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Removal of Arsenic using a Cationic polymer gel impregnated with Iron Hydroxide

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Lyndsay Troyer, Ph.D.
Science Editor
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Dear Dr. Troyer:

Please find enclosed our manuscript entitled "Removal of Arsenic using a Cationic Polymer Gel Impregnated with Iron Hydroxide", which we would like to submit for publication as a video article in Journal of Visualized Experiments (JoVE).

Arsenic is a lethal contaminant of groundwater and industrial wastewater, which has direct negative effects on public health. Treatment processes to remove arsenic are urgently needed. Although, many researchers have developed adsorbents to remove arsenic, they are not effective in natural conditions, because of a lack of selectivity. Moreover, these adsorbents lack process simplicity and cost effectiveness. Our objective is to develop an adsorbent, a cationic polymer gel loaded with iron hydroxide, which can effectively adsorb arsenic, provide selectivity and simplify production processes. The gel is also cost-effective and reusable. In this paper, we discussed the unique preparation method of the gel composite. The uniqueness is that, we added $FeCl_3$ in the middle of the synthesis of the gel so as to ensure maximum content of FeOOH inside the gel structure. We found that the gel performs effectively at natural pH levels. Also, we examined the adsorption reaction kinetics. The arsenic adsorption isotherm of the gel was also discussed, and it matched well with Langmuir isotherm. We found the maximum adsorption capacity of arsenic adsorption by our gel is higher than the other methods. In addition, one of our objectives was to examine the selectivity of arsenic adsorption by the gel. According to the Hofmeister series, Sulphate ion precedes the other ions because of its ability to penetrate the headgroup region of the monolayer and thereby disrupting the hydrocarbon packing. Therefore, we examined the selective adsorption of arsenic in the presence of Sulphate ion. We found that, the gel's performance does not deviate even if high concentration of Sulphate is present in water. Hence, the gel can adsorb arsenic selectively from natural water. In addition, the regeneration process in this study is different than the other studies because, for the desorption process, NaOH is most commonly used. But, we used NaCl for desorbing arsenic because of the harmfulness of NaOH. And the regeneration process was continued for eight consecutive days successfully. This information will be of immediate interest to researchers investigating the treatment processes to remove arsenic from water sources. We believe that JoVE is the best platform to share our results with the viewers.

This study was funded by the JSPS KAKENHI Grant Number (26420764, JP17K06892). The authors have no conflicts of interest to declare. We would like to recommend the following reviewers to evaluate our manuscript:
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Please address all correspondence to: tgoto@hiroshima-u.ac.jp. We look forward to hearing from you at your earliest convenience.

Yours sincerely,
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TITLE:

Removal of Arsenic Using a Cationic Polymer Gel Impregnated with Iron Hydroxide

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KEYWORDS:

polymer, gel, hydrogel, composite, arsenic, water, treatment, adsorption, toxic, metal, iron, hydroxide.

SUMMARY:

In this work, we prepared an adsorbent composed of the cationic *N,N*-dimethylamino propylacrylamide methyl chloride quaternary (DMAPAAQ) polymer gel and iron hydroxide for adsorbing arsenic from groundwater. The gel was prepared via a novel method designed to ensure the maximum content of iron particles in its structure.

ABSTRACT:

In this work, we prepared an adsorbent composed of a cationic polymer gel containing iron hydroxide in its structure designed to adsorb arsenic from groundwater. The gel we selected was the *N,N*-dimethylamino propylacrylamide methyl chloride quaternary (DMAPAAQ) gel. The objective of our preparation method was to ensure the maximum content of iron hydroxide in the structure of the gel. This design approach enabled simultaneous adsorption by both the polymer structure of the gel and the iron hydroxide component, thus, enhancing the adsorption capacity of the material. To examine the performance of the gel, we measured reaction kinetics, carried out pH sensitivity and selectivity analyses, monitored arsenic adsorption performance, and conducted regeneration experiments. We determined that the gel undergoes a chemisorption process and reaches equilibrium at 10 h. Moreover, the gel adsorbed arsenic effectively at neutral pH levels and selectively in complex ion environments, achieving a maximum adsorption volume of 1.63 mM/g. The gel could be regenerated with 87.6% efficiency and NaCl could be used for desorption instead of harmful NaOH. Taken together, the presented gel-based design method is an effective approach for constructing high-performance arsenic adsorbents.

INTRODUCTION:

Water pollution is a great environmental concern, motivating researchers to develop methods for removing contaminants such as arsenic from wastewaster[1]. Among all the reported methods, adsorption processes are a relatively low cost approach for heavy metal removal[2–7]. Iron oxyhydroxide powders are considered to be one of the most efficient adsorbents for extracting arsenic from aqueous solutions[8,9]. Still, these materials suffer from a number of drawbacks, including early saturation times and toxic synthetic precursors. Additionally, there is a severe adverse effect in the water quality when these adsorbents are used for a long period of time[10]. An additional separation process, such as sedimentation or filtration, is then needed to purify the contaminated water, which increases the cost of the production further[8,11].

Recently, researchers have developed polymer gels such as cationic hydrogels, microgels, and cryogels that have demonstrated efficient adsorption properties. For example, an arsenic removal rate of 96% was achieved by the cationic cryogel, poly(3-acrylamidopropyl) trimethyl ammonium chloride [p(APTMACl)][12]. Additionally, at pH 9, approximately 99.7% removal efficiency was achieved by this cationic hydrogel[13]. At pH 4, 98.72 mg/g of maximum arsenic adsorption capacity was achieved by the microgel, based on tris(2-aminoethyl) amine (TAEA) and glyceroldiglycidyl ether (GDE), p(TAEA-co-GDE)[14]. Although these gels demonstrated good adsorption performances, they failed to effectively remove arsenic from water at neutral pH levels, and their selectivities in all studied environments were not reported[15]. A maximum adsorption capacity of 227 μg/g of was measured when Fe(III)-Sn(IV) mixed binary oxide-coated sand was used at a temperature of 313 K and a pH of 7[16]. Alternatively, Fe-Zr binary oxide-coated sand (IZBOCS) has also been used to remove arsenic and achieved a maximum adsorption capacity of 84.75 mg/g at 318 K and a pH of 7[17]. Other reported adsorbents suffer from low adsorption performances, lack of recyclability, low stability, high operational and maintenance costs, and the use of hazardous chemicals in the synthesis process[4].

We sought to address the above limitations by developing a material with improved arsenic adsorption performance, high selectivity in complex environments, recycling capability, and efficient activity at neutral pH levels. Therefore, we developed a cationic gel composite of *N,N*-dimethylamino propylacrylamide methyl chloride quaternary (DMAPAAQ) gel and iron(III) hydroxide (FeOOH) particles as an adsorbent for arsenic removal. We chose to combine FeOOH with our gel because FeOOH increases the adsorption of both forms of arsenic[18]. In this study, our gel composite was designed to be non-porous and was impregnated with FeOOH during preparation. In the next section, the details of the gel preparation method, including our strategy for maximizing the content of FeOOH is discussed further.

PROTOCOL:

CAUTION: Arsenic is extremely toxic. Please use gloves, long sleeve clothing, and experimental goggles at all times during the experiment to prevent any contact of arsenic solution with the skin and eyes. If arsenic comes into contact with any part of your body, wash it immediately with soap. Additionally, please clean up the experimental surroundings regularly so that you and others do not come into contact with arsenic, even when the experiment is not being performed. The symptoms of arsenic exposure may appear after a long period of time. Prior to cleaning the equipment, first rinse it with clean water and dispose the water separately into an experimental waste container designated for arsenic. Then, clean the equipment well with detergent. To prevent arsenic contamination of the environment, take precautions while disposing of arsenic samples. Dispose of them separately into experimental waste containers designated for arsenic. After the adsorption or desorption experiment is performed, the gels contain a high amount of arsenic. Therefore, dispose of the gels separately to a designated experimental waste bin for only arsenic-containing gels.

1. Synthesis of the DMAPAAQ+FeOOH gel composite

1.1. Dry two 20 mL measuring flasks and two 20 mL beakers equipped with magnetic stir bars.

1.2. Transfer 2.07 g of DMAPAAQ (75%), 0.15 g of *N,N'*-methylene bisacrylamide (MBAA), 0.25 g of sodium sulfite and 1.68 g of NaOH to one 20 mL beaker.

1.3. Dissolve the solution wholly in distilled water as 'solvent' and stirring it for 30 min with a magnetic stir bar.

1.4. Transfer the mixture from the beaker to one 20 mL measuring flask and add distilled water to generate a 20 mL solution. Label the solution as the "monomer solution".

1.5. Similarly, take 0.27 g of ammonium peroxodisulfate (APS) and 3.78 g of $FeCl_3$ in another 20 mL beaker.

1.6. Dissolve the solution completely in distilled water and stirring it for 30 min with a magnetic stir bar.

1.7. Transfer the mixture from the beaker to another 20 mL measuring flask and add distilled water to compose a 20 mL solution. Label the solution as the "initiator solution".

1.8. Prepare the experimental setup as shown in **Figure 1**.

1.9. Transfer the solutions into the respective 20 mL separating funnels.

1.10. Purge the solutions with N_2 gas for 10 min.

1.11. Mix the solutions together, stir them in a 50 mL test tube with an electric stirrer, and then place the mixture into a chiller maintained at 10 °C for 40 min.

1.12. Take out the gel block from the test tube and place it on a flat cutting board.

1.13. Cut the gel block into a cubic shape, 5 mm in length.

1.14. Soak the gel slices with de-ionized water for 24 h to remove the impurities.

1.15. After 12 h, replace the water and soak the gel slices again.

1.16. Spread the gel slices onto a Petri dish and dry them at room temperature for 24 h.

1.17. Place the Petri dish with the gel slices in the oven at 50 °C for 24 h.

2. pH sensitivity analyses

2.1. Dry nine 40 mL plastic containers.

2.2. Measure nine 20 mg dried gel pieces and put each of them in a separate 40 mL plastic container.

2.3. Add 20 mL of a 4 mM disodium hydrogenarsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) solution to each container.

2.4. To control the pH levels, add 20 mL of NaOH solution or HCL solution with different concentrations (0.1, 0.01, 0.001, 0.0001 M) in the respective containers to maintain pH levels of 2, 6, 8, 10, 12, 13 and label them.

2.5. Keep the containers in the stirrer at 20 °C and 120 rpm for 24 h.

2.6. Collect a 5 mL sample from each container and place each sample in a plastic tube using a micropipette.

2.7. Measure the equilibrium pH for all the samples.

2.8. Measure the remaining concentration of arsenic in the solution using a high performance liquid chromatography (HPLC). Use an analytical column (4 x 200 mm), a guard column (4 x 50 mm) and a 4 mm suppressor with the following conditions:

Flowrate: 1.5 mL/min;
Amount of injected sample: 10 μL;
Column temperature: 30 °C;
Eluent solution: 2.7 mM Na_2CO_3 and 0.3 mM $NaHCO_3$;
Pump pressure: 2000 psi;
Electric conductivity detection: Suppressor method.

NOTE: We procured 1 mL of the sample into a 1 mL single-use syringe. The syringe was coupled with a syringe membrane filter (pore size: 0.22 μm, diameter: 13 mm) to discrete the microscopic fragments of the gel from the sample. About 0.7 mL of sample was instilled into the column. Distilled water was infused before the inception of injecting the samples as blank sample. Peaks denoting the existence of arsenic in the sample was detected at 13 min.

CAUTION: After injecting the sample, please leave the syringe into the suction head of HPLC for nearly 2 min with roughly 0.2-0.3 mL of sample remaining in it. Because the dust and air could penetrate the column and alter its adeptness, which possibly will result in erroneous outcome.

3. Arsenic adsorption experiment

3.1. Dry five 40 mL plastic containers.

3.2. Measure and place 20 mg of dried gel in each 40 mL plastic container.

3.3. Add 40 mL of disodium hydrogenarsenate heptahydrate ($Na_2HAsO_4{\cdot}7H_2O$) solution to each container at the following concentrations: 0.1, 0.2, 0.5, 1, 2 mM.

3.4. Keep the containers in the stirrer at 20 °C and 120 rpm for 24 h.

3.5. Collect a 5 mL sample from each container and place in a plastic tube using a micropipette.

3.6. Follow step 2.8 to assess the equilibrium arsenic levels in the solutions using HPLC.

4. Selectivity analyses of the DMAPAAQ+FeOOH gel

4.1. Dry five 40 mL plastic containers.

4.2. Place 20 mg of dried gel in each of the five 40 mL plastic containers.

4.3. Add 20 mL of a 0.4 mM disodium hydrogenarsenate heptahydrate ($Na_2HAsO_4{\cdot}7H_2O$) solution to each container.

4.4. Add 20 mL at concentrations of 0.5, 1, 2, 5, 10 mM Na_2SO_4 to the five containers.

4.5. Keep the containers in the stirrer at 20 °C and 120 rpm for 24 h.

4.6. Collect a 5 mL sample from each container and place into separate plastic tubes using micropipettes.

4.7. Follow step 2.8 to quantify the remaining concentration of arsenic in the solution using HPLC.

5. Equilibrium rate analyses

5.1. Dry seven 40 mL plastic containers.

5.2. Place 20 mg of dried gel in each of the 40 mL plastic containers.

5.3. Add 40 mL of a 0.2 mM disodium hydrogenarsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) solution to each of the containers.

5.4. Keep the containers in the stirrer at 20 °C at 120 rpm for the duration of their designated times.

5.5. Collect 5 mL samples in plastic tubes using micropipettes after 0.5, 1, 3, 7, 11, 24, and 48 h.

5.6. Follow step 2.8 to determine the equilibrium arsenic level in each solution using HPLC.

6. Regeneration analysis

6.1. Adsorption analysis

6.1.1. Dry a 40 mL plastic container.

6.1.2. Take 20 mg of dried gel and place it in the 40 mL plastic container.

6.1.3. Add 40 mL of a 0.2 mM disodium hydrogenarsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) solution to the container.

6.1.4. Keep the container in the stirrer at 20 °C and 120 rpm for 24 h.

6.1.5. Collect a 5 mL sample in a plastic tube using a micropipette.

6.1.6. Refer to step 2.8 to evaluate the equilibrium arsenic level in the solution using HPLC.

6.2. Cleaning the gel

6.2.1. Obtain a mesh sieve.

6.2.2. Carefully collect the gel pieces one at a time so that they do not break and place them in the mesh sieve.

6.2.3. Wash the gel several times (minimum five times) using de-ionized water so that any remaining arsenic on the surface of the gel is washed away.

CAUTION: The gel pieces are fragile. Handle them with care while washing and transferring them from the arsenic solution to the NaCl solution.

6.3. Desorption analyses

6.3.1. Dry a 40 mL plastic container.

6.3.2. Put the gel pieces from step 6.2 into a 40 mL plastic container.

6.3.3. Add 40 mL of a 0.5 M NaCl solution to the container.

6.3.4. Keep the container in the stirrer at 20 °C and 120 rpm for 24 h.

6.3.5. Collect a 5 mL sample in a plastic tube using a micropipette.

6.3.6. Follow the step 2.8 to evaluate the equilibrium arsenic level in the solution using HPLC.

6.4. Repetition of the process

6.4.1. After collecting the gel from step 6.3, repeat the process in the following sequence for eight complete cycles: 6.2 > 6.1 > 6.2 > 6.3 > 6.2 > 6.1 > 6.2 > 6.3.

REPRESENTATIVE RESULTS:

Figure 1 describes the experimental setup for the preparation of the DMAPAAQ+FeOOH gel. **Table 1** illustrates the compositions of the materials involved in the preparation of the gel.

Figure 2 shows the relation of contact time with the adsorption of arsenic by the DMAPAAQ+FeOOH gel. In the figure, the amount of adsorption of arsenic was examined at 0.5, 1, 3, 7, 11, 24, and 48 h. The results show that the adsorption of arsenic reaches its equilibrium after 10 h, and after 24 h of adsorption, minimal increase in the amount of adsorption of arsenic was detected.

Figure 3a,b shows the pseudo first order and pseudo second order reaction kinetics for arsenic adsorption by the DMAPAAQ+FeOOH gel. The results suggest that the correlation coefficients (R^2) for pseudo first order and pseudo second order were 0.866 and 0.999, respectively.

Figure 4 shows the pH sensitivity of the DMAPAAQ+FeOOH gel. The same amount of dry DMAPAAQ+FeOOH gel (20 mg) was immersed in arsenic solutions (0.2 mM) at different pH levels for 24 h at 20 °C and 120 rpm. The results suggest that the adsorption of arsenic was high at low and neutral pH levels and low at high pH levels.

Figure 5 shows the adsorption performance of DMAPAAQ+FeOOH. The same amount of dry DMAPAAQ+FeOOH gel (20 mg) was immersed in different arsenic solution concentrations (0.1, 0.2, 0.5. 1, 2 mM) at 20 °C and 120 rpm for 24 h. The results show that the maximum arsenic adsorption capacity of the DMAPAAQ+FeOOH gel was 1.63 mM/g. The data were also consistent with the Langmuir isotherm.

Figure 6 shows the selectivity analysis of the DMAPAAQ+FeOOH gel. The same amount of dry DMAPAAQ+FeOOH gel (20 mg) was immersed in the arsenic solution (0.2 mM) with different SO_4^{2-} concentrations (1, 2, 5, 10, 20 mM) at 20 °C and 120 rpm for 24 h. The analysis shows that the adsorption amount of arsenic decreased slightly with an increase in SO_4^{2-} concentration; however, the change was small, and at high concentrations of SO_4^{2-}, the gel still adsorbed arsenic effectively.

Figure 7 shows the regeneration experiment of the DMAPAAQ+FeOOH gel. The same amount of dry gel (20 mg) was used for eight consecutive days of experimentation. The experiment was conducted using a 0.2 mM arsenic solution at 20 °C and 120 rpm for 24 h. To perform the desorption process, the gel was then washed and immersed into a 0.5 M NaCl solution at 20 °C and 120 rpm for 24 h. The gel was regenerated successfully after eight days of continuous adsorption-desorption cycles. We calculated the regeneration efficiency from the adsorption data on day 1 and day 7; a regeneration efficiency of 87.6% was achieved.

FIGURE AND TABLE LEGENDS:

Table 1: Composition of the DMAPAAQ+FeOOH gel. This table has been adopted from *Chemosphere* [**217**, 808–815, doi: 10.1016/j.chemosphere.2018.11.050 (2019)][15] and details the materials used in preparing the DMAPAAQ+FeOOH gel.

Figure 1: Experimental setup for preparing the DMAPAAQ+FeOOH gel. This figure shows the arrangement of equipment for preparing the DMAPAAQ+FeOOH gel. Since our preparation method is unique, this figure will help researchers replicate our setup.

Figure 2: Relating the contact time with the adsorption amount between the DMAPAAQ+FeOOH gel and arsenic solution. This figure has been modified from *Chemosphere* [**217**, 808–815, doi: 10.1016/j.chemosphere.2018.11.050 (2019)][15] and shows the relationship between the adsorption amount of arsenic by the DMAPAAQ+FeOOH gel and the contact time. Additionally, it illustrates the time required for the gel to reach its adsorption equilibrium.

Figure 3: Arsenic adsorption reaction kinetics of the DMAPAAQ+FeOOH gel. (a) Pseudo first order. (b) Pseudo second order. This figure has been modified from *Chemosphere* [**217**, 808–815, doi: 10.1016/j.chemosphere.2018.11.050 (2019)][15] and shows the suitability of the kinetic model to the DMAPAAQ+FeOOH gel.

Figure 4: pH sensitivity analysis of the DMAPAAQ+FeOOH gel. This figure has been adopted from *Chemosphere* [**217**, 808–815, doi: 10.1016/j.chemosphere.2018.11.050 (2019)][15] and shows the results of the pH sensitivity analysis of the DMAPAAQ+FeOOH gel in arsenic solutions.

Figure 5: Adsorption performance of the DMAPAAQ+FeOOH gel. This figure has been modified from *Chemosphere* [**217**, 808–815, doi: 10.1016/j.chemosphere.2018.11.050 (2019)][15] and shows the arsenic adsorption amount by the DMAPAAQ+FeOOH gel at different concentrations of arsenic and the fitting of these data with the Langmuir isotherm model.

Figure 6: Selectivity analysis of the DMAPAAQ+FeOOH gel. This figure has been modified from *Chemosphere* [**217**, 808–815, doi: 10.1016/j.chemosphere.2018.11.050 (2019)][15] and shows the

arsenic adsorption selectivity of the DMAPAAQ+FeOOH gel in the presence of different concentrations of sulfate ions.

Figure 7: Regeneration analysis of the DMAPAAQ+FeOOH gel. This figure has been adopted from *Chemosphere* [**217**, 808–815, doi: 10.1016/j.chemosphere.2018.11.050 (2019)][15]. The reusability of the DMAPAAQ+FeOOH gel was examined for eight continuous days using arsenic solutions for adsorption and NaCl for desorption processes.

DISCUSSION:

The main advancement of our developed method is the unique design strategy of the gel composite. The purpose of our gel preparation method was to maximize the amount of iron content in the gel. During the preparation, we added $FeCl_3$ and NaOH to the “initiator solution” and the “monomer solution,” respectively. Once the monomer solution was mixed with the initiator solution, there was a reaction between $FeCl_3$ and NaOH, producing FeOOH inside the gel. This phenomenon ensured maximum iron content in the gel composite. Despite the advantages of this method, the gel does not form under the following conditions: 1) When the solutions are not mixed thoroughly; 2) When the amount of $FeCl_3$ exceeds 700 mol/m^3 or the initiator, APS, and the accelerator, sodium sulfite, are lower.

If the gel does not form, add the initiator and accelerator gradually and mix the solution thoroughly. If the amount of initiator and accelerator are too high, the polymer structure of the gel differs, and the desired performance cannot be achieved. When the gel starts forming, stop mixing it to avoid distorting the gel.

Previous studies have reported ineffective adsorption of arsenic at neutral pH levels. Thus, the pH sensitivity experiment in the present work was important for indicating the practical applicability of the developed gel. Our studies demonstrate that the gel adsorbed arsenic effectively and was regenerated by NaCl at neutral pH levels. Although the adsorption amount of arsenic was high at acidic pH values and low at basic pH values, the adsorption was effective at neutral pH levels (**Figure 4**). To assess the adsorption behavior under real-life conditions, we conducted other experiments at neutral pH levels.

The relationship between the gel/arsenic solution contact times and arsenic adsorption amount was studied. The DMAPAAQ+FeOOH gel achieved adsorption equilibrium at 10 h (**Figure 2**). Additionally, we examined the rate of adsorption by the DMAPAAQ+FeOOH gel with the two kinetic models, pseudo first order and pseudo second order (**Figure 3a,b**). The correlation coefficients (R^2) denoted the similarity between the experimental values and calculated values. We found that the R^2 value was higher for the pseudo second order reaction kinetics. This finding suggests that the adsorption between the arsenic solution and DMAPAAQ+FeOOH gel is a chemisorption process[19].

We performed the adsorption performance analyses at neutral pH levels. 20 mg of dry gel was immersed in the arsenic solution for 24 h at different concentrations of As(V). **Figure 5** shows the amounts of arsenic adsorbed by the DMAPAAQ+FeOOH gel. These results were consistent with the Langmuir isotherm model of adsorption. The maximum adsorption amount by the gel reached 1.63 mM/g (**Figure 5**). Notably, the developed gel outperformed previously reported adsorbents studied at neutral pH levels. We rationalize this observation by the unique structure of the gel, which enables simultaneous arsenic adsorption by both the DMAPAAQ and FeOOH units. We found that 35.5% of arsenic was adsorbed by the amino group of the DMAPAAQ+FeOOH composite and 64.4% of arsenic was adsorbed by FeOOH particles[15]. During the adsorption process, make sure that the gel is immersed into the arsenic solution completely. The high levels of arsenic adsorption by the current gel over conventional and recently studied materials demonstrate its promising utility as a highly efficient adsorbent.

Selectivity is an important property of an adsorbent because there are many competing ions in water, including Cl^-, HS^-, SO_3^{2-}, SO_4^{2-}, H_2CO_3, HCO_3^-, and CO_3^{2-} [20]. The Hofmeister series suggests that the sulfate ion (SO_4^{2-}) can disrupt hydrocarbon packing and penetrate the headgroup region of the monolayer of an adsorbent[21]. The concentration of sulfate in groundwater has been determined to be as high as 230 mg/L[22]. Therefore, if the developed gel can selectively adsorb arsenic with sulfate as a competing ion, it may be suitable for treating environmental groundwater. Thus, selectivity analyses with sulfate ions were performed and showed that the DMAPAAQ+FeOOH gel adsorbed arsenic effectively at high concentrations of sulfate (**Figure 6**). Since the adsorption amount of arsenic was similar in the absence or presence of sulfate ions, the gel may perform as effectively in groundwater as in the laboratory.

Regeneration is an important feature of any practical adsorbent because it ensures cost reductions, eco-friendliness, and usability[23]. The developed gel was regenerated successfully for eight consecutive days of experimentation (**Figure 7**). Additionally, 87.6% regeneration efficiency was achieved when the same gel was used for all eight adsorption-desorption cycles. One of the most important findings of our research was the use of NaCl in the desorption process. While NaOH is conventionally used for desorption, it can be harmful to human health. Therefore, we substituted NaOH for NaCl in our studies, which had not been reported previously.

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DISCLOSURES:

The authors have nothing to disclose.

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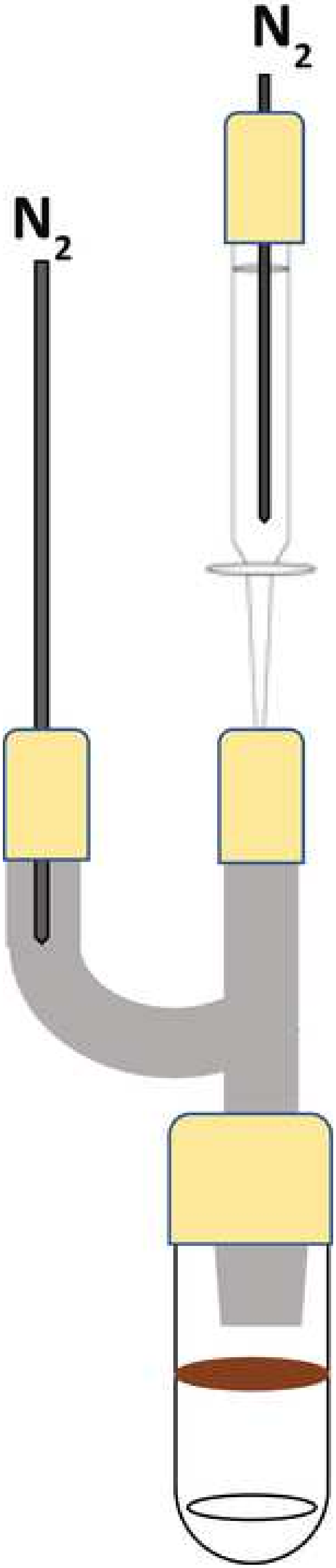
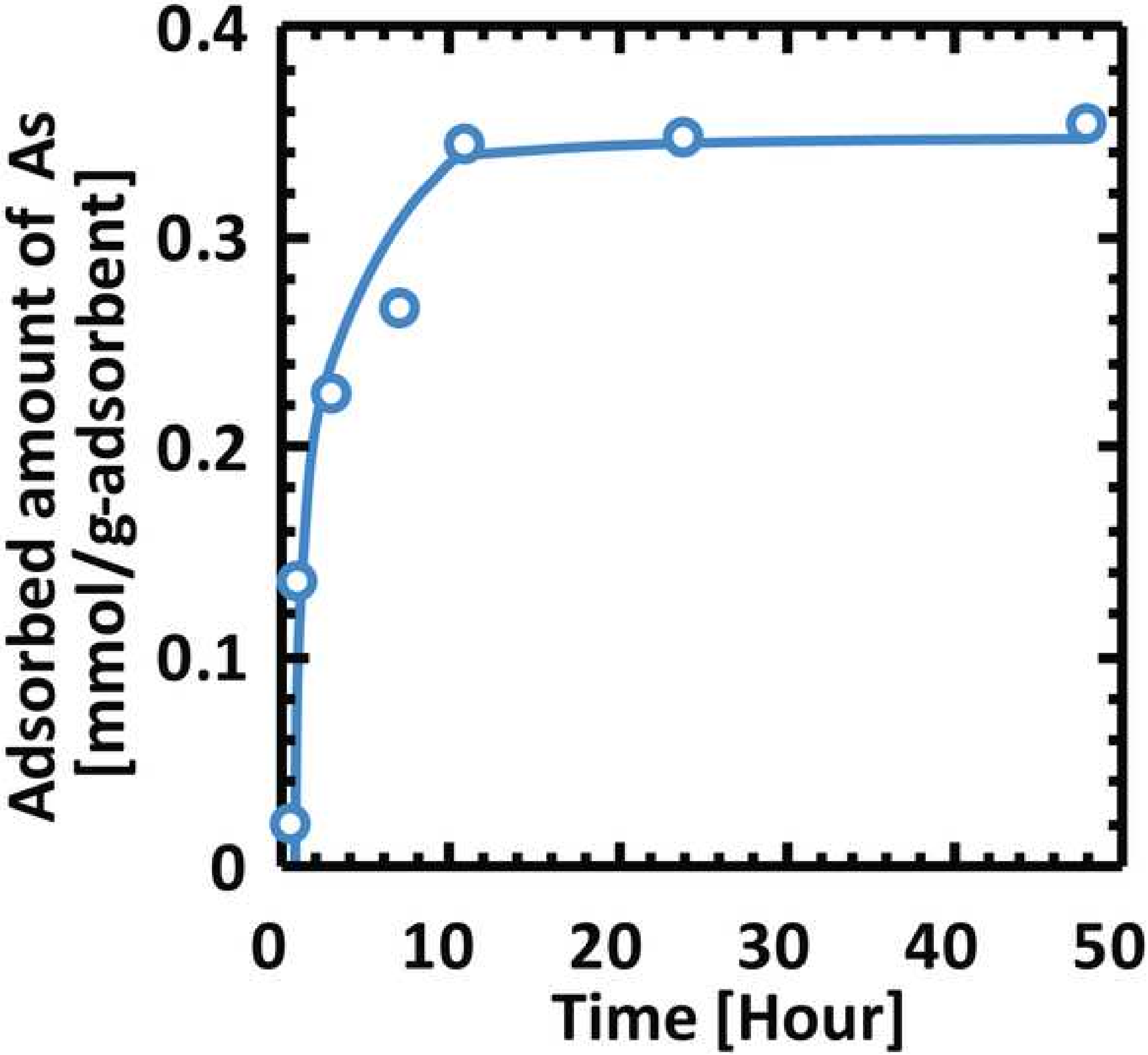

N_2
N_2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10
20
30
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50
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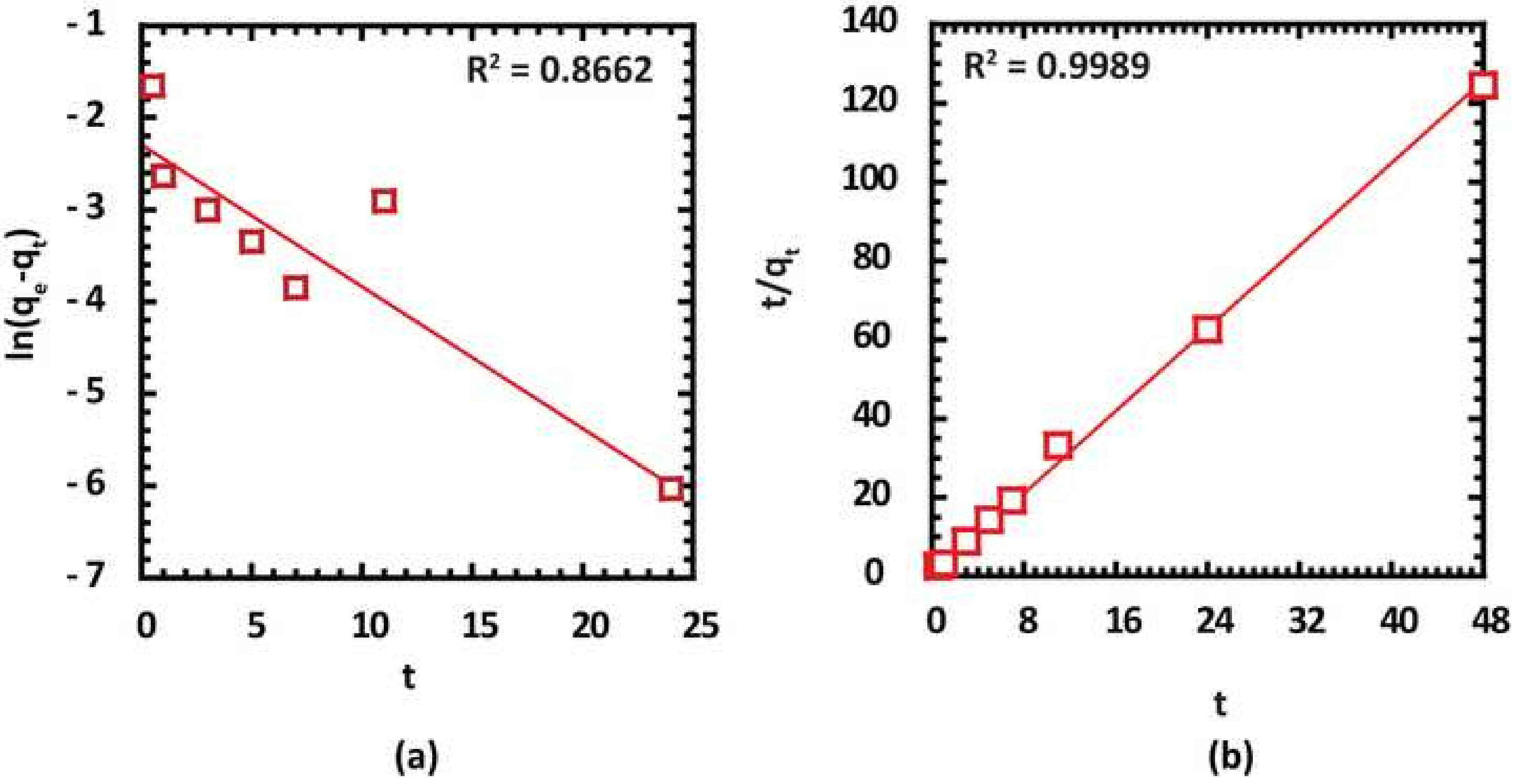
[mmol/g-adsorbent]


- 1
- 2
- 3
- 4
- 5
- 6
- 7
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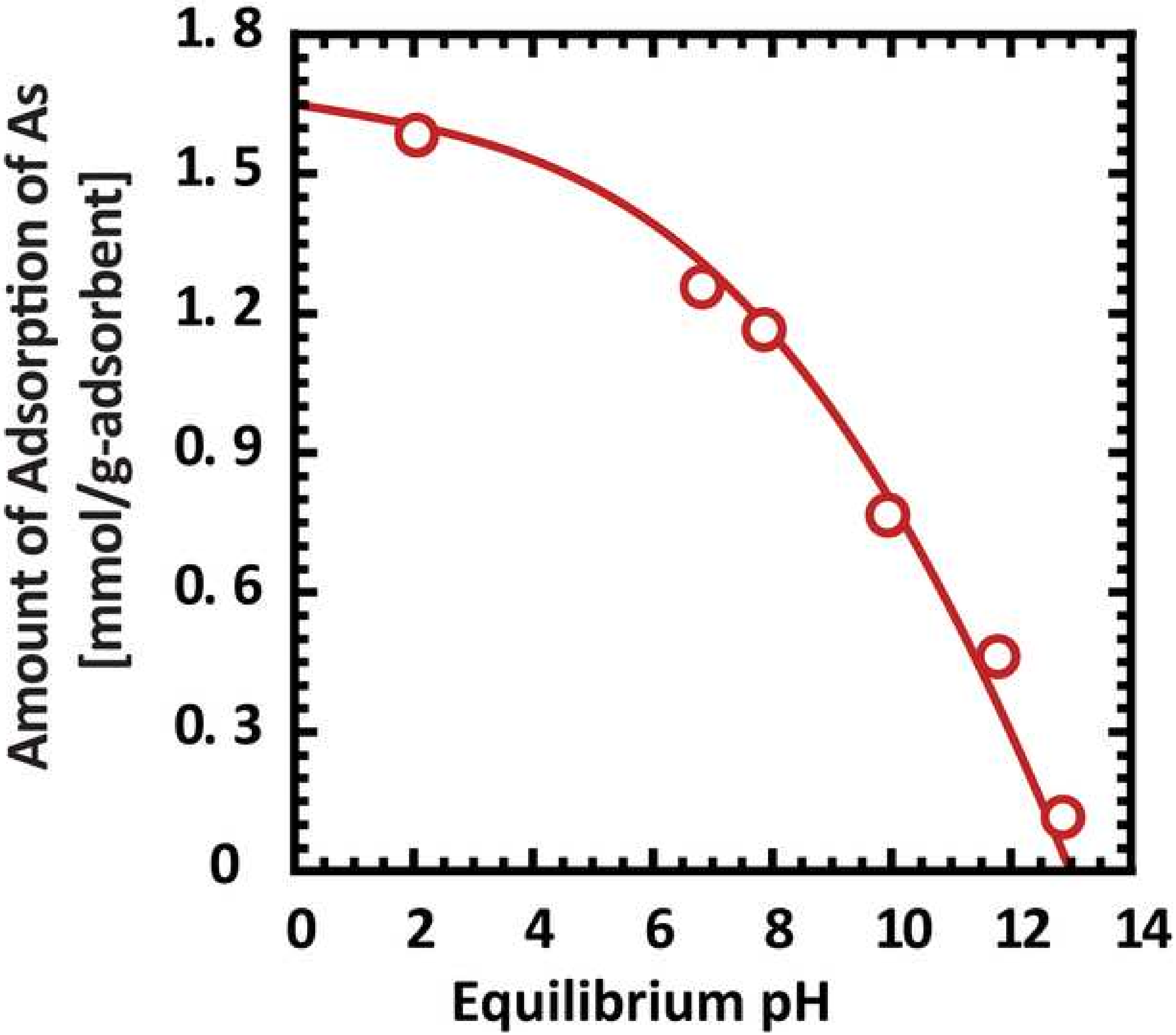
5
10
15
20
25
t
(a)
140
120
100
80
60
40
20
0
t/q_t
$R^2 = 0.9989$
0
8
16
24
32
40
48
t
(b)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1. 5
1. 2
0. 9
0. 6
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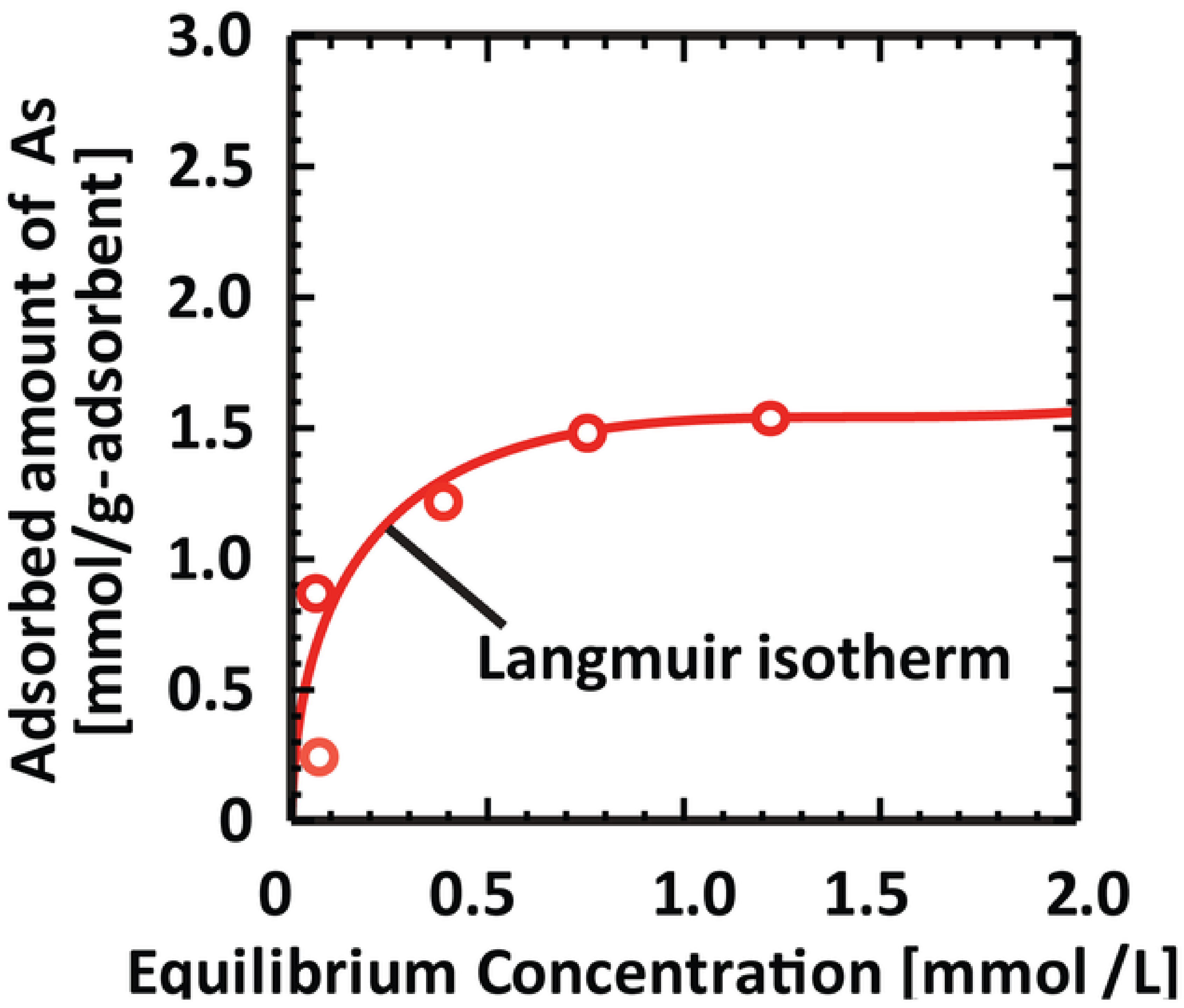
[mmol/g-adsorbent]
Equilibrium pH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2.5
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1.0
0.5
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Langmuir isotherm
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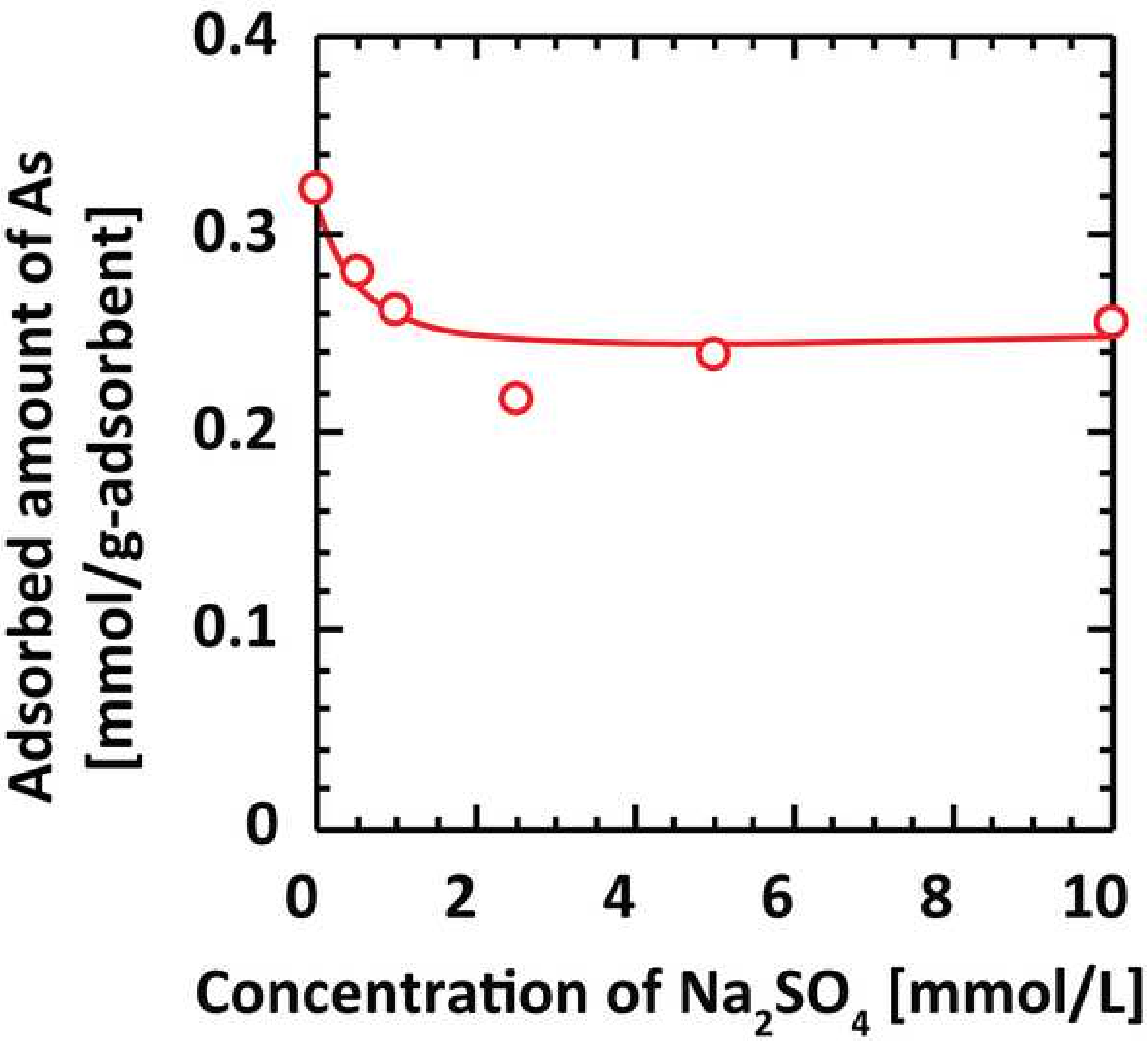
0.5
1.0
1.5
2.0
Equilibrium Concentration [mmol /L]


Adsorbed amount of As [mmol/g-adsorbent]
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8
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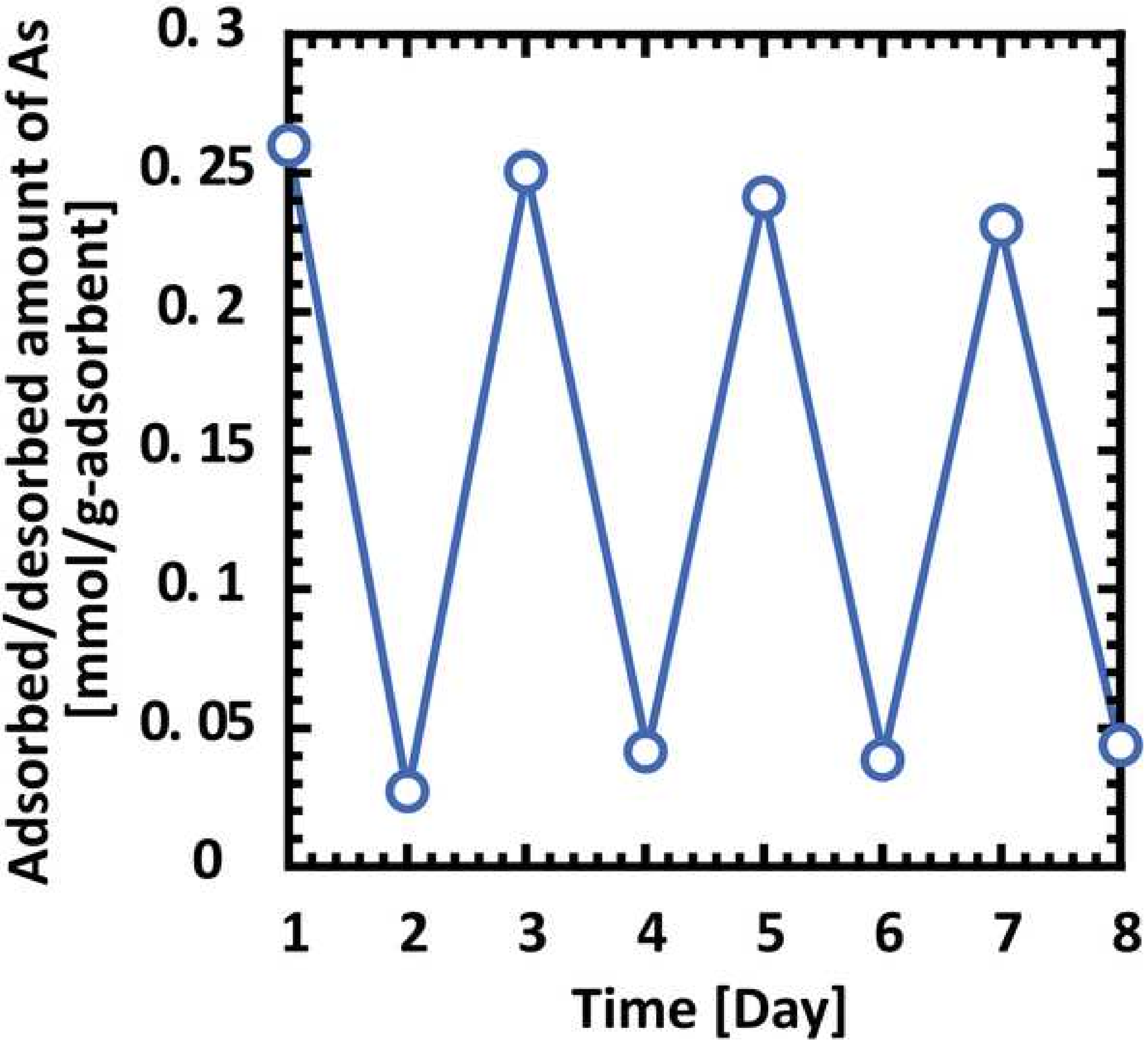
Concentration of Na_2SO_4 [mmol/L]


Adsorbed/desorbed amount of As
[mmol/g-adsorbent]
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0. 25
0. 2
0. 15
0. 1
0. 05
0
1
2
3
4
5
6
7
8
Time [Day]

	Chemical	**Quantity (mol/m^3)**
Monomer	DMAPAAQ	500
Crosslinker	MBAA	50
Accelerator	Sodium Sulfite	80
	Sodium Hydroxide (NaOH)	2100
Initiator	Ammonium peroxodisulfate (APS)	30
	Ferric Chloride ($FeCl_3$)	700

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
N,N' -dimethylamino propylacrylamide, methyl chloride quaternary (DMAPAAQ) (75% in H_2O)	KJ Chemicals Corporation, Japan	150707	
N,N' -Methylene bisacrylamide (MBAA)	Sigma-Aldrich, USA	1002040622	
Sodium sulfite (Na_2SO_3)	Nacalai Tesque, Inc., Japan	31922-25	
Sodium sulfate (Na_2SO_4)	Nacalai Tesque, Inc., Japan	31916-15	
Di-sodium hydrogenarsenate heptahydrate($Na_2HAsO_4.7H_20$)	Nacalai Tesque, Inc., Japan	10048-95-0	
Ferric chloride($FeCl_3$)	Nacalai Tesque, Inc., Japan	19432-25	
Sodium hydroxide(NaOH)	Kishida Chemicals Corporation, Japan	000-75165	
Ammonium peroxodisulfate (APS)	Kanto Chemical Co. Inc., Japan	907W2052	
Hydrochloric acid (HCl)	Kanto Chemical Co. Inc., Japan	18078-01	
Sodium Chloride (NaCl)	Nacalai Tesque, Inc., Japan	31320-05	

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Author(s):	Syed Ragib Safi, Takehiko Gotoh, Takashi Iizawa, Satoshi Nakai

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Responses to The Editorial Comments

We are thankful to the Review Editor, Dr. Bing Wu, for reviewing the manuscript carefully and providing insightful comments. Followings are the responses (in black) to each comment. The revised parts of the manuscripts are shown after the original part. The changes made in the manuscript are marked with different colors. The deducted parts from the original manuscript are shown in red, and the added parts in the revised manuscript are shown in blue.

Editorial comment: *The manuscript has been modified and the updated manuscript, **59728_R2.docx**, is attached and located in your Editorial Manager account. **Please use the updated version to make your revisions.***

Response : We would like to thank the Editor for the modification and updating the manuscript. We used the updated version and made revisions on it.

Editorial comment 1: *Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.*

Response 1: We sincerely thank the Editor to suggest us to thoroughly proofread the manuscript to get rid of spelling and grammatical mistakes. We believe that it is a chance to improve our manuscript by correcting any grammatical, typing mistakes and improving the English language. However, we could not find any mistake to the manuscript after checking it thoroughly. Previously, we got our manuscript checked by Enago English language editing service. It helped us to solve the problem of grammatical and typing errors and improved the English language usage in the manuscript.

Editorial comment 2: *Step 1.2: Please specify the solvent and the amount of solvent used to dissolve the reagents.*

Editorial comment 3: *1.3: Please specify the solvent and the amount of solvent used to dissolve the reagents.*

Response 2 and 3: We are tankful to the Editor's kind suggestion and giving us an opportunity to improve the manuscript by specifying the solvent and the amount. We apologize to the Editor, as before the initial submission, we should have defined the solvent and it's amount. However, we utilized this opportunity to rectify the mistake.

Original text

(Line no. 101-107, Page no. 3)

1.2. Transfer 2.07 g of DMAPAAQ (75%), 0.15 g of *N,N'*-methylene bisacrylamide (MBAA), 0.25 g of sodium sulfite, 1.68 g of NaOH to the 20 mL beaker and dissolve the solution well by stirring it for 30 min with a magnetic stir bar. Label the solution as the "monomer solution".

1.3. Similarly, take 0.27 g of ammonium peroxodisulfate (APS) and 3.78 g $FeCl_3$ in another 20 mL beaker and dissolve the solution well by stirring it for 30 min with a magnetic stir bar. Label the solution as the “initiator solution”.

Revised text
(Line no. 101-117, Page no. 2)

1.2. Transfer 2.07 g of DMAPAAQ (75%), 0.15 g of *N,N'*-methylene bisacrylamide (MBAA), 0.25 g of sodium sulfite, 1.68 g of NaOH to the 20 mL beaker.

1.3. Dissolve the solution wholly by combining distilled water as ‘solvent’ and stirring it for 30 min with a magnetic stir bar.

1.4. Shift the mixture from the beaker to the 20 mL measuring flask and add distilled water to generate a 20 mL solution. Label the solution as the “monomer solution”.

1.5. Similarly, take 0.27 g of ammonium peroxodisulfate (APS) and 3.78 g $FeCl_3$ in another 20 mL beaker.

1.6. Dissolve the solution completely by combining distilled water and stirring it for 30 min with a magnetic stir bar.

1.7. Relocate the mixture from the beaker to the 20 mL measuring flask and add distilled water to compose a 20 mL solution. Label the solution as the “initiator solution”.

Editorial comment 4: *2.3: What is the As(V) solution? Please specify.*

Response 4: We are appreciative to the Editor for lending us the chance to improve our manuscript. We revised the text by specifying the As(V) solution.

Original text
(Line no. 140, Page no. 3)
2.3. Add 20 mL of a 4 mM As(V) solution to each container.

Revised text
(Line no. 188-189, Page no. 3)
2.3. Add 20 mL of a 4 mM Disodium hydrogenarsenate heptahydrate ($Na_2HAsO_4.7H_2O$) solution to each container.

Original text
(Line no. 162-163, Page no. 3)
3.3. Add 40 mL As(V) solution to each container at the following concentrations: 0.1, 0.2, 0.5, 1, 2 mM.

Revised text

(Line no. 237-238, Page no. 4)

3.3. Add 40 mL Disodium hydrogenarsenate heptahydrate ($Na_2HAsO_4.7H_2O$) solution to each container at the following concentrations: 0.1, 0.2, 0.5, 1, 2 mM.

Original text

(Line no. 177, Page no. 4)

4.3. Add 20 mL of a 0.4 mM As(V) solution to each container.

Revised text

(Line no. 252-253, Page no. 4)

4.3. Add 20 mL of a 0.4 mM Disodium hydrogenarsenate heptahydrate ($Na_2HAsO_4.7H_2O$) solution to each container.

Original text

(Line no. 194, Page no. 4)

5.3. Add 40 mL of As(V) solution to each container.

Revised text

(Line no. 281-282, Page no. 5)

5.3. Add 40 mL of a 0.2 mM Disodium hydrogenarsenate heptahydrate ($Na_2HAsO_4.7H_2O$) solution to each of the containers.

Original text

(Line no. 212, Page no. 4)

6.1.3. Add 40 mL of a 0.2 mM As(V) solution to the container.

Revised text

(Line no. 300-301, Page no. 5)

6.1.3. Add 40 mL of a 0.2 mM Disodium hydrogenarsenate heptahydrate ($Na_2HAsO_4.7H_2O$) solution to the container.

Editorial comment 5: *3.6: Please add more details to your protocol steps. Please ensure you answer the "how" question, i.e., how is the step performed? Alternatively, add references to published material specifying how to perform the protocol action.*

Response 5: We are gratified to the Editor for providing us the opportunity to further improve our manuscript by adding more details to our protocol steps. We added the text of how we performed the action.

Original text

(Line no. 153-154, Page no. 3)

2.8. Measure the remaining concentration of As(V) in the solution using High Performance

Liquid Chromatography (HPLC).

Revised text

(Line no. 202-229, Page no. 3-4)

2.8. Measure the remaining concentration of arsenic in the solution using a Dionex ICS-1100 High Performance Liquid Chromatography (HPLC). We utilized Dionex IonPac AS12A (4 X 200 mm) analytical column, Dionex IonPac AG12A (4 X 50 mm) guard column and Dionex AERS 500 4mm suppressor with the following conditions:

Flowrate: 1.5 mL/min;
Amount of injected sample: 10 µL;
Column temperature: 30 °C;
Eluent solution: 2.7 mM Na_2CO_3 and 0.3 mM $NaHCO_3$;
Pump pressure: 2000 psi;
Electric conductivity detection: Suppressor method.

We procured 1mL of sample into a 1mL single-use syringe. The syringe was coupled with a syringe membrane filter (pore size: 0.22 µm, diameter: 13 mm) to discrete the microscopic fragments of the gel from the sample. About 0.7 mL of sample was instilled into the column. Distilled water was infused before the inception of injecting the samples as blank sample. Peaks denoting the existence of arsenic in the sample was detected at 13 min.

CAUTION: After injecting the sample, please leave the syringe into the suction head of HPLC for nearly 2 min with roughly 0.2-0.3 mL sample remaining in it. Because the dust and air could penetrate the column and alter it's adeptness, which possibly will result in erroneous outcome.

Original text

(Line no. 169, Page no. 4)

3.6. Measure the equilibrium arsenic levels in the solutions using HPLC.

Revised text

(Line no. 244, Page no. 4)

3.6. Follow step 2.8 to assess the equilibrium arsenic levels in the solutions using HPLC.

Original text

(Line no. 186, Page no. 4)

4.7. Measure the remaining concentration of As(V) in the solution using HPLC.

Revised text

(Line no. 262, Page no. 4)

4.7. Follow step 2.8 to quantify the remaining concentration of arsenic in the solution using HPLC.

Original text

(Line no. 202, Page no. 5)
5.6. Measure the equilibrium arsenic level in each solution using HPLC.

Revised text

(Line no. 290, Page no. 5)
5.6. Follow step 2.8 to determine the equilibrium arsenic level in each solution using HPLC.

Original text

(Line no. 218, Page no. 5)
6.1.6. Measure the equilibrium arsenic level in the solution using HPLC.

Revised text

(Line no. 307, Page no. 5)
6.1.6. Refer to step 2.8 to evaluate the equilibrium arsenic level in the solution using HPLC.

Original text

(Line no. 245, Page no. 6)
6.3.6. Measure the equilibrium arsenic level in the solution using HPLC.

Revised text

(Line no. 338, Page no. 6)
6.3.6. Follow the step 2.8 to evaluate the equilibrium arsenic level in the solution using HPLC.

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