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# Preparation and characterisation of a poly(acrylamidoglycolic acid-*co*-acrylamide) hydrogel for selective binding of Cu<sup>2+</sup> and application to diffusive gradients in thin films measurements

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## Abstract

A poly(acrylamidoglycolic acid-*co*-acrylamide) [poly(AAGA-*co*-AAM)] hydrogel was prepared by copolymerising 2-acrylamidoglycolic acid (AAGA) with acrylamide (AAM). The copolymer hydrogel composition and structure was characterised by FTIR spectroscopy and elemental microanalysis and found to contain 3.5 AAGA monomer units for each AAM monomer unit. This was similar to the monomer ratios used in the synthesis. The metal ion binding properties of the hydrogel were characterised for a range of metal ions (Cu<sup>2+</sup>, Cd<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) under varying conditions of pH, ionic strength, metal concentration and time. The hydrogel was shown to bind Cu<sup>2+</sup> and Cd<sup>2+</sup> strongly under non-competitive binding conditions, with binding capacities of 5.3 and 5.1 μmol cm<sup>-2</sup>, respectively. The binding capacity of each metal decreased, under competitive binding conditions (with a range of metal ions present at 17.8 μN), to 1.3 and 0.17 μmol cm<sup>-2</sup>, respectively, indicating stronger selectivity for Cu<sup>2+</sup>. The metal ions were readily recovered (>94%) by eluting with 2 M nitric acid solution for 24 h. The binding capacities for Cu<sup>2+</sup> and Cd<sup>2+</sup> were also found to decrease with increasing ionic strength and at pH values < 5. The copolymer was found to have an equilibrium swelling ratio (*q<sub>w</sub>*) of over 500 at a maxima of pH 5.4 and at low ionic strengths. Finally, the copolymer hydrogel was tested as a binding phase with the diffusive gradients in thin films technique. A linear mass vs. time relationship was observed for Cu<sup>2+</sup> in synthetic Windermere water with a recovery of approximately 100%. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Poly(acrylamidoglycolic acid-*co*-acrylamide); Copper binding; Diffusive gradients in thin films

## 1. Introduction

Hydrogels are three-dimensional polymer networks that are highly hydrophilic yet are insoluble in water [1]. When fully hydrated they can contain over 95% water and therefore are, in effect, parcels of water that can be easily handled. Other properties of hydrogels of interest are their capacity to allow controlled diffusion [2,3], their swelling response to changes in ionic strength, pH, and temperature [4,5], and their ability to interact with chemical species (e.g. Cu<sup>2+</sup> and Co<sup>2+</sup>) [6,7] through the polar functional groups responsible for their hydrophilic nature. Hydrogels have been used as membranes in water purification and separation [8], catheters [9], contact lenses [10], controlled release devices [11] and as components in devices for environmental analysis [12]. Of particular interest in the

latter application is the use of hydrogels with the diffusive gradients in thin films (DGT) technique [12,13].

In the DGT technique, a polyacrylamide hydrogel is used as a medium to allow only diffusional mass transport of an analyte. A polyacrylamide hydrogel is also used to encapsulate a binding agent that is selective for the analytes of interest, e.g. Chelex-100 for trace metal ions [13,14]. These two hydrogel layers are laid on top of one another within a DGT device and deployed in a solution. A diffusive gradient of the analyte species is maintained within the diffusion hydrogel layer, between the interface with the external solutions and the interface with the binding layer. The concentration at the latter is ideally zero, as the analyte species accumulates within the binding layer. This constant diffusive gradient allows the mass transport and accumulation to be quantified by Fick's law of diffusion [12]. The analyte is bound strongly to the binding layer until eluted in a form suitable for analysis.

An alternative to the use of a gel layer encapsulating a binding agent is for the gel itself to have functional groups

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that interact selectively and strongly with the analytes of interest. Here, we report the synthesis and characterisation of a new homogenous copolymer hydrogel containing glycolic acid functional groups, poly(acrylamidoglycolic acid-*co*-acrylamide) [poly(AAGA-*co*-AAM)]. A copolymer was made from the acrylamidoglycolic acid monomer with acrylamide because it had been shown to bind transition metals in aqueous solution [15]. The binding properties of this poly(AAGA-*co*-AAM) hydrogel for a range of metal ions were investigated under various conditions. The swelling response of the hydrogel to variation in pH and ionic strength was also investigated. Finally the suitability of this new copolymer hydrogel for use as a binding phase for DGT was assessed.

## 2. Experimental

### 2.1. Preparation of poly(acrylamidoglycolic acid-*co*-acrylamide) hydrogel

Poly(acrylamidoglycolic acid-*co*-acrylamide) [poly(AAGA-*co*-AAM)] hydrogel was prepared from a monomer solution containing 2.23 g of acrylamidoglycolic acid monohydrate (AAGA) (Aldrich) added to 10 ml of deionised water (Milli-Q) followed by adding 1.5 ml of 30% NaOH with constant stirring to bring the pH close to 7. The solution was then titrated with 1 M NaOH to pH 7.0. The volume of the solution was made up to 15.0 ml with deionised water (Milli-Q) and thoroughly mixed. The poly(AAGA-*co*-AAM) hydrogel was prepared by adding 780  $\mu$ l of 40% acrylamide (AAM), 800  $\mu$ l of 2% agarose-derived cross-linker (DGT Research Ltd, Lancaster, UK) [12], 70  $\mu$ l of freshly made 10% (w/w) ammonium persulphate (Bio-Rad) solution and 30  $\mu$ l of 99% *N,N,N',N'*-tetramethylethylenediamine (TEMED) (Bio-Rad) to the AAGA solution. This gave a molar ratio of 3:1 for AAGA and AAM, which was the optimum ratio for handling purposes and for the metal binding capacity. The well-mixed solution was immediately pipetted carefully into a suitable mould comprising two slightly offset, clean glass plates separated by an inert plastic spacer of known thickness (0.04 cm) held firmly together with clips. The mould was then incubated at  $60 \pm 2$  °C for 3 h, after trials to optimise the conditions. The set gel sheets were then hydrated in ultrapure water (Milli-Q) for 24 h, replenishing the water several times. They were then soaked in 10% HNO<sub>3</sub> for another 24 h (to remove any metal contamination within the gel) prior to being washed again with water. The gel sheets were cut into disks of 4.9 cm<sup>2</sup> and stored in 0.1 M NaNO<sub>3</sub> which made them easier to handle for subsequent experiments. This storage solution contained several grams of Chelex-20 resin to reduce trace metal impurities.

### 2.2. Characterisation of the poly(AAGA-*co*-AAM) hydrogel

FTIR spectra of the poly(AAGA-*co*-AAM) hydrogel were obtained using a Perkin Elmer Series 1000 FTIR spectrophotometer. The gel sample was dried in air and ground with KBr<sub>(s)</sub> (Merck). Spectra were collected by accumulating five scans at a resolution of five wave numbers.

The elemental composition of the poly(AAGA-*co*-AAM) gel was determined by elemental microanalysis on a Carlo Erba 1106 Elemental Analyser. The samples were prepared by drying them in air before analysis. The theoretical and experimental monomer ratios are best calculated from the N percentages.

### 2.3. Swelling properties of the poly(AAGA-*co*-AAM) hydrogel

The hydrogel disks were soaked in solutions of differing pH at room temperature (23 °C) for 24 h. The pH value of each solution was obtained by adding either hydrochloric acid or sodium hydroxide. After the hydrogel disks had equilibrated in each solution the degree of swelling was measured by accurately weighing each disk. For the measurement of equilibrium swelling ratio,  $q_w$ , the disks were weighed both in their hydrated and dried states. The dried gel disks were obtained by drying them in air to a constant weight. The equilibrium swelling ratio [16] was calculated from

$$q_w = m_s/m_d \quad (1)$$

where  $m_s$  and  $m_d$  are the weights of the hydrogel disks in the swollen/hydrated state and dried state, respectively. The experiments on the swelling properties of the hydrogel were also carried out as a function of electrolyte concentration as NaNO<sub>3</sub> ranging from 10  $\mu$ M to 0.10 M.

### 2.4. Metal binding properties of the poly(AAGA-*co*-AAM) hydrogel

The binding properties of poly(AAGA-*co*-AAM) hydrogel for metal ions Cu<sup>2+</sup>, Cd<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, were tested under non-competitive conditions by immersing a gel disk in a solution containing a metal ion concentration of 1.0 mM at pH 6–7 for several time periods up to 24 h. This enabled measurement of the binding capacity and also the rate of binding for each metal, provided that saturation occurred within 24 h. The amount of metal ion bound in the gel was eluted by soaking the gel in 5.0 ml of 2 M HNO<sub>3</sub> for 24 h before being diluted to an appropriate concentration with water (Milli-Q) and measured with a flame atomic absorption spectrometer (FAAS). The metal concentrations of the tested solutions were also measured by FAAS before and after the gel immersion.

To study the competitive binding of the gel, a disk was immersed in a stirred solution containing Cu<sup>2+</sup>, Cd<sup>2+</sup>, K<sup>+</sup>,

$\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , each at  $17.8 \mu\text{M}$  concentration. Elution was performed as described earlier. The effects of various conditions on the gel binding for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  were studied by changing the time of exposure (1–24 h), pH (from 0.2 to 12) and  $\text{NaNO}_3$  concentration ( $10 \mu\text{M}$ –1 M).

### 2.5. DGT performance

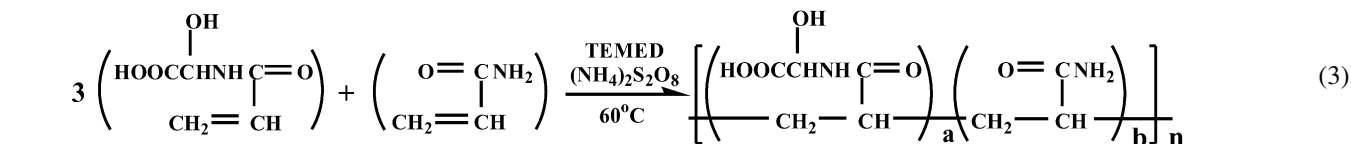
A validation test for a new DGT binding phase was undertaken according to procedures described previously [13,14]. The poly(AAGA-co-AAm) hydrogel binding layer, the PAAm hydrogel diffusive layer (preparation described below) and a wet  $100 \mu\text{m}$  Millipore cellulose nitrate filter as a protective layer were placed, in that order, into a DGT assembly [13]. Eight DGT assemblies were exposed to a well-stirred solution of  $0.79 \mu\text{M}$  of  $\text{Cu}^{2+}$  over various periods of time, up to 145 h, in synthetic lake water (Windermere, Lake District, UK) of composition:  $[\text{Mg}^{2+}] = 40.5 \mu\text{M}$ ;  $[\text{Ca}^{2+}] = 157 \mu\text{M}$ ;  $[\text{Na}^+] = 202 \mu\text{M}$ ;  $[\text{K}^+] = 17 \mu\text{M}$ ;  $[\text{Cl}^-] = 242 \mu\text{M}$ ;  $[\text{NO}_3^-] = 25 \mu\text{M}$ ;  $[\text{SO}_4^{2-}] = 85.5 \mu\text{M}$  and pH 7.2 [17]. Sufficient volume of solution was provided to ensure that the depletion of  $\text{Cu}^{2+}$  by the DGT assemblies was negligible. The mass of  $\text{Cu}^{2+}$  accumulated in the poly(AAGA-co-AAm) gel was measured by FAAS. Elution was carried out as described above.

The mass of ions,  $M$ , that accumulate in the binding gel from a solution with analyte concentration ( $C$ ), after passing through a diffusive gel layer of area ( $A$ ) and thickness ( $\Delta g$ ), over a deployment time ( $t$ ), can be predicted by the DGT equation [2,13]:

$$M = DCAt/\Delta g \quad (2)$$

Here, an experimentally determined value of the diffusion coefficient,  $D$ , was measured according to a procedure described previously [14].

The performance of the DGT measurement is assessed in two ways. Firstly, from Eq. (2), a linear relationship is expected between measured  $M$  and deployment time,  $t$ , up to the capacity of the binding gel if the DGT device is acting according to theory. Secondly, a line of best fit for  $M$  vs.  $t$  is



compared with a theoretical line derived from the actual solution concentration,  $C$  and Eq. (2). Comparison of the gradients of these lines provides an estimation of the recovery of the measurement. Recoveries  $>90\%$  are desirable with DGT.

### 2.6. Preparation of polyacrylamide hydrogel

Polyacrylamide (PAAm) hydrogel was prepared accord-

ing to a previously described procedure [18,19]. A stock solution comprising 18.75 ml of 40% acrylamide monomer (Bio-Rad), 7.50 ml of 2% agarose-derived cross-linker (DGT Research, UK), and 23.75 ml of deionised water (Milli-Q) was mixed thoroughly. PAAm gels were prepared by adding 70  $\mu\text{l}$  of freshly made 10% (w/w) ammonium persulphate (Bio-Rad) solution and 25  $\mu\text{l}$  of 99% TEMED (Bio-Rad) to 10.0 ml of the stock solution. The well-mixed solution was immediately pipetted carefully into a mould, as described in Section 2.1, but using a 0.025 cm spacer. The mould was then incubated at  $40 \pm 2^\circ\text{C}$  for 1 h. The set gels were then hydrated in ultrapure water (Milli-Q) for at least 24 h, replenishing the water several times. The gel sheets were stored in 0.01 M  $\text{NaNO}_3$  solution containing a few grams of Chelex-20 resin before use.

### 2.7. Analysis by FAAS

The concentrations of metal ions were determined by FAAS according to the standard guidelines of the manufacturers (SpectrAA-200, Varian), choosing resonance lines of sensitivity for metals of interest with deuterium background correction [20]. Instrument detection limits were  $6.29 \times 10^{-4} \mu\text{mol ml}^{-1}$  for Cu and  $1.78 \times 10^{-4} \mu\text{mol ml}^{-1}$  for Cd with an air and acetylene flame. The metals in the elution solution (5 ml) from blank poly-(AAGA-co-AAm) gels were below the instrument detection limits, meaning that there were  $<6.42 \times 10^{-4} \mu\text{mol cm}^{-2}$  Cu and  $<1.81 \times 10^{-4} \mu\text{mol cm}^{-2}$  Cd in the hydrogels.

## 3. Results and discussion

### 3.1. Structure and composition of the poly(AAGA-co-AAm) hydrogel

The poly(AAGA-co-AAm) hydrogel was prepared by copolymerising AAGA with AAm at a 3:1 molar ratio in the presence of the initiators ammonium persulphate and TEMED according to the following reaction:

FTIR and elemental analysis were undertaken to determine the composition and structure (i.e.  $a$  and  $b$ ) of the copolymer gel. The FTIR spectrum of poly(AAGA-co-AAm) with characteristic peaks is shown in Fig. 1. Peaks appear at  $1651.67 \text{ cm}^{-1}$  (C=O in carboxylic groups and amide groups),  $3443.37 \text{ cm}^{-1}$  (NH and OH in carboxylic groups and amide groups), and  $1096.28 \text{ cm}^{-1}$  (the secondary alcohol groups) [21]. These data confirmed that the poly(AAGA-co-AAm) copolymer hydrogel was

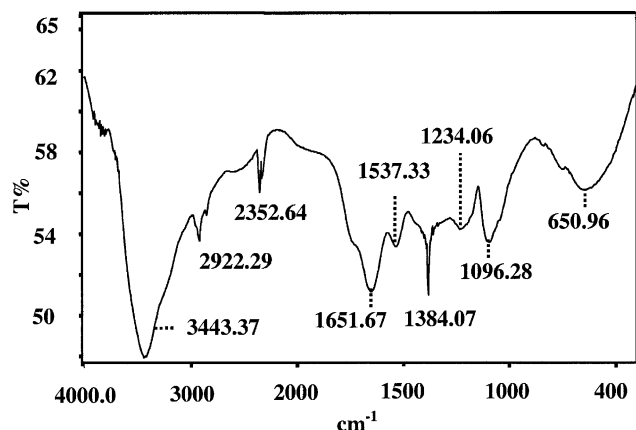
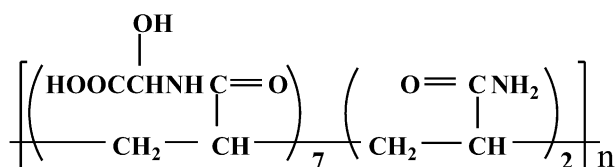


Fig. 1. FTIR spectrum of poly(AAGA-co-AAm) hydrogel with the main diagnostic peaks highlighted.

formed with functional groups from both acrylamide and AAGA.

Elemental analysis of poly(AAGA-co-AAm) gel was performed to determine the values of  $a$  and  $b$ . The elemental analysis indicated a C/N/H ratio of 4:1:0.5 (Table 1). The molar ratio of AAGA and AAm in the poly(AAGA-co-AAm) gel, as calculated from the nitrogen stoichiometry based on the data shown in Table 1, was 3.53:1 or approximately 7:2. This indicated that the copolymerisation reaction was not exactly complete, as some AAm monomers did not form part of the polymer and would have been removed during rinsing. The poly(AAGA-co-AAm) gel structure can therefore be written as follows.



### 3.2. Swelling properties of the poly(AAGA-co-AAm) gel

Since the poly(AAGA-co-AAm) gel had carboxylic acid groups on the network chain, the degree of swelling was expected to vary with pH. Fig. 2 shows the observed variation of the gel swelling ratio,  $q_w$ , with pH at 23 °C.  $q_w$  was strongly dependent on pH, which was due to dissociation of the carboxylic group on the gel network. The highest degree of swelling was reached at around pH

Table 1  
Microelemental analysis results of poly(AAGA-co-AAm)

	C%	H%	N%
Experimental values	36.96 ± 0.57	5.96 ± 0.09	10.88 ± 0.16
Theoretical values <sup>a</sup>	40.91	4.92	11.06

<sup>a</sup> Based on the monomer ratio of AAGA to AAm of 3:1.

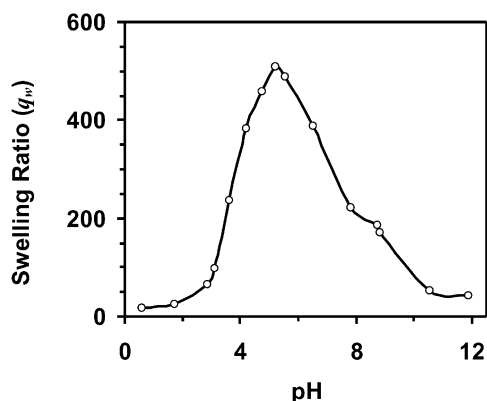


Fig. 2. Effect of pH on the equilibrium swelling ratio,  $q_w$ , of the poly(AAGA-co-AAm) hydrogel; temperature 23 °C.

5.4. A similar swelling phenomenon has been observed in other hydrogel research work [22].

As shown in Fig. 3, the poly(AAGA-co-AAm) gel was observed to swell less as the  $\text{NaNO}_3$  concentration increased. The increase of  $\text{NaNO}_3$  concentration tends to screen the attraction between the polar water molecule and the polyelectrolyte gel, thereby, decreasing the water content of the hydrogel [23].

This dependence of the swelling of the hydrogel on pH and ionic strength has implications for its use as a binding layer for DGT. The gel will need to be stored in a solution of similar pH and ionic strength to that in which the DGT assembly is to be deployed to ensure that swelling does not interfere with the measurement.

### 3.3. Metal binding properties of the poly(AAGA-co-AAm) hydrogel

#### 3.3.1. Non-competitive binding capacities

The binding properties of the poly(AAGA-co-AAm) hydrogel for metal ions were investigated initially in a non-competitive manner. The non-competitive binding capacity for each metal ion was calculated from the maximum metal ion uptake (saturation) within 24 h. The results are summarised in Table 2. The binding capacities observed

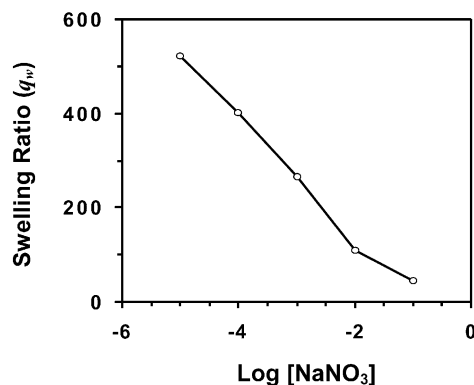


Fig. 3. Effect of ionic strength on the equilibrium swelling ratio,  $q_w$ , of the poly(AAGA-co-AAm) hydrogel; temperature 23 °C, pH 7.0.

Table 2

Non-competitive and competitive binding capacities of various metals by poly(AAGA-co-AAm) hydrogel

	Cu <sup>2+</sup>	Cd <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
Non-competitive binding capacity ( $\mu\text{mol cm}^{-2}$ )	5.3	5.1	0.78	0.85	0.68	0.82
Competitive binding capacity ( $\mu\text{mol cm}^{-2}$ )	1.3	0.17	0.027	0.024	0.024	0.027

were in the order of  $\text{Cu}^{2+} \approx \text{Cd}^{2+} \gg \text{Na}^+ \approx \text{Mg}^{2+} \approx \text{K}^+ \approx \text{Ca}^{2+}$ . This indicated that the affinity of the poly(AAGA-co-AAm) hydrogel towards the binding of transition metal ions such as  $\text{Cu}^{2+}$  ( $5.3 \mu\text{mol cm}^{-2}$ ) and  $\text{Cd}^{2+}$  ( $5.1 \mu\text{mol cm}^{-2}$ ) was stronger than that towards alkali or alkaline earth metal ions. This difference is due to the coordination bonds that form between these transition metals and the various ligands on the gel network [24].

### 3.3.2. Competitive binding capacities

In natural waters, there are many ions present. Therefore, it was necessary to collectively test the competitive binding of metal ions to the poly(AAGA-co-AAm) hydrogel before it was used for practical binding purposes. It is clearly shown, in Table 2, that the binding selectivity order was  $\text{Cu}^{2+} \gg \text{Cd}^{2+} \gg \text{K}^+ \approx \text{Mg}^{2+} \approx \text{Na}^+ \approx \text{Ca}^{2+}$  when all metal ions were present at the same normality. These results indicate much higher selectivity of the gel for  $\text{Cu}^{2+}$  ( $1.3 \mu\text{mol cm}^{-2}$ ) compared to the other ions tested under competitive binding, including  $\text{Cd}^{2+}$  ( $0.17 \mu\text{mol cm}^{-2}$ ). This result was generally supported by observations made of the change in metal binding capacity with increasing ionic strength (see below). However, it seems that the  $\text{Cd}^{2+}$  interaction is greatly reduced when  $\text{Cu}^{2+}$  is also present. The binding capacity for  $\text{Cu}^{2+}$  was comparable to capacities reported for the Chelex-100 binding gel [13] previously used with the DGT technique.

### 3.3.3. Binding rate

Metal uptake curves for non-competitive binding of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  are shown in Fig. 4. The initial concentrations of metal ions in the aqueous phase were 1.0 mM. For both metals, a rapid initial rate of uptake was

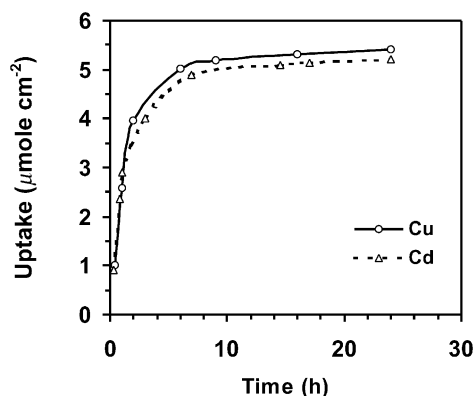


Fig. 4. Uptake of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  by the poly(AAGA-co-AAm) hydrogel at various times; temperature 23 °C, pH 7.0.

observed in the first 2 h. The linear rate of uptake during this time was  $2.64 \mu\text{mol cm}^{-2} \text{h}^{-1}$  for both  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ . The binding capacities were effectively reached within 6 h for each ion and demonstrate classic adsorption patterns. The binding rate observed here is approximately equivalent to experimental data on the binding kinetics of heavy metal ions by various sorbent systems in membrane or microsphere form (about 6 h) [25].

Note that there are several parameters which determine the binding rate, such as sorbent structural properties (e.g. size, porosity, surface area), amount of sorbent, metal ion properties (e.g. hydrated ionic radius), and initial concentration of metal ions [26]. In the case of a single disk of gel immersed in a solution, the binding rate also depended on how well-stirred the solution was. However, the binding rate obtained with the poly(AAGA-co-AAm) gel was deemed to be satisfactory for application with DGT, as was confirmed later.

### 3.3.4. Effect of pH on the binding capacity of $\text{Cu}^{2+}$ and $\text{Cd}^{2+}$

A change in pH can influence the uptake of a metal by a complexing agent. The pH influences transition metal speciation and solubility and the charge of the binding functional groups [25,27,28]. The proportion of the basic form of the glycolic acid groups, the main binding site, increases with an increase in pH. Fig. 5 shows that the binding capacity of ions first increased with increasing pH, due to a change in the ratio between the basic and acidic form of the glycolic acid groups. Interestingly the pH influenced the uptake of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  in different ways with  $\text{Cu}^{2+}$  taken up at lower pH values (1.5–4.0) and  $\text{Cd}^{2+}$  at slightly higher values (2.5–5.0). This is further evidence

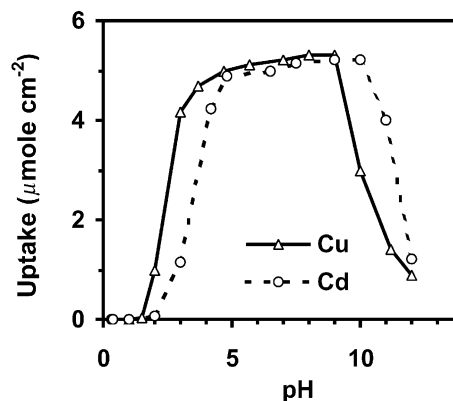


Fig. 5. Effect of pH on the binding capacity of the poly(AAGA-co-AAm) hydrogel; temperature 23 °C, time 24 h.

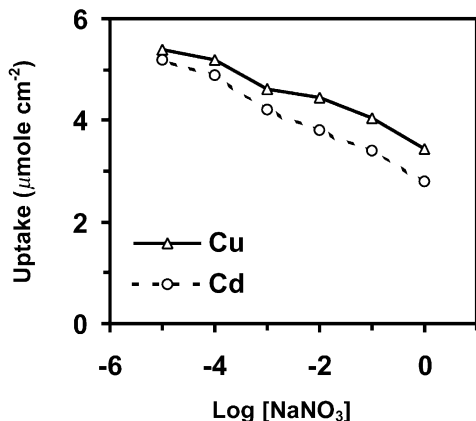


Fig. 6. Effect of electrolyte concentration on the binding capacity of the gel for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ; temperature 23 °C, pH 7.0, time 24 h.

for the selectivity of the poly(AAGA-co-AAm) hydrogel for  $\text{Cu}^{2+}$ . The binding capacities increased slightly at pH values  $>5$ , until the uptake decreased due to metal hydroxide insolubility at pH  $>9$ .

### 3.3.5. Effect of electrolyte concentration on the binding capacity of $\text{Cu}^{2+}$ and $\text{Cd}^{2+}$

Natural waters have a range of ionic strengths, so the binding behaviour of the poly(AAGA-co-AAm) gel to  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  was studied in aqueous solutions with  $\text{NaNO}_3$  concentrations ranging from 10  $\mu\text{M}$  to 0.10 M. Fig. 6 shows that the binding of  $\text{Cu}^{2+}$  to the gel was slightly stronger than that of  $\text{Cd}^{2+}$  at all electrolyte concentrations. In both cases, as expected, the binding capacity decreased with an increase in ionic strength. Even at a concentration of 1.0 M  $\text{NaNO}_3$  the binding capacities obtained were still appropriate for DGT applications.

### 3.4. Assessing poly(AAGA-co-AAm) as a binding layer for use with DGT

The poly(AAGA-co-AAm) hydrogel was tested as a binding phase with DGT for  $\text{Cu}^{2+}$ , based on its selectivity for  $\text{Cu}^{2+}$  from the metal binding experiments above. When DGT assemblies were deployed for time periods up to 150 h, the measured mass ( $M$ ) of  $\text{Cu}^{2+}$  in the gel increased linearly ( $r^2 = 0.975$ ) with time ( $t$ ) as shown in Fig. 7. This indicates that the poly(AAGA-co-AAm) binding layer was capable of reducing the  $\text{Cu}^{2+}$  ion concentration to zero at the interface between the binding and diffusive layers. In addition, the data agreed well with the theoretical line calculated from the DGT equation using the known concentration of  $\text{Cu}^{2+}$  in the experiment (0.79  $\mu\text{M}$  in synthetic Windermere water). A recovery of close to 100% was measured this way, indicating that the diffusion coefficient ( $D$ ) used was appropriate. For application in more complex systems with a range of species present for each analyte, each with their own diffusion coefficient, the results can be interpreted as a flux or as an indicative

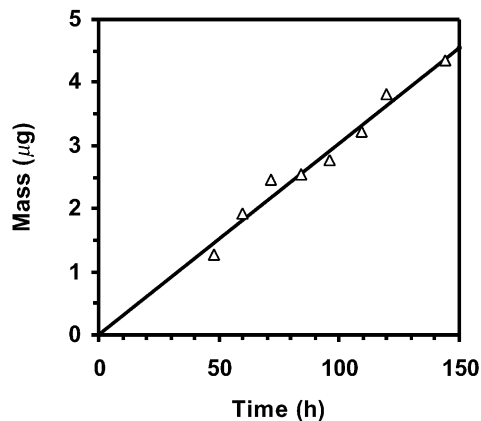


Fig. 7. Accumulation mass vs. time of DGT uptake for  $\text{Cu}^{2+}$  ion and theoretical response calculated from Eq. (2) using the solution concentration and other known parameters;  $\Delta g = 0.36$  mm,  $[\text{Cu}^{2+}] = 0.79$   $\mu\text{M}$ ,  $A = 4.9$   $\text{cm}^2$ ,  $D = 2.2 \times 10^{-6}$   $\text{cm}^2 \text{s}^{-1}$  at 23 °C.

concentration value. This is an area requiring additional research.

These two positive outcomes confirm that the poly(AAGA-co-AAm) hydrogel is suitable for use as a binding layer for  $\text{Cu}^{2+}$  ions using the DGT technique. These results indicate that the analyte concentration on the interface between diffusion gel and binding gel layer was effectively reduced to zero during the deployment, a condition of applying the DGT equation. The fact that the gel binding function groups were evenly distributed on the three-dimensional hydrogel backbone and the contact between the diffusion gels and the binding layer would have been close to an ideal two-dimensional layer, made it suitable for application to DGT.

## 4. Conclusions

A new copolymer (poly(AAGA-co-AAm)) was prepared with a 7:2 ratio of AAGA monomer units to AAm monomer units. This polymer was found to bind  $\text{Cu}^{2+}$  ions selectively with a binding capacity of 5.3  $\mu\text{mol cm}^{-2}$  for non-competitive uptake and 1.30  $\mu\text{mol cm}^{-2}$  for competitive uptake with other metal ions. This binding capacity and rapid uptake kinetics made the polymer suitable for use as a binding layer with the DGT technique. This was confirmed when a linear response was obtained for accumulated mass vs. uptake time of  $\text{Cu}^{2+}$  and a 95–100% recovery with a DGT uptake experiment.

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