



## Article

# Removal of Arsenic(III) from Water with a Combination of Graphene Oxide (GO) and Granular Ferric Hydroxide (GFH) at the Optimum Molecular Ratio

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**Abstract:** The occurrence of arsenic in water is a global problem for public health. Several removal technologies have been developed for arsenic removal from water, and adsorption onto iron oxyhydroxides is the most widely used technique. Granular ferric hydroxide (GFH) has been used mainly for As(V) removal, but it has the disadvantage that it can create a problem with the residual concentration of iron in the water. Moreover, graphene oxide (GO), which contains a large amount of reactive oxygen, exhibits high adsorbing capacity. In this study, the combined use of GO and GFH as adsorbent materials in different molar ratios was investigated in order to achieve the maximum As(III) removal from aqueous solutions. The effect of the adsorbent's dosage, pH value, contact time, initial As(III), and different molar ratios of GO/GFH was examined. As depicted, the presence of GFH enhances the use of GO. In particular, the molar ratio of GO/GFH 2:1 (i.e., 0.2 g/L GO and 0.1 g/L GFH) is chosen as optimal at pH value  $7.0 \pm 0.1$ , while the removal percentage increased from 10% (absence of GFH) to 90% with the simultaneous addition of GFH. Freundlich isotherm and pseudo-second-order kinetic models described the experimental data adequately and the highest adsorption capacity that was achieved was 22.62  $\mu\text{g/g}$ .

**Keywords:** arsenic; GFH; graphene oxide; adsorption



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## 1. Introduction

Arsenic belongs to the metalloid elements and appears in water with two oxidation states, found as oxyanions, as arsenate [As(V)] ( $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HASO}_4^{2-}$ , or  $\text{AsO}_4^{3-}$ ), or arsenite [As(III)] ( $\text{H}_3\text{AsO}_3$ ,  $\text{H}_2\text{AsO}_3^-$ , and  $\text{HASO}_3^{2-}$ ) [1], with As(III) being about 60 times more toxic than As(V) [2]. According to the World Health Organization (WHO), the maximum permissible concentration of As in drinking water is 10  $\mu\text{g/L}$  [3], while extended consumption of arsenic-containing waters leads to several health effects, such as cancer of skin, lungs, and bladder [3].

Therefore, because arsenic is hazardous to human health and occurs in large concentrations, above WHO drinking water standard limits, in many regions around the world, such as India, Bangladesh, Pakistan, Cambodia, Argentina [4–6], and others, the need to remove it from water becomes imperative. Several removal technologies [7] have been developed for arsenic removal from water, such as adsorption with activated carbons [8], coagulation [9], membranes [10,11], molecularly imprinted polymers (MIPs) [12], etc. Iron coagulation—filtration and adsorption onto iron oxyhydroxides are the most widely used techniques [9,13–17]. In many cases, there is a need for a peroxidation step to oxidize As(III) into As(V). Hence, chemical oxidants such as chlorine, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), ozone ( $\text{O}_3$ ), permanganate, hypochlorite, monochloramine, and persulfate-based systems were frequently employed to oxidize As(III) to As(V) [18–21]. On the other hand, iron oxides and

oxy-hydroxides (FeOOH) have been intensively studied as adsorbents for several years for the purification of water [18–23].

Granular ferric hydroxide (GFH), a usual porous iron adsorbent, is commercially available and commonly considered for arsenic removal [16,24,25] under both laboratory-scale and full-scale water treatment plants [24]. Several times, a powdered-sized fraction of iron-oxide-based adsorptive material was deposited on the surface of a microfiltration (MF) membrane [16]; however, this application might be increasing the cost of processing with the use of membrane.

Although GFH has a lot of applications, some disadvantages cannot be avoided while using it, such as the addition of iron to water and the relative residual concentration. When iron is present in water in higher concentrations than the limits (0.2 mg/L) [26], this has impacts on water quality, such as (a) giving water a reddish color when exposed to air, (b) giving water a nasty metallic taste, and (c) domestic pipes being clogged by iron precipitates [27]. In addition, kinetic studies with GFH suggested slow kinetics from 3 to 415 days, leading to a diffusion-controlled transport process that limits the rate of arsenic adsorption [28].

On the other hand, graphene, a two-dimensional structure, since its discovery in 2004 [29], has attracted researchers [30–33] while exhibiting a flexible, porous structure and high chemical stability. Oxidation of graphite leads to the eventual formation of graphene oxide (GO), which contains a large amount of reactive oxygen due to the presence of epoxy, carboxyl, and hydroxyl groups [34]. The benefits of using GO as a reactant in aqueous solution are its hydrophilicity because of these groups and its adsorbing capacity of several contaminants onto the benzene ring by the strong  $\pi$ - $\pi$  interaction [35].

In the present study, the main aim was to combine the two materials, i.e., graphene oxide and the commercially available GFH to develop a hybrid-type treatment, in which the advantages of both materials will be combined. As a first application of this treatment type, in the present study, As(III) removal from waters will be examined in order to evaluate the efficiency of the treatment and to gain data, which will be useful for further applications, such as in combined removal of arsenic with other contaminants, inorganic and mainly organic, for which graphene oxide has a great affinity [36]. Considering the aforementioned advantages of GO and GFH, in this study, the combined use of these two adsorbent materials in different molar ratios was investigated in order to achieve the maximum arsenic removal from aqueous solutions. To the best of our knowledge, this is the first research paper combining the use of GFH with graphene oxide for As(III) removal in water treatment applications.

## 2. Materials and Methods

### 2.1. Materials

All reagents used were of analytical grade. Sodium metarsenite ( $\text{AsNaO}_2$ ) (Merck KGaA, Darmstadt, Germany) solution was used for the preparation of simulated arsenic water. As(III) stock solution (100 mg As(III)/L) was prepared by dissolving 0.1733 g  $\text{AsNaO}_2$  in 1000 mL deionized water and stored in 4 °C for further use in the experiments. The GFH material was supplied by GEH-Wasserchemie GmbH & Co. KG, Osnabrück, Germany. The GFH material is predominantly  $\beta$ -FeOOH and  $\text{Fe}(\text{OH})_3$ , with a particle size of 0.2–2.0 mm and specific surface area (BET) of  $\sim 300 \text{ m}^2/\text{g}$  [37]. The GO was previously synthesized and used by the authors [33] according to the modified Hummer's method [38], as improved by Debnath et al. (2014) [39], with a theoretical specific surface area of  $\sim 890 \text{ m}^2/\text{g}$  [34]. pH was properly regulated by utilizing HCl solution of 37% (Panreac Quimica SLU, Barcelona, Spain) or NaOH ACS reagent  $\geq 97.0\%$  pellets (Sigma-Aldrich St. Louis, MO, USA) solutions of appropriate concentrations in the range of 0.01–0.1 M.

## 2.2. Analytical Determinations

For the determination of residual arsenic concentration, atomic absorption spectroscopy coupled with graphite furnace (Varian Zeeman AA240Z with GTA 120; Hansen Way Palo Alto, CA, USA), which has a detection limit of 1 µg/L, was used.

## 2.3. Adsorption Experiments

Adsorption experiments have been conducted by introducing a predetermined quantity of adsorbent in 15 mL Falcon tubes (10 mL is the volume of solution) containing arsenic solutions at indicated initial concentrations. Experiments were performed at a constant temperature. The suspension was agitated using a Trayster overhead shaker and Loopster rotator (IKA®-Werke GmbH & Co. KG, Staufen, Germany) at a constant stirring speed (80 rpm). The following experimental variables were examined: the pH value of the solution in the range 4.0–9.0 ± 0.1, the initial As(III) concentration in the range 25–500 µg/L, the adsorbent dose (0.2–2.0 g/L), and contact time (10–360 min for kinetics and 24 h for equilibrium). Following the adsorption experiment, the collected water samples were filtered through 0.45 µm pore size nylon filter and the examined parameters were determined in the filtrate. The results represent the mean value of results obtained by three replicated experiments. The percentage removal (%R) As(III) was determined from the following Equation (1):

$$R (\%) = \left( \frac{C_0 - C_f}{C_0} \right) \times 100\% \quad (1)$$

where  $C_0$  is the initial As(III) concentration (µg/L) and  $C_f$  is the final As(III) concentration (µg/L) after treatment.

The adsorption capacity of adsorbents ( $Q_e$ ) (µg/g) was calculated from the following Equation (2):

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where  $C_e$  is As(III) concentration (µg/L) at equilibrium,  $V$  (L) is the volume of solution, and  $m$  (g) is the mass of the adsorbent used.

### 2.3.1. Equilibrium Experiments

For the isothermal experiments, a fixed amount of adsorbent sample (g) was added to 10 mL of As(III) solution (25–500 µg/L) in 15 mL falcon tubes. The adsorption experimental results were fitted to the Langmuir and Freundlich isotherm models.

The Langmuir model associates the solid-phase adsorbate concentration ( $Q_e$ ) and the uptakes to the equilibrium liquid concentration and is expressed as Equation (3):

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where  $Q_m$  is the theoretical monolayer/maximum adsorption capacity (µg/L) and  $K_L$  is related to the energy of As(III) (L/µg) adsorption.

The Langmuir theory assumes that the adsorbent has a limited adsorption capacity ( $Q_m$ ), while the adsorbate forms a monolayer on the adsorbent surface and that there is a lack of interface between the adsorbed molecules [40].

The Freundlich model [41] outlines the inter-relation between As(III) equilibrium concentrations (µg/L) with the uptake capacities,  $Q_e$  (µg/g) of adsorbent, and is expressed as Equation (4):

$$Q_e = K_F C_e^{1/n} \quad (4)$$

where  $K_F$  is a constant related to adsorption capacity, while  $1/n$  is a constant related to the intensity of adsorption or surface heterogeneity;  $1/n = 0$  is for heterogeneous phase;  $1/n < 1$  is for a normal Freundlich isotherm; and  $1/n > 1$  indicates a co-operative adsorption.

### 2.3.2. Kinetics Experiments

Two widely used models, i.e., the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetics models, were investigated to fit the kinetics of As(III) adsorption. The calculated adsorption kinetic parameters were further analyzed to estimate the adsorption rates, as well as to determine the potential reaction mechanism. The pseudo-first-order model used for the data analysis is as shown below as Equation (5):

$$Q_t = Q_e \left(1 - e^{-k_1 t}\right) \quad (5)$$

where  $Q_e$  is the amount of As(III) adsorbed at equilibrium ( $\mu\text{g/g}$ ),  $Q_t$  is the amount of As(III) adsorbed at time  $t$  ( $\mu\text{g/g}$ ),  $k_1$  is the rate constant of the PFO model ( $1/\text{min}$ ), and  $t$  is time (min).

The pseudo-second-order model used for the data analysis is as shown below as Equation (6):

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (6)$$

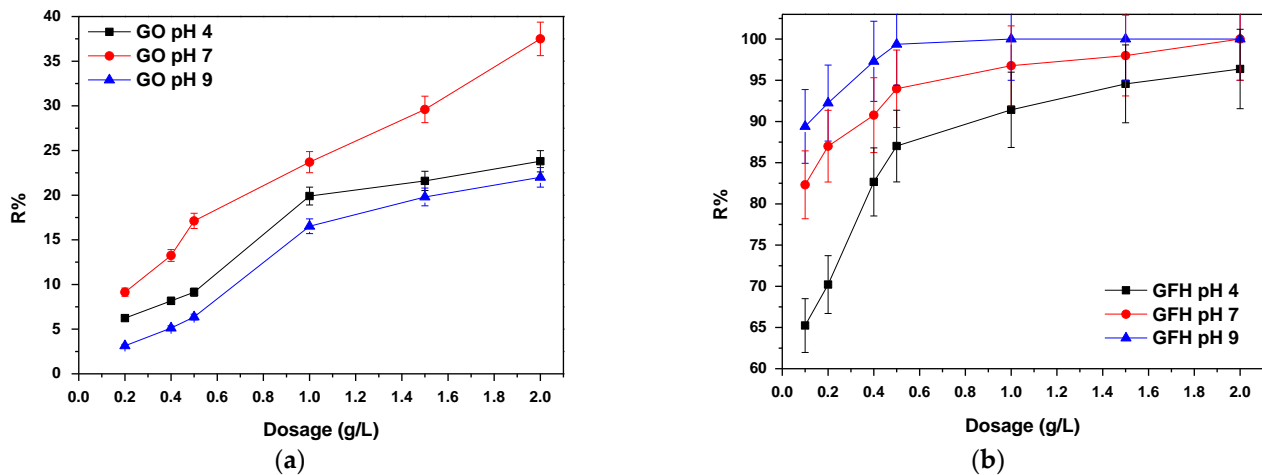
where  $Q_e$  is the amount of As(III) adsorbed at equilibrium ( $\mu\text{g/g}$ ),  $Q_t$  is the amount of As(III) adsorbed at time  $t$  ( $\mu\text{g/g}$ ),  $k_2$  is the rate constant of the PSO ( $\text{g}/(\mu\text{g min})$ ), and  $t$  is time (min).

## 3. Results and Discussion

### 3.1. Batch Adsorption Experiments

#### 3.1.1. Effect of Adsorbent Dose

Figure 1a shows the effect of GO and Figure 1b the effect of GFH dose on As(III) % removal, applying an initial As(III) concentration of  $100 \mu\text{g/L}$ .



**Figure 1.** Comparison and effect of adsorbent dose on As(III) R% removal (a) on GO and (b) on GFH; initial As(III) concentration  $100 \mu\text{g/L}$ , pH 4.0, 6.0, 7.0  $\pm$  0.1,  $T = 298 \text{ K}$ , contact time 24 h, in deionized water.

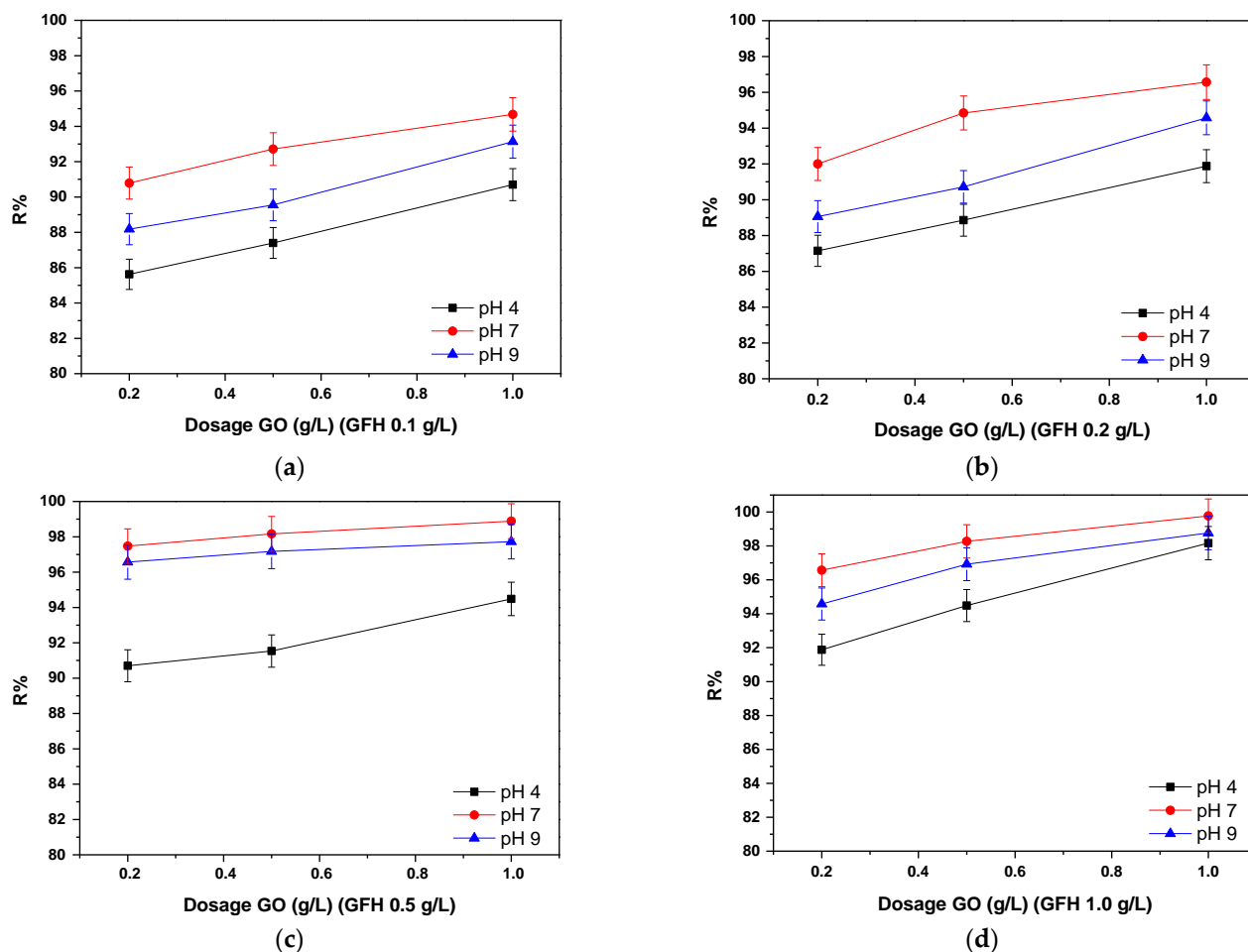
As illustrated in Figure 1a, by applying GO dosage, as the dosage of the adsorbent increased, so did the removal of As(III), especially at neutral pH values at which the efficiency is significantly higher. In particular, while in pH 4 and 9 with  $2 \text{ g/L}$  of GO, the removal reached 20%, in pH 7, it almost doubled. However, at all pH values, As(III) removal by applying only GO as the adsorbent material was low and, therefore, GO alone cannot be considered an efficient adsorbent for As(III) removal.

On the other hand, in Figure 1b, it is observed that GFH was effective in all applied doses, especially in basic pH values. Therefore, it follows that a combined use with GO in

the appropriate molecular ratio would be of interest to study to examine the effectiveness of the combined use of materials as regards As(III) removal.

### 3.1.2. Effect of the Dose Ratio of GO/GFH to the Removal of As(III) from Waters

The effect of different dose ratios of GO and GFH on the removal of As(III) is shown in Figure 2 with an initial As(III) concentration of 100 µg/L by applying several doses of GO at room temperature (298 K) at different doses of GFH (0.1, 0.2, 0.5, and 1.0 g/L) at pH 4.0 ± 0.1; 7.0 ± 0.1; and 9.0 ± 0.1. As depicted, the presence of GFH enhances the use of GO at all pH values. Even with the application of a small amount of GFH (0.1 g/L), the change in the removal efficiency of As(III) is very important. In particular, the dose mass ratio of GO/GFH 2:1 (i.e., 0.2 g/L GO and 0.1 g/L GFH) was chosen as optimal, as it was shown that, at a pH value 7.0 ± 0.1, the removal percentage increased from 10% (absence of GFH) to 90% with the simultaneous addition of 0.1 g/L GFH and 0.2 g/L GO. In addition, it is worth noting that the performance of the GFH was also enhanced, from 82% without the addition of GO and reaching 92% with their combination. In all experiments, the residual iron concentration was measured and was found to be well below the maximum permissible concentration of 200 µg/L, which is the limit of iron in drinking water.

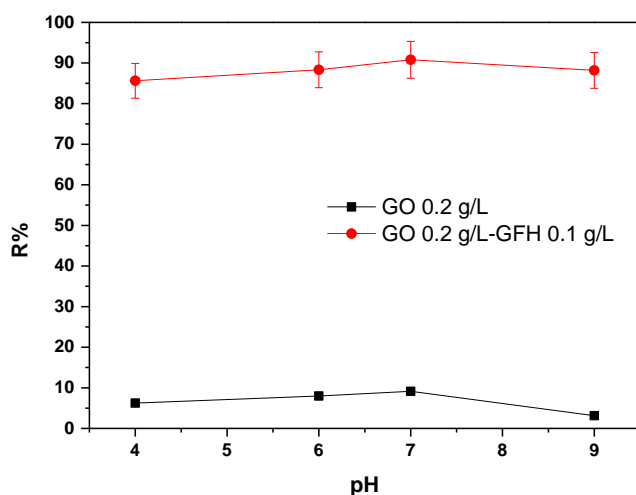


**Figure 2.** Effect of GO dosage on As(III) % removal with combined addition of several doses of GFH (a) 0.1 g/L, (b) 0.2 g/L, (c) 0.5 g/L, (d) 1.0 g/L; initial As(III) concentration 100 µg/L, pH 4.0, 6.0, 7.0 ± 0.1, T = 298 K, contact time 24 h, in deionized water.

### 3.1.3. Effect of Initial pH Solution

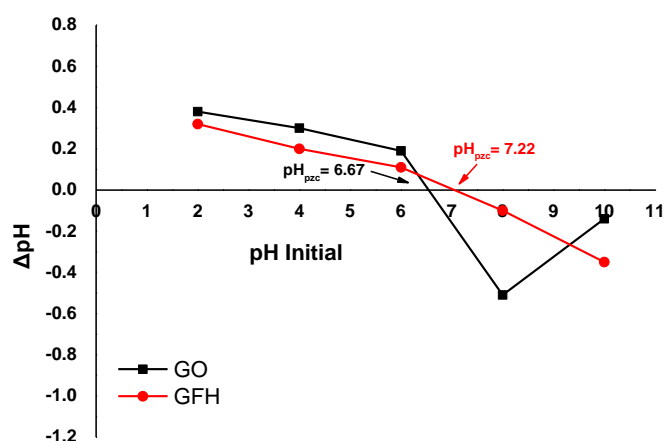
The effect of pH on the removal of As(III) was studied at different pH values of the solution ranging from 4.0 ± 0.1 to 9.0 ± 0.1 (contact time 24 h; temperature 298 K). The

optimum combination of GO/GFH, at a ratio of 2:1, was used as adsorbent. As illustrated in Figure 3, the addition of GFH enhanced the removal of As(III), particularly at pH  $7 \pm 0.1$ .



**Figure 3.** Effect of initial solution pH on the adsorption of As(III) onto the combination of GO (0.2 g/L) and GFH (0.1 g/L); initial As(III) concentration 100  $\mu\text{g/L}$ , pH  $7.0 \pm 0.1$ ,  $T = 298 \text{ K}$ , contact time 24 h, in deionized water.

In order to understand and explain the overall achieved removal, the  $\text{pH}_{\text{pzc}}$  measurements of the adsorbents were performed in the pH range of  $2.0\text{--}10.0 \pm 0.1$ .  $\text{pH}_{\text{pzc}}$  is the pH value at which the surface charge of the adsorbent changes from positive to negative, with a potential impact to the interface between the adsorbate and the adsorbent.  $\text{pH}_{\text{pzc}}$  was calculated by the relative graph of  $\Delta\text{pH}$  vs.  $\text{pH}_{\text{initial}}$ , as illustrated in Figure 4 by using pH drift method [42]. It was found that the relative  $\text{pH}_{\text{pzc}}$  values were 6.67 for GO and 7.22 for GFH, resulting in a slightly negatively charged surface of GO and slightly positively charged surface of GFH at solution pH values (pH 7.0 found in this study) greater and lower than the  $\text{pH}_{\text{pzc}}$ , respectively. At pH 7.0, As(III) with a  $\text{pK}_{\text{a}1}$  of 9.22 is mostly present as nonionic  $\text{H}_3\text{AsO}_3$  [43]; thus, at pH 7.0, adsorption of As(III) is less pH-sensitive [44] and the adsorption of nonionized As(III) takes place only through a Lewis acid–base (ligand exchange) reaction [45].

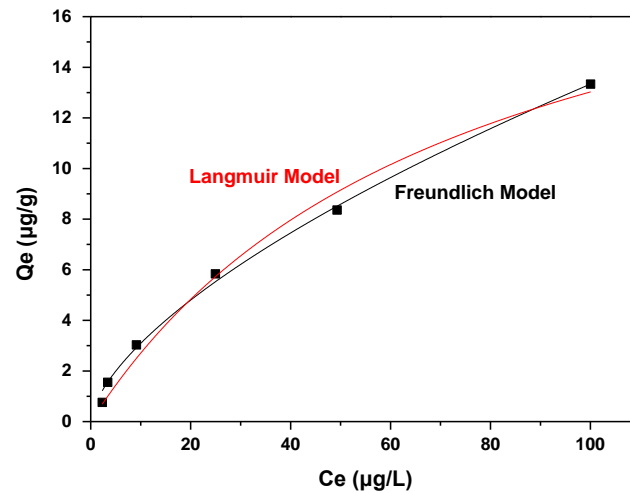


**Figure 4.** Determination of  $\text{pH}_{\text{pzc}}$  of GO and GFH using pH drift method.

### 3.2. Adsorption Isotherms

As isothermal adsorption models can describe experimental data and determine the mechanism of the adsorption process, two common isotherm models, Langmuir and Freundlich, were applied to describe the experimental results. These models are described

by two parameters that are used in order to establish the connection between the amount of arsenic adsorbed onto the combination of GO and GFH. Figure 5 provides the results for As(III) removal capacity ( $\mu\text{g/g}$ ), with initial concentration varying from 25 to 500  $\mu\text{g/L}$ , at  $\text{pH } 7.0 \pm 0.1$ , by applying the combination of 0.2 g/L GO and 0.1 g/L GFH at room temperature (298 K).



**Figure 5.** Langmuir and Freundlich isotherm models for the adsorption of As(III) (25–500  $\mu\text{g/L}$ ) onto the combination of GO (0.2 g/L) and GFH (0.1 g/L),  $\text{pH } 7.0 \pm 0.1$ ,  $T = 298 \text{ K}$ , contact time 24 h, in deionized water.

The calculated parameters from Equations (3) and (4) are shown in Table 1. As shown, the adsorption isotherm data were best fitted to the Freundlich isotherm model with a relative higher correlation coefficient ( $R^2 = 0.996$ ), indicating a multi-layer adsorption process. This model assumes the existence of interactions between adsorbed molecules. The values of  $K_F$  (0.7167) and  $1/n$  (0.6349) were calculated from the intercept and slope of the plots. For values of  $1/n$  in the range  $0 < 1/n < 1$ , adsorption is favorable, so the corresponding value obtained in this study, i.e., 0.6349, proves that the adsorbent's combination of GO/GFH with a molar ratio 2:1 is effective for As(III) adsorption and the adsorption process can be characterized as favorable. It described a heterogeneous chemisorption [41].

**Table 1.** Constants of Langmuir and Freundlich isotherm model for the adsorption of As(III) onto the combination of GO (0.2 g/L) and GFH (0.1 g/L),  $\text{pH } 7.0 \pm 0.1$ ,  $T = 298 \text{ K}$ , contact time 24 h, in deionized water.

Langmuir Isotherm Model			
$Q_m$ ( $\mu\text{g/g}$ )	$K_L$ (L/g)	$R^2$	
22.62	0.0136	0.9868	
Freundlich Isotherm Model			
$1/n$	$n$	$K_F$ ( $\mu\text{g/g}$ ) (L/ $\mu\text{g}$ ) $^{1/n}$	$R^2$
0.6349	1.5752	0.7167	0.9962

Table 1 shows the correlation coefficient for Langmuir model, which is lower than Freundlich. According to Langmuir model, the calculated adsorption capacity was 22.62  $\mu\text{g/g}$ .

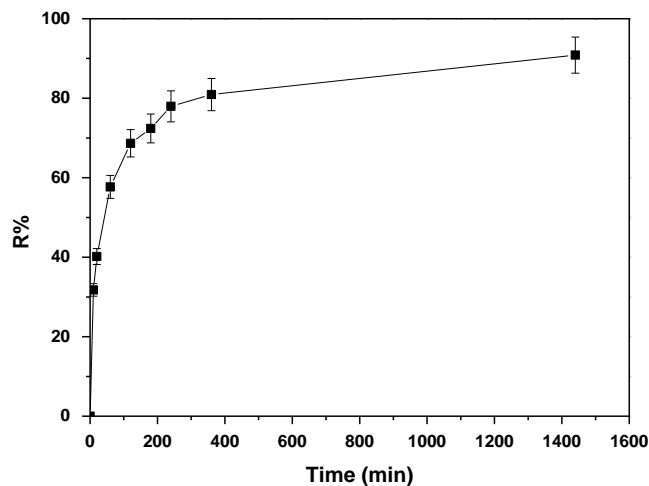
### 3.3. Effect of Contact Time and Adsorption Kinetics

The contact time is an important parameter, expressing the time required for adsorbents to reach adsorption equilibrium. For the evaluation of the adsorption kinetics,



relevant experiments were conducted at an initial As(III) concentration of 100  $\mu\text{g/L}$  at pH  $7.0 \pm 0.1$  by applying the combination of 0.2 g/L GO and 0.1 g/L GFH at room temperature (298 K).

As shown in Figure 6, the required time for achieving 50% removal of As(III) was found to be  $\sim 60$  min, reaching 80% in about 240 min. Moreover, it is observed that the equilibrium is reached after 360 min.



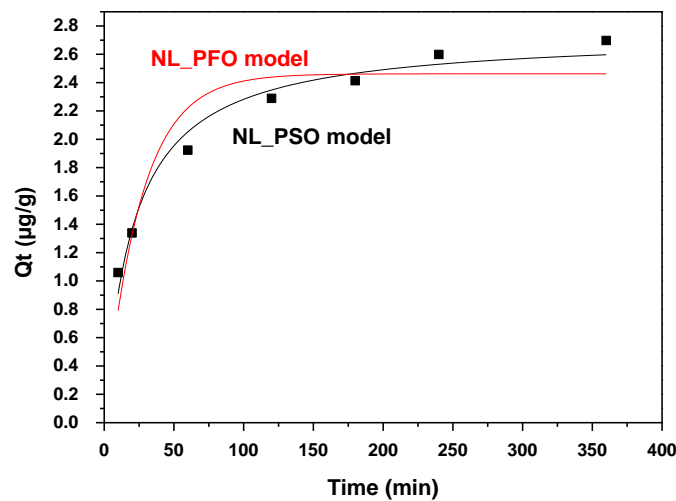
**Figure 6.** Effect of contact time on the adsorption of As(III) onto the combination of GO (0.2 g/L) and GFH (0.1 g/L); initial As(III) concentration 100  $\mu\text{g/L}$ , pH  $7.0 \pm 0.1$ ,  $T = 298$  K, in deionized water.

In addition, the kinetics of As(III) adsorption were fitted to kinetic models. Pseudo-first-order (PFO) and pseudo-second-order (PSO) models have been used for the kinetic study and the corresponding curves are illustrated in Figure 7. According to the parameters presented in Table 2, the experimental data fitted better to the pseudo-second-order model, from which a better correlation was obtained, i.e.,  $R^2 = 0.9696$  for PSO and only  $R^2 = 0.8708$  for PFO. The PSO model constants, calculated from Equation (6), are shown in Table 2, indicating that the adsorption of As(III) on a combination of GO/GFH (molar ratio 2:1) was closer to chemical adsorption and, henceforth, there is an exchanging or sharing of electrons between the adsorbate and the adsorbent [46]. This finding is in agreement with the respective findings of the application of the isotherm models, from which it was considered that As(III) removal takes place through chemisorption. In addition, the change between the calculated equilibrium adsorption capacities ( $q_{e,calc}$ ) (3.0283) and the experimental value ( $q_{e,exp}$ ) (2.7421 mg/g) was not very significant.

**Table 2.** Pseudo-first-order and pseudo-second-order kinetic parameter model for the adsorption of As(III) onto the combination of GO (0.2 g/L) and GFH (0.1 g/L), pH  $7.0 \pm 0.1$ , dosage 2 g/L,  $T = 298$  K, contact time 24 h, in deionized water.

Pseudo-First-Order Model (PFO)			
$Q_{e,exp}$ ( $\mu\text{g/g}$ )	$K_1$ ( $\text{L}/\mu\text{g}\cdot\text{min}$ )	$Q_{e,calc}$ ( $\mu\text{g/g}$ )	$R^2$
3.0283	0.0386	2.4621	0.8708
Pseudo-Second-Order Model (PSO)			
$Q_{e,exp}$ ( $\mu\text{g/g}$ )	$K_2$ ( $\text{L}/\mu\text{g}\cdot\text{min}$ )	$Q_{e,calc}$ ( $\mu\text{g/g}$ )	$R^2$
3.0283	0.0181	2.7421	0.9696





**Figure 7.** Kinetic models of pseudo-first and pseudo-second order for the adsorption of As(III) onto the combination of GO (0.2 g/L) and GFH (0.1 g/L); initial As(III) concentration 100 µg/L, pH  $7.0 \pm 0.1$ ,  $T = 298$  K, in deionized water.

#### 4. Conclusions

In the present study, GFH, a commercially available porous iron adsorbent, and GO, containing a large amount of reactive oxygen species due to the presence of epoxy, carboxyl, and hydroxyl groups, were combined in different dose ratios in order to achieve the maximum As(III) removal from aqueous solutions. The effect of the adsorbent's dosage, pH value, contact time, initial As(III), and different dose ratios of GO/GFH were examined.

According to the results, the main highlights of this manuscript can be summarized as follows: the presence of GFH enhanced the use of GO at all pH values for As(III) removal. In particular, the molar ratio of GO/GFH 2:1, by the simultaneous addition of 0.2 g/L GO and 0.1 g/L GFH, was chosen as optimal at pH value  $7.0 \pm 0.1$ , while the removal percentage increased from 10% (absence of GFH) to 90% with the simultaneous addition of GFH.

Freundlich isotherm model fitted the experimental data sufficiently with a quite high correlation coefficient ( $R^2 = 0.996$ ), indicating a multi-layer chemical adsorption process. In addition, the kinetics of As(III) adsorption on 0.2 g/L GO and 0.1 g/L GFH fitted well to the pseudo-second-order model, from which a high correlation was obtained, i.e.,  $R^2 = 0.9696$ , indicating that the adsorption of As(III) on a combination of GO/GFH (molar ratio 2:1) was closer to chemisorption and that there is an exchanging or sharing of electrons between the adsorbate and the adsorbent.

The results showed that combined use of GO and GFH can be an effective combined treatment approach for removing As(III) from water without the use of chemical reagents for As(III) oxidation, while the use of GO contributes to the need for smaller quantities of GFH, thereby reducing the final iron concentrations in the treated water, while it offers the possibility to be applied for simultaneous organic micropollutant removal, which is the main prospective of this research.

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