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TECHNICAL ARTICLE

Complexation of Ni(II) by Dimethylglyoxime for Rapid Removal and Monitoring of Ni(II) in Water

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Abstract The complexation of Ni(II) with dimethylglyoxime (DMG) entrapped within a Nafion membrane and a DMG–sol–gel matrix was studied and compared for different solutions. First and pseudo-second order kinetic models, Elovich, intra-particle, and liquid film diffusion models were applied to evaluate sorption kinetics. Complexation of Ni(II) by DMG entrapped in the polymeric materials followed a pseudo-second order kinetic model; moreover, DMG in Nafion also allowed diffusion-controlled uptake. The pseudo-second order rate constant was significantly higher for the free ligand in solution than for Ni(II) accumulation in the surface-attached DMG-Nafion. The DMG–sol–gel removal ability of Ni(II) was tested using actual mine water. The presence of interferences only insignificantly decreased the removal percentage of Ni(II), thus confirming the high selectivity of DMG towards Ni(II). Also, an electrochemical sensor modified with DMG in Nafion was investigated further for direct electrochemical determination of Ni(II) in untreated mine water. Determination errors and interference effects were low. Thus, this approach represents an effective potential solution for selective Ni(II) removal from mine water as well as a rapid and cheap sensor for on-site monitoring of Ni(II) in mine and environmental waters.

Keywords Sorption kinetics · Direct monitoring · Metals · Electrochemical sensor · Untreated mine water

Introduction

The concentration limit for Ni(II) content in environmental waters is ≈0.1 mg/L, and it should not exceed 0.02 mg/L in drinking water according to the EU Drinking Water Directive (WHO 2005). However, the European Acceptance Scheme suggested a 0.01 mg/L concentration limit for Ni(II) in drinking water (Mäkinen 2008). Precipitation and adsorption methods are generally used to remove Ni(II) from mine water. Potential adsorption agents tested include limestone (Miller et al. 2013), lignocellulose/montmorillonite nanocomposite (Zhang and Wang 2015), medlar male flowers coupled with $ZnMn_2O_4$ (Chergui et al. 2014), Amberlite (Karthika and Sekar 2013), and Acer saccharum leaves (Krishna and Gilbert 2014). However, selectivity was generally not addressed and most of these adsorbents probably have a strong affinity to other metals. A few materials, such as nanoparticles of clinoptilolite and Acer sacharum leaves, have been tested in combination with dimethylglyoxime (DMG) as a selective complexation agent for Ni(II) (Krishna and Gilbert 2014; Nezamzadeh-Ejhieh and Kabiri-Samani 2013).

Standard methods for Ni(II) detection in industrial, mining, and environmental waters also face problems. Atomic absorption spectrometry (AAS), flame photometry, inductively coupled plasma (ICP) methods, and anodic stripping voltammetry (ASV) show appropriate sensitivity and selectivity (Water Environment Federation 1999). However, sample handling often requires the use of additional chemicals and filtration, which can cause loss of

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analyte. Also, the analytical instruments needed are large and non-portable (except for ASV), and sample pretreatment and analyses are often time consuming.

ASV is a very sensitive electrochemical technique but is not suitable for determination of some metals, including Ni(II), and simple cathodic stripping voltammetry is not sensitive enough for Ni(II) determination for environmental applications. Despite many advantages and excellent results obtained by other electrochemical methods, such as differential pulse voltammetry (DPV) and square wave voltammetry (SWV), they are not yet included as standard analytical methods for metal determination. The advantage of these techniques include the possibility for miniaturization and construction of portable automated analyzers that can be used for real-time analyses in the field. These methods are also rapid and highly sensitive and their selectivity could be improved by simple modification of the working electrode.

We tested DMG incorporation into two polymeric materials: an anionic polymer and a sol–gel. Nafion is an anionic polyfluorinated polymer and is very convenient for immobilization of ligands on solid surfaces, for example on sensors, but is not suitable for preparation of bulky adsorption materials. Nafion is negatively charged and works as a cation conductor, which is convenient for the determination of metal cations and elimination of anionic interferences. Moreover, as DMG is soluble in ethanol, it can be homogenously mixed with an ethanolic solution of Nafion. Nafion films are known to be hydrophobic, but after contact with water, they become hydrophilic (Goswami et al. 2008). Ion transport appears in this hydrophilic phase at a film pore size of 1–2 nm (Barbati and Kirby 2014). The disadvantage is that metal cations then interact electrostatically with the negatively charged sulfonate groups of the Nafion, which can slow diffusion through the Nafion membrane (Xue et al. 1991).

On the other hand, sol–gels are more or less electroneutral, physically stable polymers. They form a rigid polymeric structure that can be used as a thin film for surface modification, immobilization of ligands on sensor surfaces, and for entrapment of ligands in solid-phase extraction. For example, DMG was immobilized in a sol–gel carbon composite electrode for determination of Ni(II) in river water (Wang et al. 1997) and have also been prepared for solid-phase extraction of Ni(II) from water samples (Seneviratne and Cox 2000). Acid and base catalysts are used during sol–gel preparation to control the porosity of the final material; dense films are formed by acid catalysis and porous films by base catalysis (Sinko 2010).

DMG has been tested as a surface modifier of screen-printed electrodes (SPE) for Ni(II) determination; however, none were tested in such a complex matrix as mine water nor show a complete adsorption study of Ni(II) in DMG (Bobrowski et al. 2014; Piankova et al. 2011; Wang et al. 1996). Even though the kinetics of nickel complexation by DMG has been studied in batch solution conditions (Celo et al. 2001; Xue et al. 2001), it is known that the kinetics of reactions (e.g. complexation and hybridization) with surface-attached ligands can significantly differ from those of free ligands in solution (Sekar et al. 2005). To fill this gap, we tested the kinetics of Ni(II) uptake by surface-attached DMG compared to the free ligand in solution. Preliminary results obtained with a DMG-modified carbon paste electrode (DMG/CPE) showed that DMG significantly eliminated interference effects on Ni(II) determination (Ferancova et al. 2015). In this work, we extended that study by investigating Ni(II) uptake by surface-attached DMG as well as by dissolved DMG.

The effectiveness of adsorbents developed for Ni(II) removal is usually tested at initial concentrations of 50 mg/L and higher. We have tried to fill this gap and show that the complexation of Ni(II) with DMG in sol–gel is a very effective way of removing low concentrations of Ni(II) from aqueous solutions.

Experimental Methods

Chemicals

A stock solution of 1.7 % DMG (Sigma-Aldrich) was prepared in pure ethanol (99 %). Nafion (Sigma) was used in the form of a 5 % ethanolic solution. Tetramethoxysilane (TMOS) for preparation of sol–gels was obtained from Fluka. HCl and Triton-100 used for the preparation of sol–gels were purchased from Merck. Electrochemical measurements were done in an ammonium buffer solution of pH 8.0 consisting of ammonium chloride (Sigma) and ammonia solution (Sigma). Standard solutions of Ni(II) and potential interfering metals (Fluka) were prepared at proper concentrations in an ammonium buffer solution. Natural water used for model samples was taken from a local lake (Pirttijärvi, Sotkamo, pH 6.5, conductivity 26 µS/cm). Real mine discharge water (pH 6.6, conductivity 4090 µS/cm) provided by an undisclosed Finnish mine was analyzed in the mine's internal laboratory using a standard ICP method. Results from this sample analysis are shown in supplemental Table S1.

Instrumentation

Manually operated measurements were performed using PalmSens potentiostat (PalmSens, Netherlands) connected to a PC. Electrodes used in measurements were commercial screen-printed carbon electrodes (DropSens, Spain) consisting of a 4 mm diameter carbon working electrode, a carbon counter electrode, and a silver reference electrode.

Preparation of a DMG-Modified SPE

For the entrapment of DMG in anionic polymer, 1.7 % DMG in Nafion was prepared. The surface of the working electrode was modified by drop-casting with 1 µL of DMG-Nafion solution 1 day prior to measurement and left to evaporate to dryness at room temperature, and were denoted as DMG-N/SPE.

Sol–gel was prepared in both acidic (Wang et al. 1997) and basic conditions (Seneviratne and Cox 2000). Briefly, for acidic sol–gel, TMOS was mixed with 1.7 % DMG in ethanol (ethanol without DMG for control experiments) and with 0.1 M HCl at a ratio of 1:2:0.3, respectively. For the preparation of the basic sol–gel, TMOS was mixed with 1.7 % DMG in ethanol (ethanol without DMG for control experiments) and 1 µM NH_4OH in a ratio of 1:1:1, and finally, 100 µL of Triton X-100 was added to avoid fracturing of the sol–gel. 1 µL of the sol–gel composite mixture was drop-casted onto the surface of the working electrode and kept for 24 h in the desiccator for hydrolysis and condensation reactions to occur. Fabricated acidic sol–gel electrodes were denoted as DMG-A-SG/SPE and basic sol–gel as DMG-B-SG/SPE. All modified electrodes were used as disposable sensors.

Preparation of Model and Real Water Samples

Model mine water samples for electrochemical study were prepared by diluting natural lake water that did not contain Ni(II), into an ammonium buffer at a ratio of 1:1 and spiking with a Ni(II) standard solution to a final concentration of 0.1 mg/L. Real water samples for electrochemical determination of Ni(II) were prepared by diluting the mine discharge water sample with an ammonium buffer at a ratio of 1:1 and used without further pretreatment. Real water samples for batch sorption experiment were prepared by spiking the mine discharge water with a Ni(II) standard to a final concentration of 1.0 mg/L.

Analytical Procedures

Each newly prepared DMG-N/SPE was incubated in an ammonium buffer for 6 min prior to use to hydrate the dried modifier layer and unify measurement conditions. The sensor was then transferred into the ammonium buffer containing the Ni(II), which was accumulated on the surface of a modified working electrode at open circuit conditions (i.e. no potential was applied) for 120 s under stirring. Electrochemical determination of Ni(II) was performed using DPV in the potential range of 0 to −1.5 V using a scan rate of 0.05 V/s.

Study of Sorption Kinetics

Unmodified sol–gel (SG) and DMG modified sol–gel (DMG–SG) sorption materials were prepared under basic conditions. TMOS was mixed with 1.7 % DMG in ethanol (ethanol without DMG for control experiment) and 1 µM NH_4OH in a 1:1:1 ratio, and finally, 100 µL of Triton X-100 was added. The solutions were allowed to react in the plastic test tubes for 24 h. Sol–gel monoliths that formed during the reaction were then crushed into a fine powder. Glass columns were filled with 25 mg of sol–gel powder and 5 mL of ammonium buffer containing 1 mg/L Ni(II) was applied. The signal of Ni(II) was measured using DMG-N/SPE described above. The amount of Ni(II) adsorbed was then calculated from Eq. (1):

$$q = (c_0 - c)\frac{V}{m} \tag{1}$$

where c_0 is the initial concentration of of Ni(II) in solution, c is the concentration of Ni(II) after adsorption, V is the volume of Ni(II) solution, and m is the amount of adsorbent.

For the sorption kinetics studies, 50 mg of DMG-SG powder was mixed with 10 mL of Ni(II) solution in ammonium buffer. The suspension was stirred for a given time interval and filtered through cotton wool, which did not adsorb free Ni(II) from solution.

Five kinetic models reviewed by Gupta and Bhattacharyya (2011) for sorption of metal ions were tested. First order kinetics mostly used for sorption from aqueous solution was calculated from a linearized Eq. (2):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

where q_e is the amount of accumulated Ni(II) at the equilibrium time (mg/g), q_t is the amount of accumulated Ni(II) at time t (mg/g), and k_1 is the first order rate constant (min^{-1}). This model is not suitable for characterizing the kinetic behavior of Ni(II) adsorption on solid phase adsorbents although it does describe well the ligand exchange kinetics for nickel speciation in liquid phase (Xue et al. 2001).

Pseudo-second order kinetics is often used for describing the adsorption capacity on solid phase absorbents, and the linearized dependence is expressed by Eq. (3):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where k_2 is the pseudo-second order rate constant ($\text{g mg}^{-1}\ \text{min}^{-1}$). This model was reported for adsorption of Ni(II) from solution on polyacrylamide (Mousavi et al.

2012), yeast (Padmavathy et al. 2003), hectorite clay (Ramamurthi et al. 2009), or clinoptilolite with DMG (Nezamzadeh-Ejhieh and Kabiri-Samani 2013).

Intra-particle diffusion kinetic models describe the transport process in solution to a sorbent. The linearized model is expressed by Eq. (4):

$$q_t = k_i t^{\frac{1}{2}} + C \tag{4}$$

where k_i is the intra-particle diffusion rate constant (mg g^{-1} $min^{-0.5}$) and C is related to boundary layer thickness. When C = 0, i.e. linear dependences have zero intercept, the sorption process is controlled by diffusion. This model has been previously used to study diffusion kinetics of Ni (Krishna and Gilbert 2014; Mousavi et al. 2012; Ramamurthi et al. 2009).

The Elovich kinetic model is mostly used for the characterization of chemisorption in heterogenous systems (Wu et al. 2009). Linear dependence is expressed by Eq. (5).

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{5}$$

where α and β are Elovich rate coefficients (g mg^{-1} min^{-2} and mg g^{-1} min^{-1}, respectively). The Elovich model was also tested for Ni(II) adsorption on kaolinite and montmorilonite (Gupta and Bhattacharyya 2008).

Liquid film diffusion model describes the diffusion of reactant in the liquid film surrounding the sorbent particles and was applied for the kinetic study of adsorption of Ni(II) and other metals on kaolinite (Gupta and Bhattacharyya 2008). Diffusion kinetic model is given by Eq. (6).

$$\ln(1 - F) = -k_{fd}t \tag{6}$$

where F is the fractional attainment of equilibrium, expressed by q_t/q_e, and k_{fd} is the film-diffusion rate coefficient (min^{-1}).

Results and Discussion

DMG Immobilized in Nafion—Application in a Ni(II) Sensor

Uptake of Ni(II) by Surface-Attached DMG-Nafion

The kinetics of accumulation of Ni(II) in DMG was studied using the dependence of the DPV signal on the accumulation time measured at DMG-N/SPE. The DPV signal corresponds to the reduction of Ni(II) accumulated on the electrode surface to metallic Ni(0). The area under the DPV peak divided by the scan rate corresponds to the electric charge needed for this reaction (Hianik et al. 2005), which is proportional to the amount of Ni(II) accumulated on the electrode surface. The accumulation kinetics were studied at different temperatures in the range of 5–30 °C to simulate real on-site application. This temperature range also follows from the fact that the temperature dependence of the voltammetric current below 5 °C was not linear and the kinetics was very slow; while at temperatures higher than 30 °C, the stability of DMG-Ni(II) complex was significantly decreased. Figure 1 shows the dependence of electric charge (Q) needed for the reduction of Ni(II) to Ni(0) on the electrode surface. It can be seen that decreasing temperatures significantly affect the time needed to reach equilibrium. At 30 °C, an accumulation time of 60 s was sufficient to saturate the electrode surface, while at 5 °C, the surface was saturated after 200 s. Voltammetric signals of Ni(II) were also decreased with decreasing temperature; however, this phenomena was expected as it is known that the voltammetric signal decreases between 1.5 and 2.2 % per °C (Thomas and Henze 2001).

The effect of temperature on the accumulation kinetics of Ni(II) in the surface-attached DMG was studied from the time dependence of accumulated Ni(II), q (calculated from the electric charge). First and pseudo-second order kinetic models as well as intra-particle, Elovich, and liquid film diffusion models were selected for these studies (Fig. 2). Calculated kinetic parameters are listed in Table 1.

The first-order kinetic model proved unsuitable for characterization of our system. The q_e obtained deviated significantly from the experimentally observed data (Fig. 3a) and the linearity was very poor (Fig. 3b). This behavior was expected as the ligand is surface-attached. On the other hand, the pseudo-second order kinetic model described the Ni(II) binding by surface-attached DMG very well. Values of q_e obtained from the kinetic model deviated from experimental data only slightly over the entire range of temperatures, and the linearity of dependence $t/q_e = f(t)$ was very stable and more than 0.98, confirming that

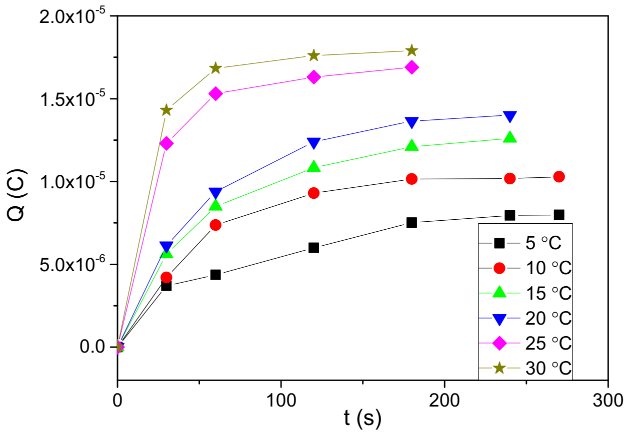
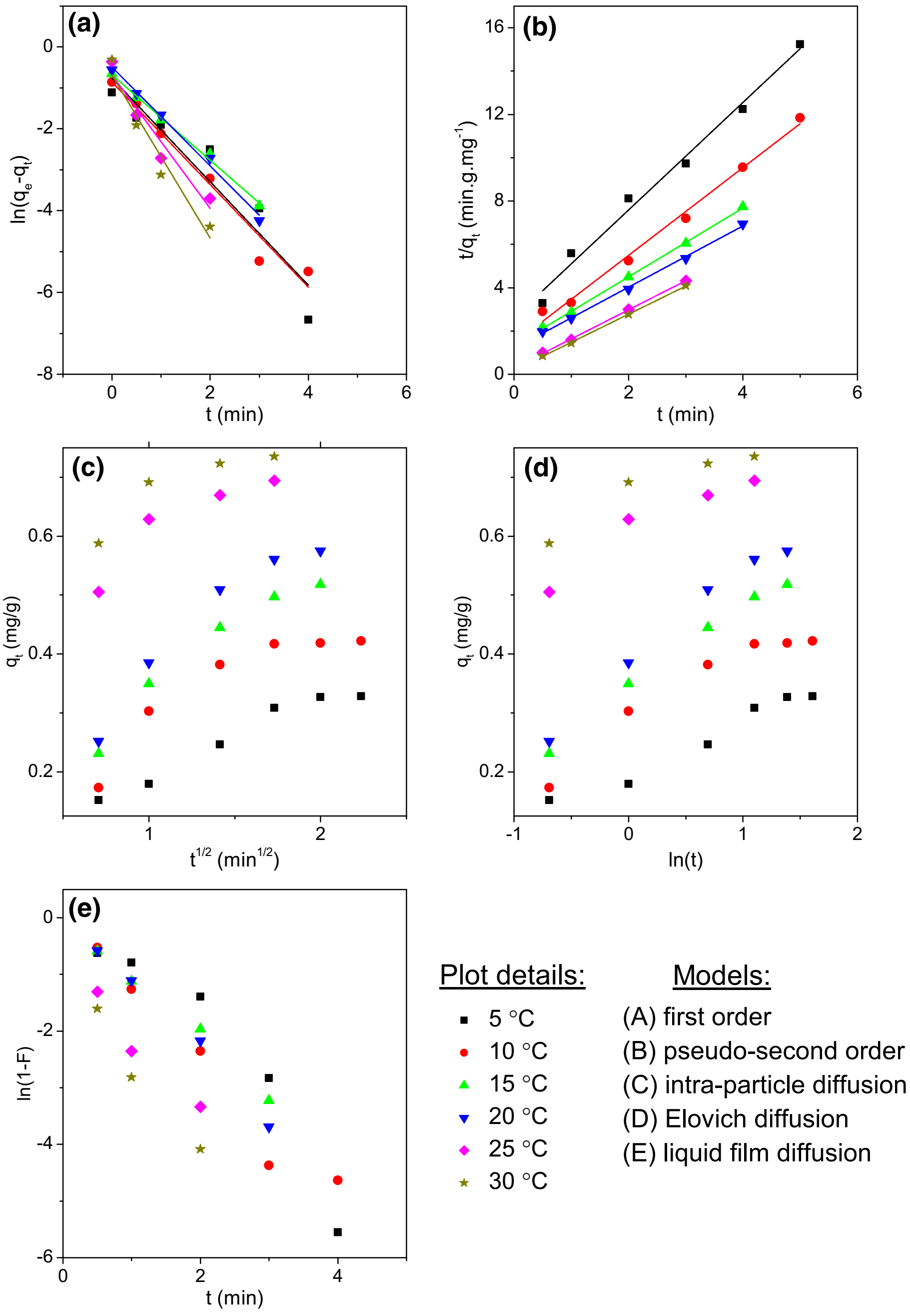


Fig. 1 Dependence of reduction charge (Q) of Ni(II) complexed by surface-attached DMG in Nafion on accumulation time

Fig. 2 Kinetic plots for Ni(II) complexation by DMG-N obtained from different kinetic models



chemisorption was the rate-controlling step over the range of temperatures tested (Fig. 3b). Values of the pseudo-second order rate constant were similar in the temperature range of 5–20 °C. After 20 °C, the kinetics of Ni(II) binding by DMG sharply increased.

Kinetics of nickel diffusion within the Nafion film was affected by electrostatic interactions as well as by the presence of DMG, which coordinately binds Ni(II). This complex mechanism of Ni(II) uptake by DMG-N was confirmed by the dependences of the intra-particle diffusion model (Fig. 2c), which did not show sufficient linearity and did not have a zero intercept over the entire range of studied temperatures. However, if we consider the complex transport of Ni(II) involving more control steps, such as diffusion of Ni(II) into the film and then diffusion within the pores of the film, dependences can be divided into two regions where the first part has good linearity (r^2 between 0.955 and 0.995) and a zero intercept, thus showing diffusion control of the Ni(II) uptake up to 120 s of contact time. Longer contact time led to more complex behavior, including mass transport and pore diffusion. The Elovich diffusion model did not show sufficient linearity.

Table 1 Kinetic parameters for Ni(II) accumulation in DMG-N/SPE at different temperatures

	Parameter	Temperature/ °C					
		5	10	15	20	25	30
Experimental data	q_e (mg/g)	0.37	0.48	0.52	0.58	0.74	0.74
Kinetic model data							
First order	k_1 (s^{-1})	0.049	0.048	0.040	0.046	0.063	0.076
	q_e (mg/g)	0.464	0.423	0.506	0.610	0.502	0.499
	r^2	0.882	0.964	0.993	0.991	0.913	0.923
Pseudo-second order	k_2 (g mg^{-1} s^{-1})	36.67	44.28	31.97	28.07	104.1	158.7
	q_e (mg/g)	0.411	0.502	0.629	0.707	0.744	0.771
	r^2	0.984	0.991	0.999	0.997	0.999	0.999
Intra-particle diffusions	k_i (mg g^{-1} $s^{-0.5}$)	0.018	0.021	0.028	0.032	0.022	0.017
	C (mg/g)	0.054	0.109	0.107	0.114	0.417	0.522
	r^2	0.971	0.812	0.925	0.903	0.742	0.712
Intra-particle diffusion (linear part)	k_i (mg g^{-1} $s^{-0.5}$)	0.023	0.036	0.042	0.047	0.085	0.095
	r^2	0.996	0.993	0.997	0.998	0.994	0.988
Elovich diffusion	β (mg g^{-1} s^{-1})	0.088	0.111	0.139	0.130	0.102	0.080
	r^2	0.958	0.920	0.987	0.976	0.882	0.837
Liquid phase diffusion	k_{ef} (s^{-1})	0.019	0.021	0.018	0.019	0.040	0.048
	r^2	0.935	0.986	0.997	0.996	0.997	0.996

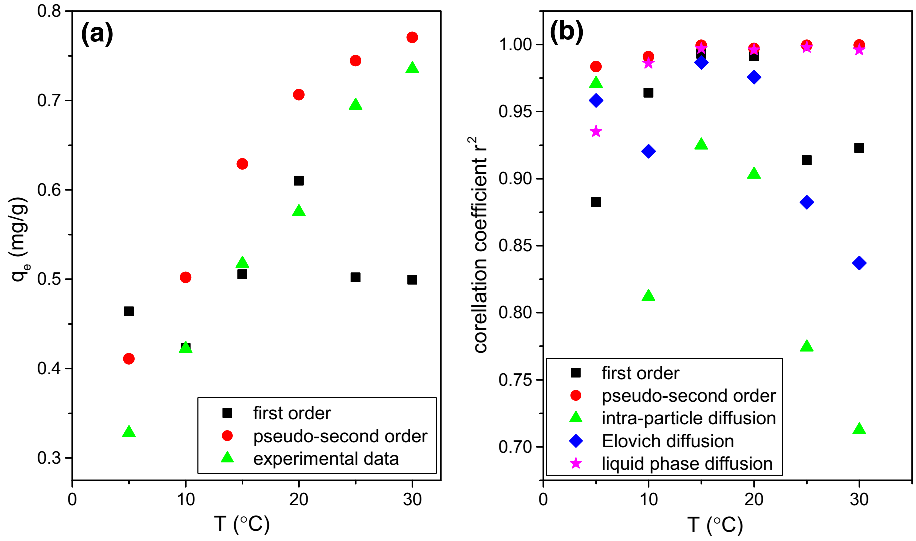


Fig. 3 **a** q_e obtained from first-order and pseudo-second order kinetic model compared to experimental data; **b** Linearity of different kinetic models

This could be due to the short time needed to reach equilibrium as the Elovich equation was reported to be applicable only for the initial adsorption rate when the system is far from equilibrium (Gupta and Bhattacharyya 2008). Finally, the liquid film diffusion model also describes the kinetics of accumulation of Ni(II) to the surface-attached DMG very well. Obtained time dependences are linear over the entire range and have almost zero intercepts at all studied temperatures (Fig. 2e). This result also confirms the complex transport of Ni(II) and that diffusion significantly affects sorption kinetics in surface-attached DMG in Nafion.

Effect of Interferences and Analysis of Model and Actual Water Samples

The effect of two main competing cations, Zn(II) and Cu(II), on the time dependence of Ni(II) uptake in the surface-attached DMG was investigated. Both interfering cations were used at a concentration of 0.1 mg/L, i.e. the same as the Ni(II) concentration. The results show that these cations did not affect the kinetics of the Ni(II) uptake (Fig. 4). This is important for application of DMG-N/SPE for determination of Ni(II) in mine and other industrial waters. It must also be pointed here that many metals, such

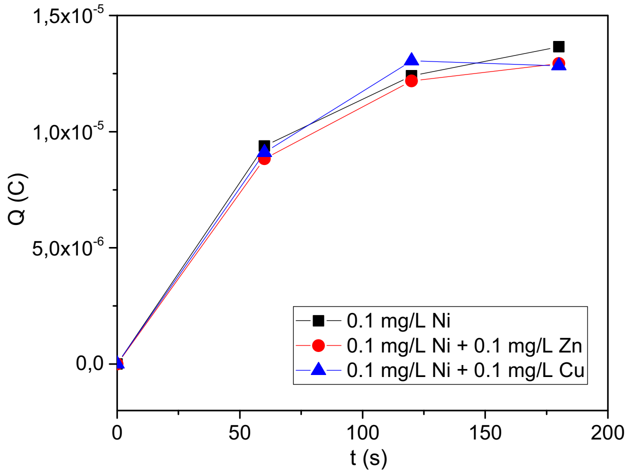


Fig. 4 Effect of Zn(II) (*circles*) and Cu(II) (*triangles*) on uptake of Ni(II) (*squares*) by surface-attached DMG in Nafion

as Cu(II), precipitate at higher concentrations under the experimental conditions, which would help to decrease the amount of potential interferences.

To test the performance of DMG-N/SPE in a real water matrix, we first prepared a model water sample using natural lake water spiked with 0.1 mg/L Ni(II). Measurements were made at laboratory conditions using the standard addition method (Fig. 5a) with RSD of 5.6 % (calculated from four measurements). This result demonstrated that the natural water matrix does not affect the selectivity and sensitivity of the DMG-N/SPE.

Water samples were obtained from an undisclosed Finnish mine. Standard analysis by ICP-OES performed in the mine's internal laboratory showed the concentration of Ni(II) to be 0.18 mg/L. The pH, conductivity, and concentrations of other cations are listed in Table S1. Here, we want to highlight that the mine water was used without any pretreatment, just diluted with an ammonium buffer solution to provide the required pH. Results from the standard addition method (Fig. 5b) showed the concentration of Ni(II) in the undiluted sample to be 0.165 mg/L, which corresponds to a low error of 8.3 %. This water sample also contained many potential interfering ions in higher concentrations than the concentration of Ni(II): Al (threefold), Ca (300-fold), Fe (17-fold), Mg (450-fold), Mn (17-fold), Na (2500-fold), and Zn (twofold). The low level of error demonstrates that these ions did not significantly affect the uptake of Ni by surface-attached DMG and that the DMG-N/SPE sensor is suitable for direct determination of Ni(II) in mine waters without pretreatment. The complexation reaction between Ni(II) and DMG gave the required selectivity.

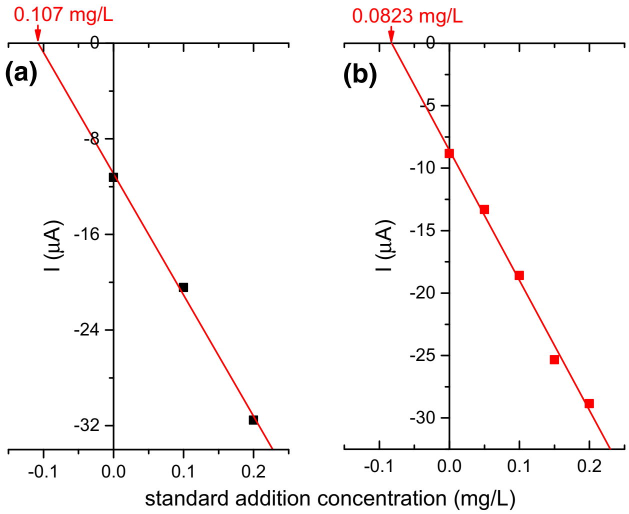


Fig. 5 **a** Analysis of model water sample; **b** Analysis of real water sample. Conditions: ammonium buffer pH 8.0, DMG-N/SPE, accumulation 120 s at O.C. conditions, DPV, 0.05 V/s. Real sample diluted with buffer at a ratio of 1:1. Evaluation using standard addition method

DMG Immobilized in Sol–Gel—Study of Ni(II) Removal

Uptake of Ni(II) by Surface Attached DMG–Sol–Gel

DMG modified sol–gels prepared by acidic or alkaline condensation did not provide sufficient sensitivity and the signal of Ni(II) was very small. However, we obtained higher signals for acidic sol–gel, and the experiment confirmed the significant role of film porosity (Elkady et al. 2014) on uptake of Ni(II) in the surface-attached DMG. Accumulation of DMG/SG towards Ni was also proved. Therefore, we continued performing the batch sorption kinetic studies of Ni(II) in DMG–SG.

Batch Uptake Studies

Sol-gels form rigid structures that can, in some cases, change the ability of ligands to bind to a target molecule. The ability of DMG in sol–gel to complex with Ni(II) was first tested by simple solid phase extraction in a glass tube. A calibration curve obtained for Ni(II) standards in the concentration range of 0.06–0.5 mg/L on DMG-N/SPE (slope = −88.5 µA L/mg; intercept = −4.11 µA; r^2 = 0.996) was used to determine Ni(II) concentrations before and after the adsorption experiment.

During extraction, the color of the DMG/sol–gel changed from white to red, confirming the formation of the DMG-Ni(II) complex in the ratio of 2:1. The results showed that 96 % of the Ni(II) was extracted from the solution. Sol–gel alone had less, but still significant, affinity towards Ni(II); 23 % of the Ni(II) was extracted by unmodified sol–gel. This result confirmed that DMG in a sol–gel structure preserves its ability to bind with Ni(II).

In the next experiment, we tested the effects of initial Ni(II) concentration and contact time on Ni(II) uptake. The same kinetic and diffusion models as were used for DMG-N were also applied in this part of the study. Figure 6 shows that the initial concentration of Ni(II) had a significant effect on the time needed to reach equilibrium and also on the removal percentage. When the initial concentration of Ni(II) was 0.1 mg/L, equilibrium was reached within 30 s, while in the case of 1.0 mg/L Ni(II) solution, 240 s of contact was needed. On the other hand, the removal percentage was only 48 % for 0.1 mg/L Ni(II), while 98 % was reached for 1.0 mg/L solution. At an initial Ni(II) concentration of 100 mg/L, the removal percentage was slightly decreased to 95 % (measured after 30 min of contact). These results show that DMG/sol–gel is a promising adsorptive material applicable for lower and higher concentrations of Ni(II), with removal percentages comparable or better than other sorbents (see supplemental Table S2. Moreover, the required contact time and adsorbent dose are much less.

The best fit for both Ni(II) concentrations was obtained using a pseudo-second order kinetic model. The theoretical value of q_e was also obtained with this model, and agreed very well with the experimental value for both initial Ni(II) concentrations. Parameters obtained from data fitting using this kinetic model are listed in Table 2.

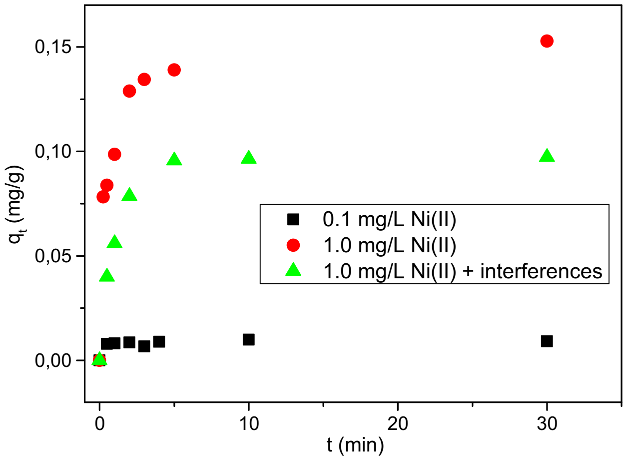


Fig. 6 Dependence of Ni(II) uptake in DMG-SG on contact time when initial concentration was 0.1 mg/L (*squares*) and 1.0 mg/L (*circles*) and the effect of interfering metals [1 mg/L Cu(II) + 1 mg/L Zn(II)] on adsorption of 1 mg/L of Ni(II) (*triangles*)

Effect of Interferences and Extraction of Ni(II) from Model Sample

To investigate the effects of common interfering metals, mixtures of Ni(II), Zn(II), and Cu(II) was extracted using DMG/sol–gel. 87 % of the Ni(II) was extracted from the metal mixture, confirming the very high affinity of DMG towards Ni(II). However, interfering metals can occupy binding sites in the sol–gel, thus decreasing the efficiency of Ni(II) extraction. As previously mentioned, Cu(II) forms a hydroxide precipitate at pH 8, which at high Cu(II) concentrations becomes remarkable. This precipitate, however, did not affect the extraction efficiency towards Ni(II). The effect of precipitates of other metals was not studied as the stability constant of their complexes with DMG is very low; instead, they form hydroxide precipitates that can be removed by filtration before Ni(II) extraction. As expected, the pseudo-second order rate constant was reduced in the presence of interfering metals (Table 3). Surprisingly, very good linearity and q_e were also obtained for the first order kinetic model.

As the available mine water did not contain sufficiently high Ni(II) concentrations, the sample was spiked with a Ni(II) standard to provide a final concentration of 1.0 mg/L. The concentrations of potential interferences with respect to the Ni(II) concentration were: Ca (488-fold), Fe (threefold), Mg (81-fold), Mn (threefold), and Na (457-

Table 3 Kinetic parameters for Ni(II) uptake by DMG–sol–gel in presence of interfering metals

Experimental model	q_e (mg/g)	0.096
Pseudo-first order	k_1 (s^{-1})	1.950
	q_e (mg/g)	0.091
	r^2	0.993
Pseudo-second order	k_2 (g mg^{-1} s^{-1})	9.131
	q_e (mg/g)	0.114
	r^2	0.999
Intra-particle diffusion	k_i (mg g^{-1} $s^{-0.5}$)	0.036
	C (mg/g)	0.019
	r^2	0.908
Elovich diffusion	β (mg g^{-1} s^{-1})	40.39
	r^2	0.983
Liquid phase diffusion	k_{ef} (s^{-1})	0.014
	r^2	0.993

Table 2 Kinetic parameters for Ni(II) uptake by DMG–sol–gel at different initial concentrations

Initial Ni(II) conc., mg/L	Experimental q_e, mg/g	Parameters from pseudo-second order kinetic model		
		q_e, mg/g	k_2, g/mg min	r^2
0.1	0.0091	0.0092	575.4	0.997
1.0	0.150	0.155	14.6	0.999

fold). A contact time of 600 s was used and Ni(II) concentration before and after extraction was measured using DMG-N/SPE. The results show a removal percentage of 86 %, which agrees well with our result from the interference study and confirms the excellent selectivity of DMG–SG towards Ni(II).

Conclusions

We studied the uptake of Ni(II) by DMG surface-attached to Nafion and entrapped in sol–gel and dispersed in solution. Nafion was used to immobilize DMG on the surface of SPEs. The accumulation of Ni(II) in surface-attached DMG followed a pseudo-second order kinetic model at temperatures of 5–30 °C. Ni(II) mobility was also controlled by intra-particle diffusion for a short time. However, film diffusion in pores predominates after that; thus, the film diffusion model fits the kinetic dependences well.

Kinetic studies allowed us to develop a rapid, sensitive, and selective sensor and voltammetric method for direct determination of Ni(II) in untreated mine water with low interference effects. DMG-N/SPE showed excellent analytical performance and proved successful for Ni(II) determination in natural lake and actual mine water. Ni(II) concentrations were determined using the standard addition method with a low error rate of 8.3 %.

The sol–gel matrix was used to prepare an adsorptive material for removing Ni(II) from solution. Batch uptake studies showed that initial Ni(II) concentrations significantly affected the contact time needed to reach equilibrium as well as the Ni removal percentage. The optimum initial concentration of Ni(II) was 1.0 mg/L, at which the removal percentage reached 98 % within 5 min. An increase of the initial concentration to 100 mg/L slightly decreased the removal percentage to 95 % after 30 min. Therefore, we can conclude that DMG/SG is a promising adsorbent for low as well as higher concentrations of Ni(II). Ni(II) adsorption in DMG/SG follows a pseudo-second order kinetic model.

The presence of interfering metals, Cu(II) and Zn(II), decreased the pseudo-second order rate constant and affected the kinetic behavior of Ni(II). However, the extraction efficiency of DMG-SG in their presence decreased only slightly—a removal percentage of 86 % was obtained for Ni(II) extraction from discharged mine water.

The removal of Ni(II) and its on-site determination is very challenging. We showed that DMG-N/SPE possess the required sensitivity and selectivity. Sensor preparation should be simple and inexpensive, since in general, screen-printed sensors can be mass produced for a few cents, and their modification for this application requires low cost chemicals (≈ 1 euro/g of DMG). Similarly, DMG in sol–gel preserves its high ability to selectively extract Ni(II) from water. Thus, this work demonstrates an effective potential solution for both low-cost selective removal of Ni(II) and a rapid and cheap sensor for on-site Ni(II) monitoring in mine and environmental waters.

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