

## Electroactive Behavior Assessment of Poly(acrylic acid)-Graphene Oxide Composite Hydrogel in the Detection of Cadmium

Areli Bejarano-Jiménez,<sup>1</sup> Vladimir A. Escobar-Barríos,<sup>1</sup> J. Mieke Kleijn,<sup>2</sup> Cesar A. Ortíz-Ledón,<sup>1</sup> Luis F. Cházaro-Ruiz<sup>1</sup>

<sup>1</sup>División de Ciencias Ambientales, Instituto Potosino de Investigación Científica y Tecnológica, A.C., Camino a la Presa San José 2055, Lomas 4<sup>a</sup> Sección, San Luis Potosí, SLP, México CP 78216

<sup>2</sup>Laboratory of Physical Chemistry and Colloid Science, Wageningen University, 6703HB Wageningen, The Netherlands  
 Correspondence to: L. F. Cházaro-Ruiz (E-mail: luis.chazaro@ipicyt.edu.mx)

**ABSTRACT:** Super absorbent polymers of acrylic acid-graphene oxide (PAA-GO) were synthesized with different percentage of chemical neutralization (0, 10, and 20%) of the acrylic acid monomer before its polymerization. The influence of their swelling and adsorption/desorption capacity of cadmium ions in aqueous solutions were studied and revealed that the GO enables greater mechanical stability in the materials. The PAA hydrogels, with the same degrees of neutralization, were also prepared without GO to compare with the composites. Additionally, carbon paste electrodes (CPE) modified with the composites PAA-GO were used to assess and compare their adsorption properties with cadmium(II). The anodic stripping voltammetry (ASV) peak, in the differential pulse voltammetry mode, for cadmium oxidation was found to be influenced by the presence of GO into the polymer, and also by their percentage of neutralization. The accumulation of cadmium(II) on the surface of the modified CPEs was performed under open-circuit conditions taking an account the preconcentration time of the metal cation. The presence of GO enhances the electrical signal of the electrodes in short times of immersion in cadmium(II) solutions. This property contributed to get linear responses of the CPEs modified with the composites, which were influenced by their degrees of neutralization. The PAA-GO 10N electrode with 10% of neutralization combined the influence of GO and the degree of neutralization in the same matrix, and also showed good performance in terms of its mechanical stability, it was chosen for preliminary studies on the selectivity of the electrode toward Zn(II) and Cu(II). © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40846.

**KEYWORDS:** cadmium(II); differential pulse voltammetry; modified carbon paste electrode; poly(acrylic acid)-graphene oxide composites hydrogels

Received 4 October 2013; accepted 6 April 2014

DOI: 10.1002/app.40846

### INTRODUCTION

The polymer poly(acrylic acid) (PAA) has received much attention in applications where its properties are used for adsorption of toxic metal ions in aqueous solutions. PAA contains carboxylic acid groups,  $-\text{COOH}$ , which in the ionized state can form complexes with heavy metal ions.<sup>1</sup> Linear hydro soluble PAA has been used as a model in a study of the binding properties of particular natural organic macromolecules such as humic substances using polarography.<sup>2</sup> The binding properties of a high molecular weight hydro soluble PAA ( $3 \times 10^6 \text{ g mol}^{-1}$ ) with cadmium(II) and lead(II) were confirmed and compared for copper(II) and nickel(II) by Peeret et al.<sup>3</sup> using polarography. It appeared that the binding properties of PAA ( $3 \times 10^6 \text{ g mol}^{-1}$ ) increased in the following order, depending on the metal ion:  $\text{Ni(II)} < \text{Cd(II)} < \text{Cu(II)} < \text{Pb(II)}$ .<sup>3,4</sup>

PAA can also occur as an insoluble three-dimensional cross-linked polymer network that swells by absorbing water up to hundreds of times its own weight, and that is why it is called a superabsorbent.<sup>5</sup> PAA hydrogels have a variety of applications including drug delivery devices,<sup>6</sup> biomaterial for tissue engineering,<sup>7</sup> in agriculture,<sup>8</sup> and waste water treatment,<sup>9</sup> based on the ability of the hydrogel to absorb water and to adsorb and retain dissolved substances, such as dyes<sup>1</sup> and heavy metal ions that have environmental impact.<sup>10</sup>

Other important properties of PAA hydrogels are their ability to control diffusion process, and their swelling/deswelling response to ionic strength, pH, temperature, and electric field.<sup>11</sup> Water absorption capacity and elastic properties of PAA hydrogels are dependent on the percentage of neutralization of the total concentration of acrylic acid (AA) monomer and the quantity of crosslinker during preparation.<sup>12–14</sup>

Additional Supporting Information may be found in the online version of this article.

© 2014 Wiley Periodicals, Inc.

Polymer gels have certain disadvantages in terms of structural, mechanical, thermal, and electrical properties. Clays,<sup>15</sup> metallic nanoparticles,<sup>16</sup> or different carbonaceous materials, like fullerenes, carbon nanotubes, and recently graphene oxide (GO), are among the materials that have been added to the PAA hydrogel matrix in order to improve its mechanical and physical properties.<sup>17,18</sup> The GO incorporated into the polymer matrix reinforces the resulting materials.<sup>19–22</sup>

The GO sheets easily disperse in an aqueous solution due to the presence of hydroxyl and epoxide functional groups on the basal planes, as well as carbonyl, and carboxyl on the sheet edges,<sup>23</sup> which facilitates the synthesis of PAA-GO polymer composites.<sup>17</sup> Several reports on GO-polymer composites have been published, but as far as we know, no report has been published about the modification of carbon paste electrodes (CPEs) with PAA-GO polymer composite hydrogels to study their interactions with heavy metals from water. The aim of this article was to assess the interaction with Cd(II) of PAA-GO composites, which were prepared using different percentages of neutralization of the starting concentration of the AA monomer prior their polymerization and denominated PAA-GO 0N, PAA-GO 10N, PAA-GO 20N, with 0%, 10%, and 20% degree of neutralization, respectively. These composites can pre-concentrate metal ions on the electrode surface by electrostatic attraction and complexation mechanisms.<sup>13</sup> For comparison, CPEs modified with pure PAA hydrogels prepared with the same degrees of neutralization but without GO, named as PAA 0N, PAA 10N, PAA 20N, were also studied. CPEs in combination with a suitable electrochemical technique have been shown to be widely applicable in studying heavy metals.<sup>24</sup> The advantages of using CPEs include the fact that they are inexpensive, they offer a wide potential window, and a low background current,<sup>25</sup> and in addition, it is possible to modify the electrode with different organic, inorganic, and biological products with the aim of increasing their sensitivity and selectivity in order to determine heavy metals.<sup>26–28</sup> In this article, it is shown that the use of CPEs in combination with anodic stripping voltammetry (ASV) procedures such as differential pulse voltammetry (DPV) is a very suitable approach to determine the interaction and the binding capacity of PAA-GO polymers when exposed to Cd<sup>2+</sup> solutions. Notwithstanding the above, studying the interaction between the heavy metals and the composite hydrogel can be considered to be an estimate of what happens in its native state, because it contains components that can interact with the heavy metals. These properties make the composites good candidates of new materials capable to change the electrode surface with analytical properties for sensor application. Similarly, the electrochemical behavior of Cu<sup>2+</sup> and Zn<sup>2+</sup> on the modified carbon paste electrodes (MCPEs) combined with linear ASV during this project is presented.

## EXPERIMENTAL

### Chemicals and Materials

Graphite powder (diameter particle size < 20 μm) was obtained from Sigma Aldrich; AA was purchased from Sigma Aldrich; azobisisobutyronitrile (AIBN) was obtained from DuPont; methylenebisacrylamide (MBA) from Alfa Aesar; paraffin oil ( $\rho = 0.88 \text{ g cm}^{-3}$ )

from Alfa Aesar, and KNO<sub>3</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, CuNO<sub>4</sub>·5H<sub>2</sub>O from Merck. GO was purchased from Graphene Supermarket on-line store. All materials were used as received. All solutions were prepared with deionized water (18.1 MΩ cm<sup>-1</sup>). A HCl 1N solution was used to adjust the solution pH value to desired pH = 5. Information concerning the characterization of the composites by IR has been included in the Supporting Information.

### Methods

**Potentiometric Titration of GO.** To determine quantities of GO's protic functional groups (carboxyls, lactones, lactols, and in some cases carbonyls), classical Boehm titrations were applied<sup>29</sup> by using an automatic Metler Toledo (T 70) titrator. In four reaction vessels, a sample of 0.005 g was placed and 25 mL of a 0.1N solution of, respectively, NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH, and NaOC<sub>2</sub>H<sub>5</sub> were added. The solutions were continuously stirred for 5 days. After that, they were titrated with 0.1N HCl. During the titration, N<sub>2</sub> was continuously led through the solution to eliminate interference with atmospheric CO<sub>2</sub>. The titration with NaOH gives the concentration of all acidic groups (carboxylic, lactonic, and phenolic groups), the Na<sub>2</sub>CO<sub>3</sub> neutralizes the carboxylic and lactonic sites, whereas the NaHCO<sub>3</sub> neutralizes only the carboxylic sites. The number of protic groups (meq/g) was calculated with the eqs. (1) and (2).

$$ASC = \frac{V_{in}(C_{in} - C_{fin})}{m} \times 1000 \quad (1)$$

$$c_{fin} = \frac{V_T C_T}{V_m} \quad (2)$$

where ASC = active sites concentration (meq g<sup>-1</sup>), V<sub>in</sub> = initial volume of the neutralizing solution (L), C<sub>in</sub> = initial concentration of the neutralizing solution (eq L<sup>-1</sup>), C<sub>fin</sub> = final concentration of the neutralizing solution (eq L<sup>-1</sup>), m = mass of GO (g), V<sub>T</sub> = volume of the titrant solution (mL), C<sub>T</sub> = concentration of the titrant solution (eq L<sup>-1</sup>), and V<sub>m</sub> = volume of the neutralizing solution with GO (mL).

**Electrochemical Equipment.** The electrochemical evaluation was carried out with a μAutolab Type II, equipped with a computer with the General Purpose Electrochemical Software (Ecochemie B-V, Utrecht, The Netherlands), System Version 4.9. Also a potentiostat/galvanostat Biologic, equipped with a computer with the EC-Lab V10-10 software, was used. All experiments were carried out under nitrogen atmosphere at room temperature. A three-electrode cell was used for electrochemical experiments, with the MCPEs as the working electrode, a graphite bar as auxiliary electrode, and a Ag/AgCl/KCl(sat) as reference electrode. To avoid contamination of the reference electrode, a salt bridge containing a free analyte electrolyte solution of KNO<sub>3</sub> 0.2M was used.

**Synthesis of the Graphene Oxide/Polymer Composite Materials.** The synthesis of PAA-GO hydrogel composites was carried out by the following procedure: First, a solution of the AA monomer in deionized water was prepared (3.6 mol L<sup>-1</sup>), and then a molar fraction of 0, 10, or 20% was neutralized with sodium hydroxide (0.0, 0.36, and 0.72 mol L<sup>-1</sup>, respectively) before polymerization. A free radical polymerization was initiated at 75 °C, under constant stirring, using AIBN (0.05 g as

initiator. After 1.5 min, 10 mL of GO aqueous suspension were added in order to obtain a concentration of GO sheets into the polymer matrix of 1 wt %; 2.5 min later, the cross-linking agent MBA (0.049 g) was added into the mixing solution. The reaction was maintained with vigorous stirring for 20 min, and as the temperature slowly increased until reaching 92 °C, thus the mixture became a brown jelly. The resulting products were denominated according to their corresponding degree of neutralization as it was explained above, PAA-GO 0N, PAA-GO 10N, and PAA-GO 20N. Also, hydrogels without GO were synthesized following the same procedure and were named as PAA 0N, PAA 10N, and PAA 20N. After polymerization, the resulting materials were washed several times with deionized water in order to remove any residual reagents and dried at 60 °C for 5 days.

#### Scanning Electron Microscopy (SEM) Studies of the Hydrogels.

These analyses were performed with environmental electron microscope ESEM QUANTA 200, using GSED detector and 950 MPa. In this case, the samples were tested being swollen with deionized water.

#### Water Absorption of the Hydrogels in Deionized Water.

Deionized water (400 mL) was added to 0.1 g of dry hydrogel. The polymer was allowed to swell for 10 min. The swollen gel was then separated by filtering through a 100-mesh aluminum screen for 2 h. The swollen gel was weighed and the maximum water absorption was calculated by the equation as follows. The percentage of water absorption ( $Q$ ) is  $[(B - A)/A](100\%)$  where  $A$  and  $B$  are the weights of the dry polymer (g) and the swollen polymer (g), respectively.<sup>30</sup> A similar procedure was separately repeated with gel swelling times of 20, 40, 60, 80, 100, 120, 150, 180, 210, 240, and 270 min.

#### Influence of the Percentage of Neutralization of the Hydrogel on the Sorption and Desorption of Cadmium Ions.

Adsorption experiments with the hydrogels were carried out by placing about 0.1 g of PAA and PAA-GO composites into 80 mL of  $\text{Cd}(\text{NO}_3)_2$  solutions at pH = 5 with an initial concentration of 20 mg  $\text{L}^{-1}$  and left stirring. After equilibrium was reached, metal inside the hydrogel was determined. Aliquots of metal ions were withdrawn and analyzed after suitable dilution every hour. The desorption capacity of the swollen hydrogels and composites was determined into acidic medium at pH = 2, and the aliquots were withdrawn every 15 min. Finally, cadmium concentrations were measured by inductively coupled plasma optical emission spectrometry Varian 730-ES.

Uptakes of metal ions onto hydrogel systems can be calculated from the following relation (3)

$$\text{mgCd}^{2+} / \text{g}_{\text{hydrogel}} = \frac{(C_i - C)}{m} V_t \quad (3)$$

where  $C_i$  and  $C$  are the initial and the equilibrium concentrations of metal ions in mg  $\text{L}^{-1}$ ,  $V_t$  is the total volume of metal solutions in liters, and  $m$  is the mass of the dry polymer in grams.

**Electrode Preparation.** For the preparation of the CPEs, the PAA-GO composites and PAA polymers were crushed to pass a <150 mm sieve. High purity graphite powder (0.56 g), paraffin

oil (0.4 g), and PAA-GO composites (0.04 g) were hand mixed in an agate mortar. The optimal ratio of graphite, composites, and oil was obtained by studying the response of the MCPES using a typical reversible redox system made up of 0.01 mol  $\text{L}^{-1}$   $\text{K}_4[\text{Fe}(\text{CN})_6]$  in  $\text{KNO}_3$  0.2 mol  $\text{L}^{-1}$ .<sup>24</sup> The CV response using the reversible system is very similar to blank CPE. The resulting pastes were packed into plastic tubes (2 mm diameter and 7 cm long). Electrical contact was achieved by inserting a copper wire into the packed plastic tube. The surface was renewed before each experiment by pushing an excess of paste out of the tube and polishing the new surface with filter paper.

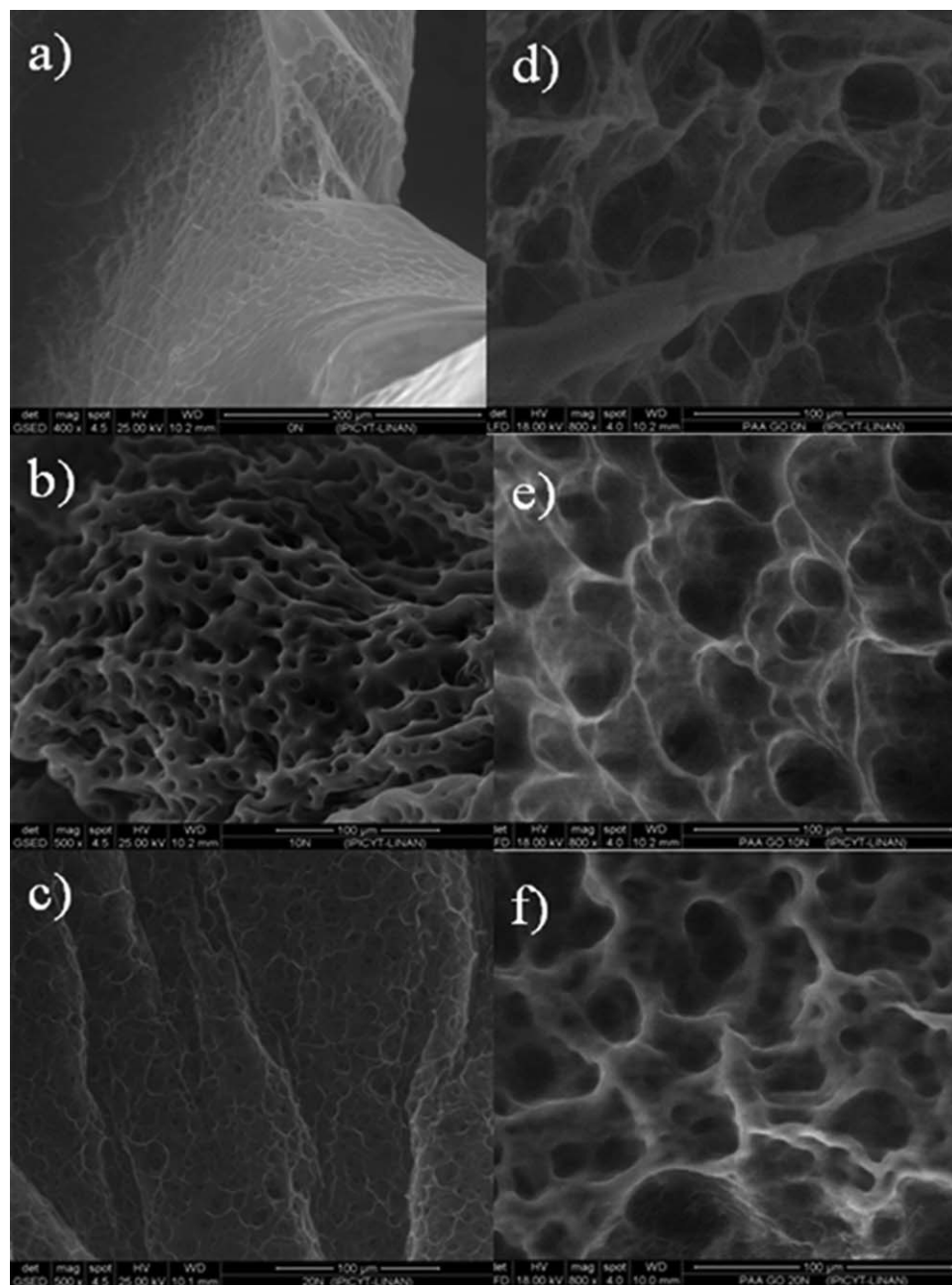
**Electroanalytical Procedures.** The analysis of  $\text{Cd}^{2+}$  using DPV was carried out in a 0.2 mol  $\text{L}^{-1}$   $\text{KNO}_3$  electrolyte solution (pH 5) using the following steps after purging with nitrogen for at least 10 min: (a) In a pre-treating procedure of the surface of the electrodes, a  $-1.0$  V potential was applied for 20 s, followed by a DPV sweep from  $-1.0$  to 0.5 V (with 100 mV  $\text{s}^{-1}$  scan rate, 100 mV pulse amplitude, and 2 ms pulse period). This procedure suppresses undesirable background currents within the potential range of interest<sup>24</sup> and enhances the sensitivity of the electrodes. (b) In order to pre-concentrate the metal ion at the activated surface of the MCPE, it was immersed for a pre-determined time in a solution of  $1 \times 10^{-3}$  mol  $\text{L}^{-1}$   $\text{Cd}(\text{NO}_3)_2$  (pH = 5), under agitation and with open circuit conditions. (c) Afterward, the MCPE was rinsed and immersed again in the electrolyte solution without cadmium, and a reduction potential of  $-0.9$  V was applied for 40 s, followed by the recording of the anodic differential pulse voltammogram by scanning from  $-0.9$  to 0.5 V (with 30 mV  $\text{s}^{-1}$  scan rate, 100 mV pulse amplitude, and 12.4 ms pulse period). A reduction time of 40 s showed the highest signal-to-background (S/B) ratio for stripping voltammetry, increasing the reduction time to 60 s did not change the S/B ratio. Therefore, the time for the electrochemical reduction of  $\text{Cd}^{2+}$  was fixed to 40 s. At the end of this process, the electrode surface was renewed and the cycle started again.

## RESULTS AND DISCUSSION

### Characterization of the Composite Polymer Materials

Through *in situ* polymerization, GO nanosheets have been successfully incorporated into many kinds of polymer matrix.<sup>18</sup> The *in situ* polymerization was made to ensure an efficient dispersion of GO in the polymer matrix. The concentration of GO sheets in the polymer matrix was 1 wt %. The pure poly(acrylic acids) (PAA 0N, PAA 10N, PAA 20N) were transparent but they turned a black color after addition of the GO, which suggests that the GO sheets were well dispersed in the polymer matrix through the *in situ* polymerization process. As a representative example, see the pictures in Supporting Information Figure S3 for the color change by the pure PAA 10N with the addition of GO in the PAA-GO 10N composite. The surfaces of the polymers and the composites showed shiny and uniform surfaces suggesting that the addition of the GO can be well dispersed. The infrared spectra of hydrogels PAA 0N, PAA 10N, PAA 20N and the composites with GO are shown in the Supporting Information (Figures S1 and S2).

SEM images of pure and composites hydrogels shown in Figure 1 revealed that all the samples are like a sponge and exhibit a



**Figure 1.** SEM images of the swollen hydrogels (A) PAA 0N, (D) PAA-GO 0N, (B) PAA 10N, (E) PAA-GO 10N, (C) PAA 20N, and (F) PAA-GO 20N. Magnification 100  $\mu\text{m}$ , except for PAA 0N which is 200  $\mu\text{m}$ .

three-dimensional network. The sponge like morphology confirms the enhanced water retention of the hydrogels, because this porous structure allows water retention. The hydrogel PAA 0N shows a wrinkled texture, whereas for PAA-GO 0N composite the pore structure is much clearer. This important difference suggests that the presence of GO in the composite leads to the formation of more and larger channels than in the hydrogel. The samples PAA-GO 10N and PAA-GO 20N exhibit a similar sponge like morphology with a thicker undulating structure due to the presence of the GO, which may suggest that the GO is acting as a crosslinking agent.<sup>17</sup> The images of the PAA-GO composites show that the pores of the composites are larger than those of the PAA gels.

The concentration of the protic functional groups (e.g.,  $-\text{COOH}$ ,  $-\text{OH}$ ), obtained from Boehm titration of GO dispersions are listed in Table I. It is observed that the quantity of carboxylic groups is higher than the other oxygenated groups, and they can offer new crossover points among the polymeric matrix. In addition, besides providing grafting points for polymerization, the functional groups on GO also offer hydrogen bonding with the PAA hydrogel resulting in a greater mechanical stability of the composite materials.<sup>15</sup> As a representative example, see the image in Supporting Information Figure S3 for the volume change by the dried materials, pure PAA 10N, and the PAA-GO 10N composite after absorbing the deionized

**Table I.** Quantity of Protic Groups on Graphene Oxide, Determined by Boehm Titrations

Oxygenated groups	Carboxylic	Lactone	Phenol	Carbonyl
Quantity (meq g <sup>-1</sup> )	0.875	0.375	0.0	1.25

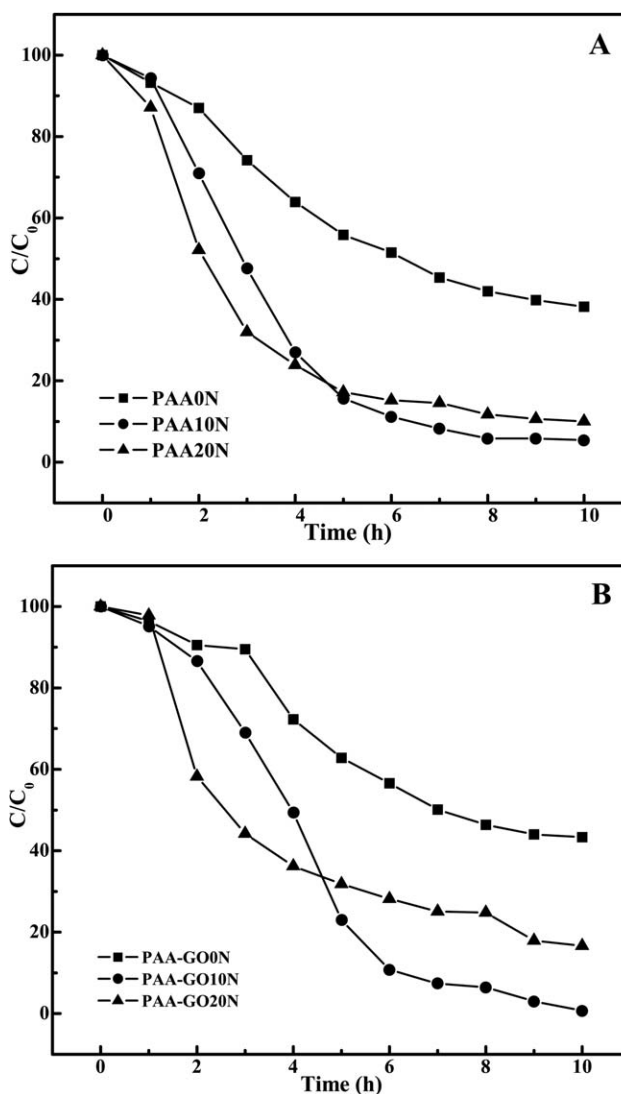
water. The 1 wt % of GO has influence on the size attained by the composite (17488%) after exposing it to the same volume of deionized water during the same exposure time of 120 min as the pure PAA 10N (4249%). A similar situation was observed with PAA-GO 0N (411%), i.e., its size after absorption of water is smaller than the PAA 0N gel (590%) after 120 min. On the contrary, it was observed that the swelling capacity of the PAA-GO 20N composite (5663%) was higher than PAA 20N (2781%) after 120 min. The hydrogels prepared with the highest degree of neutralization are more brittle and start to break during handling over 1.5 h of swelling, whereas the hydrogel composites have no fragmentation after the absorption of water up to 240 min (PAA-GO 0N (581%), PAA-GO 10N (7258%), and PAA-GO 20N (8566%)). This result has confirmed that GO enables greater mechanical stability in the materials, as the flakes could be acting as crosslinking points.<sup>17</sup>

The acrylate monomers polymerize less readily than AA, because the ionized monomers react more slowly in the propagation step of polymerization. Therefore, the neutralization can induce shorter polymeric chains. The degree of neutralization has also an effect on the crosslinking density. It has been observed that the water absorption capacity decreases with increasing degree of neutralization of AA which can be associated with an increase in the crosslink density.<sup>14</sup> In this study, the results of swelling indicate that the water absorption capacity increases with increasing degree of neutralization in the composite gels which can be associated with the repulsing charges among the polymeric chains, which facilitates the water diffusion into the polymeric chains.

On the other hand, when a superabsorbent is in contact with an aqueous solution, a charge in the material is generated due to the release of protons from the active groups, which in this case is the carboxyl group. The distribution of this charge to the pH of the solution affects the material's ability to retain ions compromising ion adsorption. The determination of the pH of the solutions in equilibrium with pure PAA hydrogels was performed and increased in the following order: 3.58 (PAA 0N) < 3.78 (PAA 10N) < 3.92 (PAA 20N). It is seen that the greater the percentage of neutralization, the higher the pH, because in contact with an aqueous solution the Na<sup>+</sup> from the -COONa groups goes into solution and the -COO<sup>-</sup> stays as it is. The swelling capacity of the gels and their charge were taken into account for the preparation of the MCPs, as it is discussed in the following paragraphs.

#### Uptake of Cd<sup>2+</sup> into Hydrogels

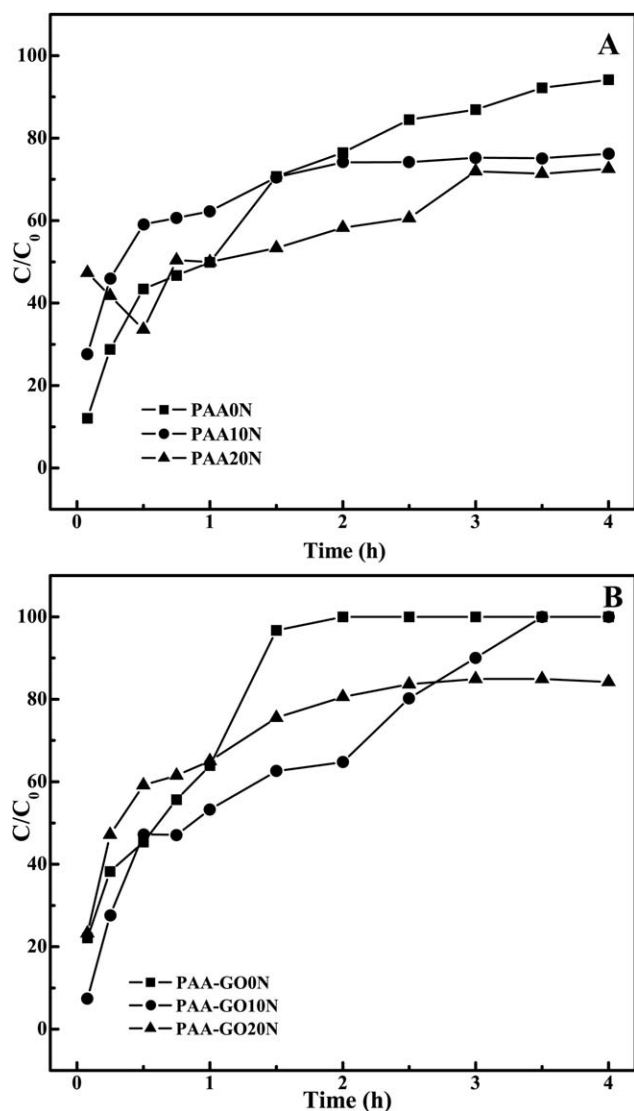
Batch experiments were carried out to determinate the Cd<sup>2+</sup> adsorption and desorption capacity of the hydrogels and composites (see Figures 2 and 3, respectively). It was observed that



**Figure 2.** Uptake of cadmium ions by (A) pure PAA hydrogels and (B) PAA-GO composites in initial concentration of Cd<sup>2+</sup> = 20 mg L<sup>-1</sup>, solution at pH = 5. Plots of concentration of cadmium vs. sorption time.

the concentration adsorption capacities of the hydrogels follow this order: PAA-GO 0N < PAA 0N < PAA-GO 20N < PAA 20N < PAA 10N < PAA-GO 10N. For the materials with 10 and 20% of neutralization, the adsorption capacity is higher than for the unneutralized gels. This can be explained because in comparison with unneutralized materials, there are more sites where cadmium can be bound to active groups. On the other hand, 20% of neutralization can induce shorter polymeric chains,<sup>26</sup> resulting in lower number of binding sites for cadmium in PAA 20N and PAA-GO 20N than in PAA 10N and PAA-GO 10N hydrogels.

The desorption capacity of the swollen hydrogels and composites is important because the metal ion could be recovered from these materials in short times. The desorption process of the pure PAA 0N hydrogel was slower than for the PAA-GO 0N composite. The first one reached saturation equilibrium around 3 h, whereas for the second one it was achieved in 1.5 h. It was

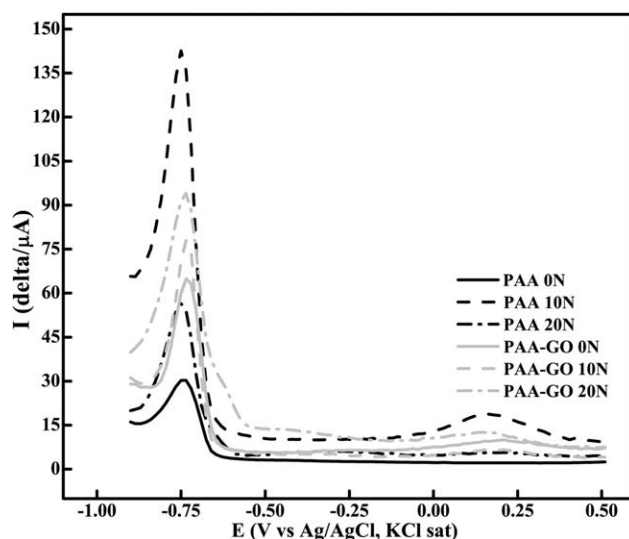


**Figure 3.** Desorption of cadmium ions from (A) pure PAA hydrogels and (B) PAA-GO composites in initial concentration of  $\text{Cd}^{2+} = 20 \text{ mg L}^{-1}$  solutions at pH = 5. Plots of concentration of cadmium vs. desorption time.

also observed that with PAA 10N and PAA 20N materials the equilibrium was reached in 3 h, but there was not total desorption of  $\text{Cd}^{2+}$ . In contrast, the PAA-GO 10N composite presented a complete desorption up to 3.5 h. The kinetics of metal ion release process from PAA 20N gel is relatively slower compared with the PAA-GO 20N composite and both hydrogels presented no complete desorption, with  $\sim 80\%$  of the recovery of cadmium into the solution. It is possible that certain number of carboxyl groups in the hydrogel remains bound with metal ion due to the electrical charge, generated from the exchange between the metal ion in the external solution and  $\text{Na}^+$  from the polar groups in the polymer chain.

#### Electrochemical Analysis with Carbon Paste Electrodes Modified with Hydrogels

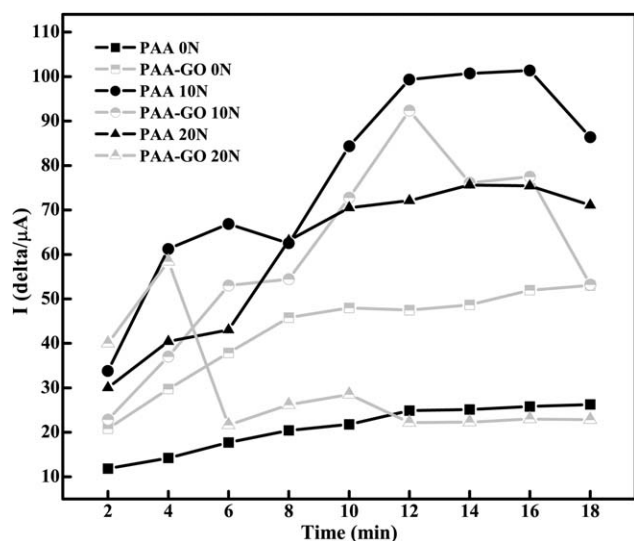
The electrochemical detection of  $\text{Cd}^{2+}$  has been investigated by DPV and linear stripping voltammetry in solutions at pH = 5 to ensure that it is the predominant species.<sup>4,31</sup> This value of the



**Figure 4.** Differential pulse voltammetry response of cadmium on MCPES immerse in  $0.2 \text{ mol L}^{-1} \text{ KNO}_3$  solution, after an exposure time of 4 min to a  $1 \times 10^{-3} \text{ mol L}^{-1} \text{ Cd}(\text{NO}_3)_2$  solution. Reduction potential at  $-0.9 \text{ V}$ , during 40 s, scan rate  $\nu = 100 \text{ mV s}^{-1}$ .

pH is above the one that was found for the pure polymers which ensures that the charge of the materials is negative and promotes the electrostatic interactions between the hydrogel and the metal cations. As a comparison, the voltammogram of the unmodified CPE in the reference solution ( $\text{KNO}_3$ ,  $0.2 \text{ M}$ , pH = 5) shows no oxidation-reduction response (Supporting Information Figure S4). The voltammetric response after exposing the CPE to the  $\text{Cd}^{2+}$  solution for 4 min shows a broad peak of very low intensity, which is difficult to assign to a redox reaction. This means that cadmium(II) uptake by the CPE is not significant and proves that all oxidation-reduction data obtained on the MCPES with this technique is exclusively associated with the modifiers of the electrodes.

Figure 4 shows the DPV response to  $\text{Cd}^{2+}$  for all MCPES obtained after activation and exposure to a  $1 \times 10^{-3} \text{ mol L}^{-1} \text{ Cd}^{2+}$  solution for 4 min. The voltammograms present a peak around  $-0.75 \text{ V}$ , corresponding to the oxidation of cadmium. The different heights of the anodic current peaks ( $I_{\text{ap}}$ ) are the result of the different amounts of cadmium adsorbed on the surface of the MCPES.  $I_{\text{ap}}$  varies according to the type of hydrogel contained in the electrode and follows this order  $\text{PAA } 0\text{N} < \text{PAA } 10\text{N} < \text{PAA-GO } 0\text{N} < \text{PAA-GO } 10\text{N} < \text{PAA-GO } 20\text{N} < \text{PAA } 20\text{N}$ . The anodic peaks of PAA 0N and PAA-GO 0N are found around the same potential, which suggests that  $\text{Cd}(\text{II})$  is bound to the hydrogels through functional groups with similar binding properties. In the case of PAA 10N and PAA 20N, MCPES the anodic peaks appear around  $-0.75 \text{ V}$ , whereas for their counterparts with GO these appear at slightly less negative potentials, which suggests that each material shows somewhat different interactions with cadmium(II), probably for the neutralized materials a complexation process was taken place. When the CPE voltammogram is compared with the voltammetric peaks obtained with the MCPES, a considerable difference is seen, which means that the preconcentration of cadmium mainly occurred in the active sites added to the

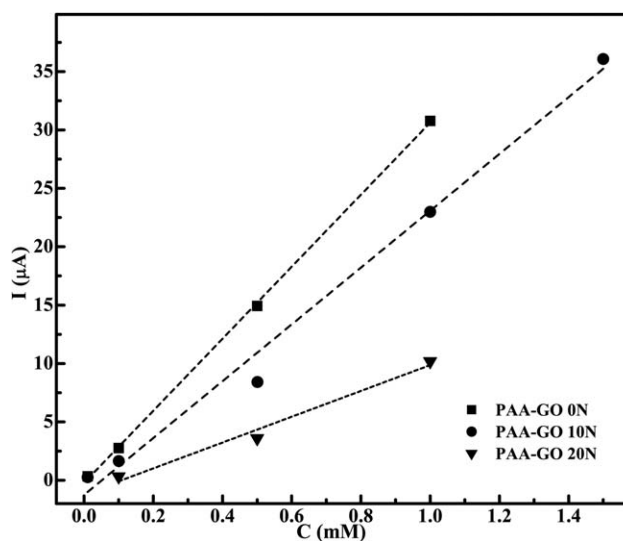


**Figure 5.** Dependence of cadmium uptake (anodic peak current) vs. immersion time of the modified carbon paste electrodes in  $0.2 \text{ mol L}^{-1} \text{ KNO}_3$  and  $1 \times 10^{-3} \text{ mol L}^{-1} \text{ Cd(NO}_3)_2$  solution. Reduction potential at  $-0.9 \text{ V}$ , during  $40 \text{ s}$ , scan rate  $\nu = 100 \text{ mV s}^{-1}$ .

MCPE by the pure hydrogels and the composites. Because the anodic peak around  $-0.75 \text{ V}$  is present on the MCPEs, the studies were focused on that peak.

It is clear that the degree of neutralization of the AA monomer prior the preparation of PAA polymer as well as the presence of the GO influences the  $\text{Cd(II)}$  detection, as described in the previous paragraphs. It should be noted however that reproducible results were difficult to attain for MCPEs produced with the same composite hydrogels, especially with PAA-GO 10N and PAA-GO 20N composites. This is most likely because the particles of the hydrogel composite are not identical in shape due to differences in their density distribution which can influence the degree of swelling on the surface of the electrode. In order to reproduce the results, the preconcentration and voltammetric processes of the ion were repeated several times.

The results described in this article indicate that GO can indeed play a role as an electrochemical sensitizer for cadmium detection. The effect of GO was clearly seen from the different voltammetric responses of the modified electrodes. The heights of the anodic peaks after  $\text{Cd}^{2+}$  uptake by the MCPEs, versus their immersion time in the solution of  $1 \times 10^{-3} \text{ mol L}^{-1} \text{ Cd(NO}_3)_2$ , is shown in Figure 5. Generally, the anodic peak shows a clear increase for longer exposure times to  $\text{Cd}^{2+}$  solution of almost all the modified electrodes. It takes  $\sim 8$  to  $10 \text{ min}$  for the PAA 10N and PAA-GO 10N electrodes to take up the equilibrium adsorbed amount of  $\text{Cd}^{2+}$ . For the PAA 0N electrode, the equilibrium was achieved only after  $12 \text{ min}$ . In contrast, the PAA-GO 0N anodic peak showed fluctuations over the whole range of exposure times. The cause for this is not clear. The signals of the PAA-GO 0N (curve) and PAA-GO 10N (curve) are higher than those for PAA 0N (curve) and PAA 10N (curve), thus it can be proposed that GO can successfully increase the electrochemical signals. The observed increase in the anodic peak current, using GO, represents the larger micro-



**Figure 6.** Calibration graph: anodic peak current as a function of  $\text{Cd}^{2+}$  concentration in the exposure solution for the PAA-GO modified carbon paste electrodes. Exposure time  $6 \text{ min}$ , reduction potential at  $-0.9 \text{ V}$ , during  $40 \text{ s}$ , scan rate  $\nu = 100 \text{ mV s}^{-1}$ .

scopic area of the modified electrode, resulted by the presence of GO. However, the peak currents at the PAA-GO 20N electrode are lower than those at the other MCPEs after  $12 \text{ min}$  which suggests that the  $\text{Cd}^{2+}$  is released from the polymer matrix due to the degree of swelling of the polymer, which is much higher than that of the other materials, facilitating migration of ions.

The higher peak currents obtained with the MCPEs containing the composites PAA-GO 0N and PAA-GO 10N compared with the ones modified with pure PAA 0N and PAA 10N hydrogels can be attributed to higher number of active sites that can act as ligands with cadmium ions. According to the Boehm titration results, these extra active sites can be functional groups such as hydroxyl, carboxyl, carbonyl, and lactone present in the structure of GO incorporated in the polymer matrix. In addition, the graphite is a  $\pi$  system with a high electron density, which promotes attraction of cations as cadmium(II), or other metals. Also, the GO may contribute to sites where electron transfer can take place. As a result, not all  $\text{Cd}^{2+}$  ions have to diffuse out from the polymer matrix to come into contact with the carbon paste, to be detected in the ASV procedure. Besides that, during the application of the reduction potential, reduced GO may be generated, a material that is known to be up to eight orders of magnitude more conductive than the starting GO. According to Pumera,<sup>32</sup> GO is reduced below  $-0.60 \text{ V}$  vs.  $\text{Ag/AgCl}$  approximately, reaching a maximum at  $-0.87 \text{ V}$ , with a consequent increase in the conductivity, which would lead to better electronic transfer in materials containing GO.<sup>33</sup>

The electrode modified with the PAA-GO 20N polymer presented the lower peak currents after  $10 \text{ min}$ . As it was mentioned before, 20% of neutralization in PAA can induce shorter polymeric chains and reduce the degree of crosslinking,<sup>34</sup> resulting in a lower number of binding sites for cadmium and less

**Table II.** Cadmium Concentration Range and Equations of the Calibration Curves for the PAA-GO Modified Carbon Paste Electrodes

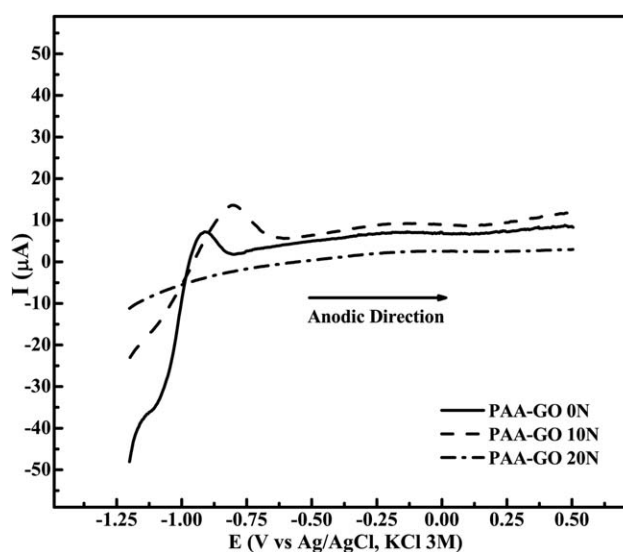
Electrode	Concentration (mmol L <sup>-1</sup> )		Equation	Ad. R. square
	Min	Max		
PAA-GO 0N	0.01	1	$y = -0.2151 + 30.84x$	0.99
PAA-GO 10N	0.01	1.5	$y = -1.2472 + 24.33x$	0.98
PAA-GO 20N	0.1	1	$y = -1.1944 + 11.06x$	0.96

adsorption of this metal ion compared with the pure PAA 20N hydrogel. Also, when the polymer is PAA-GO 20N a competition between the water absorption and the formation of complex with metal can be generated inside the hydrogel. The water absorption dominates and the solution increases its concentration of metal ions. This can explain that the PAA-GO 20N electrode took up cadmium in short times (4 min), but it can be easily released at longer times. This result concurs with the observed faster desorption of this metal cation from this composite in batch experiments.

Figure 6 shows the calibration plots for the PAA-GO-MCPEs, obtained with standard solutions of Cd<sup>2+</sup> by an exposure time of the modified electrodes into the solutions of 6 min. Based on the results shown in Figure 5 at this time of immersion, the composite gels have nearly reached the adsorption equilibrium. In addition, a total assay time of 6 min represents a quite rapid method for the determination of cadmium. In Table II, the equations of the linear fits of the data for each electrode are listed together with the concentration ranges that gave a good linear fit ( $r^2 > 0.96$ ). The fitting curves confirmed that anodic current peaks are due to the stripping of Cd<sup>2+</sup> and show that the method can also be applied for the detection of this metal ion. The calibration plot was found to be linear between 0.01 and 1.5 mM with slope of 24.33  $\mu\text{A mM}$  for the PAA-GO 10N modified electrode. For the PAA-GO 0N modified electrode, the plot was linear between 0.01 and 1 mM with the highest slope of 30.84  $\mu\text{A mM}$ . At 1 mM of concentration, this electrode reaches a saturation state as it is observed in Figure 5. On the other hand, the calibration plot associated with PAA-GO 20N electrode was found to be linear in a shorter range of concentration between 0.1 and 1 mM with the lowest slope value of 11.06  $\mu\text{A mM}$  for the three electrodes. The slope of the calibration curve decreases with the increasing of the degree of neutralization of the composite modifier, which is consistent with what is observed in Figure 5. At higher degree of neutralization, it seems more difficult to perform the detection of cadmium ion in solution with PAA-GO 20N electrode. It is possible that not all the cadmium adsorbed onto the polymeric matrix was redissolved in the solution due to the reoxidation.

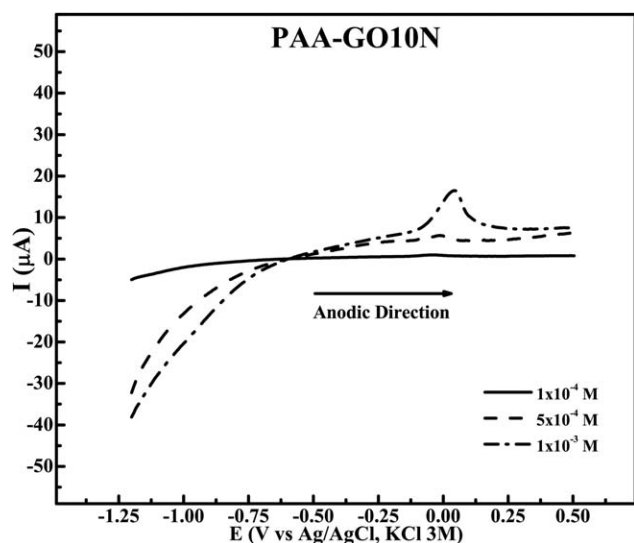
Although, the PAA gel is not a selective ligand, the immobilization of GO into its matrix and the change of its neutralization percentage are techniques that can provide certain selectivity toward the analyte of interest. In studies of the swelling of poly(acrylic acid-co-itaconic acid) 80/20 hydrogels, it was observed that the sorption of zinc is higher than the one with copper at pH = 4.7.<sup>30</sup> The metal ion sorption is pH dependent

and in agreement with the carboxylic proton-metal ion exchange process. These authors also studied the swelling of poly(acrylic acid-co-itaconic acid) hydrogels loaded with Cu<sup>2+</sup> and Zn<sup>2+</sup>, and it was observed that the swelling of hydrogels loaded with zinc is higher and faster (higher kinetics constant) than those loaded with copper. They also reported that the rate of water diffusion through the hydrogel was slower than that of the unloaded one due to the superficial barrier formed by metal complexes. In order to test the selectivity of the composite gels, in this work, the linear ASV procedure using the MCPEs was carried out with these metal ions. Based on the results obtained for the calibration of electrodes modified with composites shown in Figure 6, and the desorption of cadmium(II) from composites in Figure 3(B), the PAA-GO 10N electrode was chosen to perform the study of selectivity. This electrode combines the properties of GO and the influence of the percentage of neutralization. Additionally, Figure 7 shows the linear anodic stripping voltammograms for the three different PAA-GO-MCPEs electrodes immersed for 6 min into a Zn(NO<sub>3</sub>)<sub>2</sub> 1 × 10<sup>-3</sup> mol L<sup>-1</sup> solution and then transferred to an electrolytic solution without Zn(II). It is seen that the PAA-GO 20N electrode shows no current peak, whereas for the other two electrodes different values for peak currents  $I_p$  were obtained, which are significantly lower than those found for cadmium (Figure 4), and a significant difference in the peak potential  $E_p$  is



**Figure 7.** LASV response of zinc on PAA-GO-MCPEs in 0.2 mol L<sup>-1</sup> KNO<sub>3</sub>, Zn(NO<sub>3</sub>)<sub>2</sub> 1 × 10<sup>-3</sup> mol L<sup>-1</sup>, exposure time of 6 min, reduction potential at -1.2 V, reduction pulse time 40 s, at scan rate of  $v = 50 \text{ mV s}^{-1}$ .





**Figure 8.** Linear anodic stripping voltammetry response of copper on PAA-GO 10N modified carbon paste electrode in  $0.2 \text{ mol L}^{-1} \text{ KNO}_3$ , and the mixture  $\text{Zn}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_3)_2$  (1 : 1) in different concentrations of these ions  $1 \times 10^{-4}$ ,  $5 \times 10^{-4}$ , and  $1 \times 10^{-3} \text{ mol L}^{-1}$ . Immersion time of the electrode: 6 min, reduction potential at  $-1.2 \text{ V}$ , during 40 s, scan rate  $\nu = 50 \text{ mV s}^{-1}$ .

noticed too. However, the  $I_p$  associated with PAA-GO 10N electrode is the highest and gave another reason to use this electrode in mixtures with zinc(II) and copper(II). Figure 8 shows the voltammetric response of the modified electrode after 6 min of exposure to a mixed solution of the ions  $\text{Zn}^{2+}$ - $\text{Cu}^{2+}$  (1 : 1) at different concentrations. It is seen that at  $\sim 0.0 \text{ V}$  a peak appears and corresponds to the anodic stripping of  $\text{Cu}^0$  in solutions with no zinc and copper ions. In contrast, the peak associated with the oxidation of the  $\text{Zn}^0$  does not appear at any concentration used for the mixture of ions. This suggests that the MCPE has some selectivity for metal ions, and probably more affinity for  $\text{Cu}^{2+}$  because the anodic stripping behavior of  $\text{Zn}^{2+}$  is not observed. It has been observed that the binding affinity of poly(acrylic acid-co-itaconic acid) is higher for Zn(II) than for Cu(II).<sup>30</sup> But in this study, there was not recovery of zinc and the recovery of copper is much lesser, i.e., the anodic peak of its oxidation has lower current intensity than the one from cadmium(II) (see Figures 4 and 5). The interference of these ions at the same concentration is not too high. This indicates that the PAA-GO 10N electrode is more selective for  $\text{Cd}^{2+}$  than the tested potential interfering ions, which is the subject of further investigations.

## CONCLUSIONS

The voltammetric responses of Cd(II) show that the uptake of this ion by the MCPEs depends on the degree of neutralization of the AA monomers before its polymerization to obtain PAA hydrogel or the composites with GO. Furthermore, the CPES exhibit different adsorption capacities when modified with PAA-GO composites than with the parent PAA hydrogel. This phenomenon may be due to a higher number of active sites in the composites and/or to an enhanced electron transfer because of the presence of reduced GO, which facilitates the detection of

Cd(II). In addition, the graphite is a  $\pi$  system with a high electron density, which promotes attraction of metal cations. The sensitivity shown by different electrode configurations for Cd(II) and preliminary selectivity in the different concentrations and mixtures of Zn(II) and Cu(II) ions used, suggests that this kind of electrodes may be used as environmental sensors.

## ACKNOWLEDGMENTS

The authors acknowledge the financial support from CONACYT and also by SEP-CONACYT project 169634. A. Bejarano-Jiménez is grateful to CONACYT for the Master and International Research Stay Grants (No. 375980). The authors thank Herman van Leeuwen (Wageningen University, The Netherlands) for helpful discussions. The authors thank the technical assistance of Dulce Partida, Guillermo Vidriales, Juan Pablo Rodas, and Gladys Labrada from IPICYT. They also thank the Division de Ciencias Ambientales of IPICYT for the grant received for writing this article, and Jonathon Simon for checking the English language.

## REFERENCES

- Tang, Q.; Wu, J.; Sun, H.; Fan, S.; Hu, D.; Lin, J. *Polym. Compos.* **2009**, *30*, 1183.
- Van Leeuwen, H.; Cleven, R.; Buffle, J. *Pure Appl. Chem.* **1989**, *61*, 255.
- Peeret, S.; Morlay, C.; Cromer, M.; Vittori, A. *Water Res.* **2000**, *34*, 3614.
- Morlay, C.; Cromer, M.; Vittori, A. *Water Res.* **2000**, *34*, 455.
- Liu, Z.; Miao, Y.; Wang, Z.; Yin, G. *Carbohydr. Polym.* **2009**, *77*, 131.
- Elviraa, C.; Manoa, J. F.; San Románb, J.; Reisa, R. L. *Bio-materials* **2002**, *23*, 1955.
- Anamul Haque, Md.; Kurokawa, T.; Gong, J. P. *Polymer* **2012**, *53*, 1805.
- Li, A.; Wang, A.; Chen, J. *J. Appl. Polym. Sci.* **2004**, *94*, 1869.
- Bekiari, V.; Sotiropoulou, M.; Bokias, G.; Lianos, P. *Colloids Surf. A* **2008**, *312*, 214.
- Nursel, P.; Güner, A.; Güven, O. *J. Appl. Polym. Sci.* **2002**, *85*, 376.
- Safronov, A. P.; Shakhnovich, M.; Kalganov, A.; Kamalov, I. A.; Shklyar, T. F.; Blyakhman, F. A.; Pollack, G. H. *Polymer* **2011**, *52*, 2430.
- Ilavsk, M.; Fährnich, J.; Nedbal, J.; Bouchal, K. *Polym. Bull.* **1996**, *37*, 791.
- Schosseler, F.; Ilmain, F.; Candau, S. J. *Macromolecules* **1991**, *24*, 225.
- Kiatkamjornwong, S.; Wongwatthanasatien, R. *Macromol. Symp.* **2004**, *207*, 229.
- Kabiri, K.; Zohuriaan-Mehr, M. *J. Polym. Adv. Technol.* **2003**, *14*, 438.
- Harada, T.; Hirashima, Y.; Suzuki, A.; Goto, M.; Kawamura, N.; Tokita, M. *Eur. Polym. J.* **2005**, *41*, 2189.

17. Shen, J.; Yan, B.; Li, T.; Long, Y.; Li, N.; Ye, M. *Soft Matter* **2012**, 81831.
18. Zhu, Z. Q.; Sun, H. X.; Qin, X. J.; Jiang, L.; Pei, C. J.; Wang, L.; Zeng, Y. Q.; Wen, S. H.; , La P. Q.; Li, A.; Deng, W. Q. *J. Mater. Chem.* **2012**, 22, 4811.
19. Zhang, L.; Wang, Z.; Xu, C.; Li, Y.; Gao, J.; Wang, W.; Liu, Y. *J. Mater. Chem.* **2011**, 21, 10399.
20. Hu, N.; Wei, L.; Wang, Y.; Gao, R.; Chai, J.; Yang, Z.; Kong, E. S.-W.; Zhang, Y. *J. Nanosci. Nanotechnol.* **2012**, 12, 173.
21. Yang, Z.; Gao, R.; Hu, N.; Chai, J.; Cheng, Y.; Zhang, L.; Wei, H.; Kong, E. S.-W.; Zhang, Y. *Nano-Micro Lett.* **2012**, 4, 1.
22. Tai, Z.; Yang, J.; Qi, Y.; Yan, X.; Xue, Q. *RSC Adv.* **2013**, 3, 12751.
23. Dreyer, D. R.; Park, S.; Bielawski, C. W.; Ruoff, R. S. *Chem. Soc. Rev.* **2010**, 39, 228.
24. Švancara, I.; Vytras, K.; Kalcher, K.; Walcarius, A.; Wang, J. *Electroanalysis* **2009**, 1, 7.
25. Švancara, I.; Schachl, K. *Chem. Listy* **1999**, 9, 490.
26. Gismera, M. J.; Hueso, D.; Procopio, J. R.; Sevilla, M. T. *Anal. Chim. Acta* **2004**, 524, 347.
27. Svancara, I.; Vytras, K.; Barek, J.; Zima, J. *Crit. Rev. Anal. Chem.* **2001**, 31, 311.
28. Thobie-Gautier, C.; Lopes da Silva, W. T.; Rezende, M. O. O.; Murr, N. E. *J. Environ. Sci. Health Part A* **2003**, 38, 1811.
29. Boehm, H. P.; Diehl, E.; Heck, W.; Sappok, R. *Angew. Chem. Int. Ed. Engl.* **1964**, 3, 669.
30. Katime, I.; Rodríguez, E. *J. Macromol. Sci. Pure Appl. Chem.* **2001**, A38, 543.
31. Rangel-Mendez, J. R.; Streat, M. *Water Res.* **2002**, 36, 1244.
32. Pumera, M. *Chem. Soc. Rev.* **2010**, 39, 4146.
33. Kauppilaa, J.; Kunnas, P.; Damlin, P.; Viinikanoja, A.; Kvarnströma, C. *Electrochim. Acta* **2013**, 89, 84.
34. Mayoux, C.; Dandurand, J.; Ricard, A.; Lacabanne, C. *J. Appl. Polym. Sci.* **2000**, 77, 2621.