs}{Ci} \right) \times 100 \tag{1}$$

where:

C_i is the initial solution concentration (µmol/mℓ)
C_s is the solution concentration after adsorption.

These extraction efficiencies were achieved with a smaller total volume of the mixture (from 12.93 to 10.55 mℓ), though the volume of monomer used was greater than that used in the previous study (Rammika et al., 2011) i.e. before optimisation. Table 2 shows that the optimum crosslinker to monomer molar ratio was 3.3:1.0, which is in the range of 3.0:1.0 to 20.0:1.0 as reported by others (Yan and Ramström, 2005; Zhu et al., 2007; Yu and Mosbach, 2000; Zhang et al., 2005; He et al., 2007; Spivak, 2005).

The lower ratio of crosslinker to monomer can be attributed to the fact that the styrene monomer was added as a crosslinking monomer. The effect of the styrene was evident in Run 3 where the polymer did not form. This was mainly because the molar ratio of styrene to DVB was too high (1.0:0.1). However, the polymer formed, though with low extraction efficiency, when the ratio was reversed, as can be seen for Run 7 (Table 1) where the molar ratio was changed to 1.0:9.0. A polymer was expected to be formed in Run 3, but with lower absorption capacity than in Run 7, as the only difference between Runs 3 and 7 was the volume of porogen. The optimum volume of porogen was 8.0 mℓ compared to the 10.0 mℓ that was used without optimisation (Rammika et al., 2011). The extraction efficiency of Ni(II) increased from 99.35 to 99.91% after varying the amounts of template, monomer and ligand (Table 3).

The optimal monomer to template molar ratio that was obtained from Run 7 was 0.6:1.0, which differed from the 2.83:1.0 to 5.0:1.0 reported for other studies (Yan and Ramström, 2005; Yu and Mosbach, 2000; Zhang and Li, 2006; He et al., 2007; Kim and Spivak, 2003; Andersson et al., 1999; Chu and Lin, 2003; Spivak, 2005), or the 2.0:1.0 that was used without optimisation (Rammika et al., 2011). The optimal

Table 3
The uniform design experiment showing how the variations of NiSO$_4$·6H$_2$O, DMG and 4-VP affect recovery (n=3)

Run	[a]Mass of NiSO$_4$·6H$_2$O (g)	[b]Mass of DMG (g)	[c]Volume of 4-VP (mℓ)	Molar ratio (a:c:b)	%Recovery
1	0.158	0.650	0.409	1.0:6.0:9.3	97.28
2	0.316	0.372	0.363	1.0:2.7:2.7	85.49
3	0.473	0.093	0.318	1.0:1.6:0.4	86.3
4	0.105	0.743	0.272	1.0:6.0:16	97.61
5	0.263*	0.465*	0.227*	1.0:2.0:4.0	99.35
6	0.421	0.186	0.182	1.0:1.0:1.0	88.63
7	0.526	0.836	0.136	1.0:0.6:3.6	99.91
8	0.210	0.557	0.091	1.0:1.0:6.0	99.13
9	0.368	0.279	0.045	1.0:0.3:1.7	94.37

Amounts used in previous study: Rammika et al. (2011)

Table 4 Analytical quality control parameters determined using the SEP-3 certified referenced groundwater							
Wavelength (nm)	Calibration linearity R^2	Certified concentration (mg/ℓ)	Concentration found (n=3) (mg/ℓ)	Relative error (%)	%RSD (n=6)	LOD (µg/mℓ) (n=5)	LOQ (µg/mℓ) (n=3)
231.60	0.9967	0.8980 (0.007)	0.8972 (0.0011)	-0.0891	3.87	0.0002 (0.0015)	0.0004 (0.002)

Standard deviations in brackets

Table 5 Analytical quality control parameters determined using the BCR-142R certified referenced sandy soil							
Wavelength (nm)	Calibration linearity R^2	Certified concentration (mg/ℓ)	Concentration found (n=3) (mg/ℓ)	Relative error (%)	%RSD	LOD (mg/ℓ)	LOQ (mg/ℓ)
231.60	0.9994	64.5 (0.007)	64.2714 (0.0013)	-0.3544	2.2919	0.0003 (0.002)	0.0009 (0.002)

Standard deviations in brackets

molar ratio of $NiSO_4 \cdot 6H_2O$ to 4-VP to DMG was 1:0.6:3.6 which is slightly different from the predicted value of 1:2:2 (similar to that for Run 2; Table 3) or 1:2:4, the ratio that was employed with nickel chloride hexahydrate to 2-(diethyl-amino) ethyl methacrylate to 8-hydroxyquinoline (Romani et al., 2009[a]). According to the scheme proposed by Daniel et al. (2003), 2 molecules of 4-VP react with 1 metal atom and 2 molecules of DMG are used to hold the metal atom in place via donation of electrons by nitrogen atoms. The total masses of $NiSO_4 \cdot 6H_2O$ and DMG were higher than that used without optimisation but the volume of 4-VP was very much lower. Comparing the benefits of increasing the concentrations of template, monomer, ligand and porogen to the resulting increase in extraction efficiency, it can be said that the concentrations of reactants in Run 8 can still be used.

From Fig. 1, the optimum mass of initiator was 40.0 mg. This mass is close to that reported by other authors (Romani et al., 2008; Romani et al., 2009a; Ersoz et al., 2004; Otero et al., 2009; Praveen et al., 2005) but lower than that in some reports (Gladis and Rao, 2004; Romani et al., 2009b). There was no polymer formed when 10.0 mg of initiator were used. The optimum mass is lower than that which was previously used without optimisation (Rammika et al., 2011). The optimisation of initiator was conducted in 24 experiments with 8 levels and 3 replicates. The number of experiments could have been less if the uniform design experimental method was used for optimisation of Ni(II)-DMG IIP.

Analysis of CRMs

Table 4 gives the quality control parameters regarding the determination of nickel concentrations in groundwater CRM, while Table 5 gives the quality control parameters regarding the determination of nickel concentrations in sandy soil CRM. Accuracy of the determinations, expressed as relative error between the certified and the observed values of the reference materials, was < 0.4%. The precision of these measurements, expressed as relative standard deviation on 5 independent determinations, was also satisfactory, being lower than 4% in all cases. The limit of detection (LOD) of the Ni(II)-DMG IIP was found to be 0.0002 ± 0.0001 µg/mℓ while the limit of quantification (LOQ) was found to be 0.0004 µg/mℓ in water samples. In soil, the LOD was found to be 0.0003 ± 0.0001 µg/mℓ while the LOQ was found to be 0.0009 µg/mℓ in water samples. In all cases, there was an improvement in terms of

Table 6 Analysis of BCR-142R certified reference material				
CRM	Certified Ni(II) conc. value (µg/mℓ)	Ni(II) conc. in sample (µg/mℓ) (n=3)	Amount of Ni(II) added (µg/mℓ) (n=3)	% Recovery
BCR-142R	64.5	62.6314	0, 5, 10	-, 99, 99

Table 7 Enrichment factors (EFs) of Ni(II)-DMG IIP in aqueous samples (n=3)		
Type of water sample	EF (Before optimisation)	EF (After optimisation)
Sea	18	21
Town River	3	5
Village River	11	13
Treated sewage	6	7
Untreated sewage	2	3

accuracy, precision, LOD and LOQ relative to the results obtained ((Rammika et al., 2011) before optimisation. The extraction efficiencies of the spiked CRM material were good (Table 6).

Analysis of water samples

The Ni(II)-DMG IIP was used to trap the Ni(II) ions in water samples. The results were compared to what was obtained before optimisation (Rammika et al., 2011); enrichment factors were significantly increased (Table 7).

Analysis of soil samples

The Ni(II)-DMG IIP was used to enrich Ni(II) ions in soil samples. All soil samples were complex as estimated from the ratios evaluated with the digested and undigested samples (Table 8). Sand was less complex than loam soils A and B but had higher concentrations of Cu(II) than Ni(II); however, the extraction efficiency for Ni(II) was still high (Table 9). The soil samples had higher concentrations of Zn(II) than Ni(II) and loam soil B had the same concentration of Ni(II) as that of Co(II), but the extraction efficiency obtained with the Ni(II)-DMG-IIP was 100%. The enrichment factor (EFs) was 2 in mine tailing samples and ranged from 27 to 40 in soil samples.

Table 8
Enrichment factors (EFs) of Ni(II)-DMG IIP in soil samples and mine tailing samples (n=3)

Type of sample	[a]Ni(II) concentration in the sample (µg/mℓ) (digested)	[b]Ni(II) concentration obtained without digestion (µg/mℓ)	[c]Ni(II) conc. value obtained when using Ni(II)-DMG-IIP (µg/mℓ)	EF*	Ratio (b/a)
Loam A	0.3909	0.0156	0.4286	27	0.04
Loam B	0.4571	0.0183	0.5178	28	0.04
Sand	0.0342	0.0010	0.0402	40	0.03
Mine tailings	13.53	12.46	21.06	2	0.92

$$* \quad EF = \frac{c}{b}$$

Table 9
Composition of the soil samples (n=3)

Sample	Ni(II) (µg/mℓ)	Co(II) (µg/mℓ)	Cu(II) (µg/mℓ)	Zn(II) (µg/mℓ)	Na(I) (µg/mℓ)	K(I) (µg/mℓ)	Ca(II) (µg/mℓ)	Mg(II) (µg/mℓ)
Loam A	0.1076	0.0625	0.0770	3.432	8.899	90.68	399.0	54.20
Loam B	0.0964	0.0915	0.0770	4.820	9.332	92.95	280.6	59.04
Sand	0.033	0.0074	0.8033	3.113	30.25	17.43	5316	86.52

Table 10
Composition of the mine tailing samples (n=3)

Ca(II) (µg/mℓ)	Mg(II) (µg/mℓ)	K(I) (µg/mℓ)	Na(I) (µg/mℓ)	Co(II) (µg/mℓ)	Cu(II) (µg/mℓ)	Fe(II) (µg/mℓ)	Ni(II) (µg/mℓ)	Pd(II) (µg/mℓ)	Zn(II) (µg/mℓ)
12607.4	2595.3	612.6	442.9	0.8	10.1	246.3	13.5	1.8	1.1

* EFs were calculated as shown in Eq. (2):

$$EF = \frac{c}{b} \qquad (2)$$

where:
c is the Ni(II) concentration obtained when using Ni(II)-DMG IIP (µg/mℓ)
b is the Ni(II) concentration obtained without digestion (µg/mℓ).

Enrichment factors indicate an up to 40-fold improvement in extraction efficiencies for soil samples and up to 2-fold for mine tailing samples, respectively, when using the Ni(II)-DMG-IIP, which is a considerable improvement in terms of access to the Ni(II) ions.

Analysis of mine tailing samples

Finally, the performance of the Ni(II)-DMG-IIP in trapping Ni(II) ions was tested with mine tailing samples. The extraction efficiencies for Ni(II) ions from mine tailing samples were high (99%), with a percentage enrichment factor of 2%, considering the high background concentrations of Ca(II), Mg(II), K(I), Na(I), Cu(II) and Fe(II) that were present in the sample (Table 10). The matrix complexity of the mine tailings was estimated to be lower than that of soil samples, as shown by the ratio of Ni(II) concentrations in the digested and undigested samples. In addition, the amount of Co(II), which competes severely with Ni(II) in reactions is low (Griffing et al., 1947; Yang and Black, 1994; Kumbasar and Sahin, 2008). Therefore, it was shown that this Ni(II)-DMG IIP can successfully be used to trap Ni(II) from mine tailings.

Conclusion

The uniform design experimental method was successfully applied to optimise Ni(II)-DMG IIP in terms of the molar ratios of crosslinker to monomer, monomer to template, template to ligand and the amount of porogen, using few experiments than required by conventional methods. Comparison with the optimisation results for the initiator optimised using the conventional method indicates that the uniform design experimental method is efficient and effective. The optimised Ni(II)-DMG IIP gave higher extraction efficiencies for Ni(II) ions in water compared to those obtained prior to optimisation of the polymer. High extraction efficiencies were also obtained in soil and mine tailing samples. The composition of the mine tailings indicated a need for sample pre-concentration, which can be achieved by an optimised Ni(II)-DMG IIP. The polymer was validated by CRMs and the results were satisfactory. The polymer therefore offers a good opportunity for use as a sorbent in SPE for water, soil and mine tailing samples. The optimisation process has enabled the use of lower volumes and masses of reagents, while maintaining sorbent effectiveness, thus enabling the production of cheaper SPE sorbents.

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