



Article Sorption Capacity of AlOOH/FeAl₂ Composites towards As(V)

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Abstract: The treatment of wastewater from arsenic compounds is an important and urgent problem. Composite nanostructures consisting of boehmite and iron compounds have a high adsorption capacity towards As(V) specie. In this work, the adsorption properties of nanostructured composites prepared by the oxidation of bimetallic Al/Fe nanoparticles with different iron contents were investigated. As a result of oxidation, boehmite AlOOH nanosheets are formed, with the resultant FeAl₂ nanoparticles being distributed on the surface of boehmite nanosheets. The nanostructured composites prepared from Al/Fe nanoparticles containing 20 wt% Fe have been found to show the highest adsorption capacity towards As(V) specie, being 248 mg/g. The adsorption isotherms are most accurately described by the Freundlich model, with the arsenic adsorption process obeying pseudo second order kinetics. As a result of the study, the optimal ratio of Al and Fe in Al/Fe nanoparticles has been determined to obtain an AlOOH/FeAl₂ composite adsorbent with a developed and accessible surface and a high sorption capacity towards As(V). This allows us to consider this material as a promising adsorbent for the removal of arsenic compounds from water.

Keywords: bimetallic nanoparticle; iron; arsenic adsorption; boehmite; nanostructures; oxidation; composites



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1. Introduction

The pollution of groundwater and wastewater with heavy metals is a common environmental threat, as dissolved ions of toxic elements become a risk factor for human health [1–4]. Arsenic is one of the most abundant contaminants with high toxicity in groundwater worldwide. The presence of arsenic in groundwater requires special attention when assessing the quality of drinking and mineral waters. As groundwater is the main source for drinking water treatment, the removal of arsenic from groundwater is urgently needed.

The most abundant forms, which are commonly found in water, are arsenite (oxidation state +3) and arsenate (oxidation state +5) [4,5]. Removal of As(III) species (arsenite) from contaminated water is a more difficult process than removal of As(V) ones (arsenate). Thus, at pH 6–9, arsenite is mostly in an undissociated form (H₃AsO₃), whereas negatively charged anions (H₂AsO₃⁻⁷, HAsO₃⁻² and AsO₃⁻³) are only detected at high pH [6,7]. As a result, H₃AsO₃ is removed from the water less efficiently, so, commonly, arsenite is oxidized to arsenate beforehand. Due to this, most of the arsenic decontamination technologies are aimed at the efficient removal of arsenate, as it is present at pH values above 2 in the form of H₂AsO₄⁻ and HAsO₄⁻² anions, which are easy to remove [8–10].

Several common methods are used for arsenic removal, which include: ion exchange, coagulation, electrochemical purification, membrane technologies, adsorption, etc. [2,11–19]. Adsorption technologies for arsenic wastewater treatment are widely used due to their advantages, such as ease of operation, commercial benefits, etc. Various materials capable of efficient arsenic removal have been described in the literature. Mesoporous aluminum oxide with a specific surface area of $307 \text{ m}^2/\text{g}$ and a uniform pore size of 3.5 nm

has been shown to uptake 121 mg/g As(V) and 47 mg/g As(III), respectively [20], being stable in the pH range of 3–7. Nanocrystalline TiO₂ has been found to be also an effective arsenic adsorbent due to its high specific surface area and high affinity for arsenate [21]. Cerium oxide with a specific surface area of 198 m²/g exhibited a high affinity for both As(V) and As(III) [22], with the sorption capacities in neutral medium reaching 107 mg/g and 170 mg/g, respectively.

Iron oxides also have a high affinity for arsenic, which makes them the most promising arsenic adsorbents [23–26]. However, a number of disadvantages, such as low specific surface area or diffusion limitations, contribute to the need for the development of new composite materials for the removal of arsenic from water [27–30]. Thus, materials based on active carbon/magnetite Fe₃O₄ were investigated [27–29]. These materials have a specific surface area of up to 1240 m²/g, with the maximum adsorption capacity varying from 32.57 mg/g [28] to 455 mg/g [27]. The adsorption characteristics of AlOOH/AlFe composite material towards As(V) were recently investigated [30]. The high specific surface area of 247 m²/g and the mesoporous structure of the material are responsible for its adsorption capacity being more than 200 mg/g As(V).

Previously, a material representing bimetallic Al/Fe nanoparticles with 10 wt.% Fe content has been reported, and the influence of the conditions of oxidation with water on the morphology of the resulting nanostructures and their adsorption characteristics with respect to arsenic (V) specie relations was studied [31]. Nanosheet structures obtained by the oxidation of Al/Fe particles with water at 60 °C have been shown to have a higher adsorption capacity than platelet-like and rod-like nanostructures obtained under hydrothermal conditions and in humid air, respectively. The obtained nanosheet structures are porous, with a specific surface area of about 330 m²/g and a positive zeta potential, which contributes to the electrostatic attraction of arsenic species in an anionic form. In comparison, aluminum oxide itself, obtained by the oxidation of electro-explosion Al nanoparticles by water, is able to adsorb up to 75 mg/g As(V).

In the present work, the influence of AlFe₂ content in AlOOH/AlFe₂ composites on the sorption characteristics towards arsenic was considered for the first time. The optimal Al/Fe ratio in the nanoparticles in order to obtain an AlOOH/AlFe₂ composite with high sorption capacity towards As(V) has been established.

2. Materials and Methods

Bimetallic Al/Fe nanoparticles were obtained by electrical explosion of twisted wires (EETW) of the corresponding metals in argon medium according to the technique reported previously [32]. The EETW method is based on the destruction of a metal wire subjected to a high-current pulse with a current density in the range 10^{6} – 10^{9} A/cm². The wire heats up and then explodes, giving off metal vapor and liquid metal droplets forming nanoparticles on cooling. The common method for EETW is to use an LC circuit to set the required energy input into the wire.

Table 1 presents the electrical explosion parameters to obtain Al/Fe composites.

-	Sample –	Wire Diameter, mm		Wire Length,	CE	TT 1-37	D MDa		
		Fe	Al	mm	С, µг	υ, κν	r, wira		
	Al90Fe10	0.1	0.45	90	3.2	31	0.3		
	A180Fe20	0.1	0.35	75	2.0	27	0.3		
	A170Fe30	0.1	0.25	60	1.2	25	0.3		

Table 1. The electrical explosion parameters to obtain Al/Fe composites.

Nanostructured adsorbents under study were prepared by oxidation of bimetallic Al/Fe nanoparticles with water at 60 °C for 1 h, according to the technique reported previously [31].

XRD phase identification analyses of nanostructured materials under study were carried out using an XRD 6000 diffractometer (Shimadzu, Kyoto, Japan) in 2 θ in the area of 10–90° at 25 °C by using CuK α (λ = 1.54 Å) radiation. XRD qualitative phase analysis was performed with the Powder diffraction file (PDF) database PDF-2 Release 2014.

The crystalline structure, phase composition and morphology of the nanostructured materials were studied by the transmission electron microscopy technique using a JEM-2100 transmission electron microscope integrated with an X-Max energy dispersive spectrometer (Oxford Instruments, Abingdon, UK).

Zeta potential measurements were performed in deionized water at 25 °C and various pH values using a Zetasizer Nano ZSP instrument equipped with an auto-titration unit, MPT-2 (Malvern Instruments Ltd., GB, Malvern, UK), with the use of Zetasizer Software v7.11. For this measurement, a 20 mg powder weight was placed in 10 mL of deionized water and treated in an ultrasonic bath (VU-09-YA-FP-0.3, Ferroplast, Yaroslavl, Russia) for 30 s. Then, 1 mL aliquot was taken and placed in the U-shaped cuvette of the instrument and measured in automatic mode.

Specific surface area and porous structure of the nanostructured materials under study were determined by Brunauer–Emmett–Teller (BET) nitrogen adsorption/desorption method using a Sorbtometer M specific surface analyzer (Katakon, Novosibirsk, Russia).

For investigation of adsorption kinetics, a 50 mg weight of nanostructured composite adsorbent was placed in sodium arsenate solution with a concentration of 400 mg/L and dwelled for different time intervals under continuous stirring. The mixtures were then centrifuged at 3500 rpm for 10 min and the arsenic concentration in the supernatant was measured. The arsenic concentration was determined by the inversion voltammetry method by first reducing As(V) to As(III). Measurement was performed using a voltametric analyzer, TA-Lab (TomAnalit, Tomsk, Russia), with an electrochemical measurement system including gold-carbon working and silver chloride reference electrodes. The background electrolyte was Trilon B solution (0.01 mol/L) with the limit of detection being 0.5 μ g/L. The amount of adsorbed arsenic specie for a certain period of time was calculated by Equation (1):

$$q_t = \frac{(C_0 - C_t) * V}{m} \tag{1}$$

where q_t (mg/g) is the amount of As(V) adsorbed per mass of sorbent at any time, C_0 and C_t (mg/L) are the concentrations of As(V) at initial and any time *t*, respectively, *V* is the volume of the solution (L) and *m* is the adsorbent weight (g).

Sodium arsenate stock solution (500 mg/L) has been prepared and the sodium arsenate solutions with the desired concentration were prepared by serial dilution of the stock solution to determine an adsorption isotherm. Then, 50 mg nanostructured composite adsorbent weights were placed in 50 mL sodium arsenate solutions with different concentrations. Adsorption experiment was carried out under continuous stirring for 60 min. Then, the solutions were centrifuged at 3500 rpm for 10 min and measurements were carried out. Adsorption capacity q_e (mg/g) was calculated by Equation (2):

$$q_e = \frac{(C_0 - C_e) * V}{m} \tag{2}$$

where q_e (mg/g) is the amount of As(V) adsorbed per mass of sorbent at equilibrium, V (L) is the volume of the solution, C_0 and C_e (mg/L) are initial and equilibrium concentrations of the solute, respectively, and m (g) is adsorbent weight.

3. Results and Discussion

According to the TEM/EDX data presented, Al/Fe nanoparticles are of spherical shape and contain both aluminum and iron (Figure 1a–c). The iron/aluminum ratios in Al-10Fe, Al-20Fe and Al-30Fe particles correspond to the theoretical ones and are 11.8 wt.% [31], 20.6 wt.% and 31.0 wt.%, respectively (Figure 1a–c, pie charts). As can be seen from the images, aluminum and iron are distributed throughout the particles. According to the phase diagram of the Al-Fe system [33], Al is well dissolved in α -Fe, forming wide regions of solid solutions with a BCC structure. Due to the fact that nanoparticles in EETW can be formed from both gas and liquid phases [32], the presence of both metals in individual nanoparticles is quite natural.



Figure 1. TEM images (left), EDX mapping for elements Al and Fe of initial Al/Fe nanoparticles (center) and elemental percentage (right) for: (**a**)—Al-10Fe; (**b**)—Al-20Fe; (**c**)—Al-30Fe.

Al/Fe powders have been found to obey the log-normal particle size distribution (Figure 2). The average sizes of the nanoparticles were determined to be (85 ± 1) nm, (97 ± 1) nm, (97 ± 1) nm for Al-10Fe, Al-20Fe and Al-30Fe, respectively.



Figure 2. Histograms of the nanoparticle size distribution for: (a)—Al-10Fe; (b)—Al-20Fe; (c)—Al-30Fe.

XRD phase analysis shows aluminum and iron in the Al/Fe nanoparticles presenting in the form of aluminum metal with a standard lattice parameter (4.049 Å) and FeAl₂ intermetallide, respectively (Figure 3). With increasing iron content in the Al/Fe nanoparticles, the intensity of the FeAl₂ intermetallide peaks increases.



Figure 3. XRD phase analysis patterns of Al/Fe nanopowders.

When oxidized with water, Al/Fe nanopowders form boehmite nanosheets 2–5 nm thick and planar sizes up to 200 nm assembled into agglomerates up to 2 μ m in size (Figure 4). The boehmite nanosheet structures are formed also when water oxidizes Al nanoparticles obtained by the electrical explosion of Al wire [34]. In modern concepts, the oxidation of aluminum with water proceeds by an electrochemical mechanism, wherein aluminum acts as an anode, and intercrystalline defects can serve as a cathode. A reduction of water with the formation of hydroxide ions and the release of hydrogen takes place at the cathode. At the anode proceeds the oxidation of aluminum, which begins with the destruction of its crystal lattice and ends with the release of Al³⁺ simple or complex hydrated ions into solution [34]. In weakly alkaline medium are formed monomers [Al(OH)₃(OH₂)₃] giving [A1₄(OH)₁₂(OH₂)₅] seeds, which are transformed into distorted tetramers, [Al₄O(OH)₁₀(OH₂)₅], yielding in the boehmite nanosheet structures.

According to TEM-EDX data, iron species are uniformly distributed on the nanosheet surface. With increasing iron content, the appearance of opaque inclusions of 10–20 nm in size is observed in the oxidation reaction products (Figure 4c).

Broadened peaks characteristic of fine crystalline boehmite are observed in XRD patterns of nanosheet agglomerates [35], and peaks characteristic of FeAl₂ intermetallide are also identified (Figure 5).

The obtained results indicate that $FeAl_2$ intermetallide within nanoparticles does not react with water and is located on the boehmite nanosheet surface. Probably, during the formation of boehmite nanosheets, intermetallide particles released after the dissolution of reacting aluminum become located in the nanosheet agglomerates. Also, with increasing iron content in the Al/Fe nanoparticles, the intermetallide particles located on the boehmite nanosheet surface are enlarged.

One of an adsorbent's important characteristics is a surface charge, which can be evaluated through the zeta potential of particles. The nanostructured composite adsorbents have been found to show a positive zeta potential in the range of a pH from 3 to 9, which should contribute to the electrostatic interaction of the nanostructured composite adsorbent with arsenic anions. At the same time, with increasing Fe content in the adsorbent samples, no significant changes in the character of the curves or changes in the point of zero charge



value were observed (Figure 6). The pH of the point of zero charge for AlOOH/FeAl₂ (10%) is 9.15, for AlOOH/FeAl₂ (20%) it is 8.75 and for AlOOH/FeAl₂ (30%) it is 8.83.

Figure 4. TEM images and EDX mapping for elements Al, O and Fe of the Al/Fe nanoparticle oxidation products: (a)—Al-10Fe; (b)—Al-20Fe; (c)—Al-30Fe.



Figure 5. XRD patterns of the Al/Fe nanoparticle oxidation products for: (**a**)—Al-10Fe; (**b**)—Al-20Fe; (**c**)—Al-30Fe.





The positive surface charge of the nanostructures in a wide pH range can promote the adsorption of arsenic anionic species due to electrostatic interaction.

Figure 7a–c show low-temperature nitrogen adsorption–desorption isotherms for the nanostructured composite adsorbents prepared. The isotherms are of type IV, according to the IUPAC classification [36,37], with a pronounced hysteresis loop, which characterizes slit shape pores in the adsorbent samples. Increasing the iron content in composite adsorbent samples leads to a decrease in the specific surface: for AlOOH/FeAl₂ (10%), the value of the specific surface is 330 m²/g, for AlOOH/FeAl₂ (20%)–282 m²/g and for AlOOH/FeAl₂ (30%)–255 m²/g. Pore size distributions for all composite adsorbent samples (Figure 7d) are characterized by pronounced maxima in the region of 4 nm.



Figure 7. Nitrogen adsorption–desorption isotherms for the nanostructured composite adsorbents AlOOH/FeAl₂ (10%) (**a**) [31], AlOOH/FeAl₂ (20%) (**b**), AlOOH/FeAl₂ (30%) (**c**) and pore size distributions (**d**): 1—AlOOH/FeAl₂ (10%); 2—AlOOH/FeAl₂ (20%); 3—AlOOH/FeAl₂ (30%).

The adsorption of arsenate on the nanostructured composite adsorbents as a function of contact time is shown in Figure 8. Adsorption proceeds rather fast and reaches equilibrium in about 60 min for all synthesized adsorbent samples (Figure 8).



Figure 8. Adsorption kinetics curves of As(V) on the nanostructured composite adsorbents (pH 7.0, initial As(V) concentration 400 mg/L): (a)—AlOOH/FeAl₂ (10%); (b)—AlOOH/FeAl₂ (20%); (c)—AlOOH/FeAl₂ (30%).

As a rule, pseudo first and pseudo second order kinetic models of adsorption kinetics are used to describe adsorption kinetics [38,39]. The pseudo first order model is expressed by Equation (3):

$$\frac{dq}{dt} = k(q_e - q_t) \tag{3}$$

The integration of Equation (3) takes into account boundary conditions ($q_t = 0$ for t = 0, $q_t = q$ for t = t) and returns Expression (4):

$$q_t = q_e \left(1 - e^{-kt} \right) \tag{4}$$

The pseudo second order model is expressed by Equation (5)

$$\frac{dq}{dt} = k(q_e - q_t)^2 \tag{5}$$

The integration of Equation (5) takes into account boundary conditions, and returns Expression (6):

$$q_t = \frac{q_e^2 kt}{1 + q_e kt} \tag{6}$$

The linear forms of the pseudo first and pseudo second order kinetics equations have the form:

$$ln(q_e - q_t) = lnq_e - k_1 t \tag{7}$$

and

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(8)

respectively.

The kinetic parameters of arsenate adsorption on the nanostructured composite adsorbents fitted according to the pseudo first order and pseudo second order models are presented in Table 2. Figure 9 shows the plots of the linear forms of pseudo first and pseudo second order kinetic models for the nanostructured composite adsorbents.

Kinatic Paramators	Reaction Order				
Killetit i alailleteis —	Ι	II			
	AlOOH/FeAl ₂ (10%)				
q _e , mg∕g	114.81	127.57			
k	0.0792	0.0009			
R ²	0.5516	0.9935			
	AlOOH/FeAl ₂ (20%)				
q _e , mg/g	248.79	271.11			
k	0.1178	0.0007			
R ²	0.8657	0.9969			
	Alooh/H	FeAl ₂ (30%)			
q _e , mg/g	248.97	274.35			
k	0.1124	0.0006			
R ²	0.8050	0.9948			

Table 2. Kinetic parameters of arsenic adsorption on the nanostructured composite adsorbents.



Figure 9. The linear forms of the pseudo first (**a**) and pseudo second order adsorption kinetic models (**b**) kinetic models for the nanostructured composite adsorbents: 1—AlOOH/FeAl₂ (10%); 2—AlOOH/FeAl₂ (20%); 3—AlOOH/FeAl₂ (30%).

According to the values of determination coefficients R^2 for the fitted kinetic parameters, the adsorption of arsenate on the nanostructured composite adsorbents can be assumed to be better described by the pseudo second order model equation. This indicates that the adsorption rate is determined more by the availability of adsorption centers on the adsorbent surface than by the concentration of solute. At the same time, different iron content in the samples does not noticeably affect the adsorption rate.

The adsorption isotherms of arsenate are shown in Figure 10. As can be seen, the adsorption isotherm curves show similar shapes, which indicates the same adsorption mechanism for all composite adsorbents. An increase in iron content in the nanostructured composite adsorbents from 10 to 20 wt.% leads to an increase in adsorption capacity from 112 mg/g to 248 mg/g, and a further increase in iron content, up to 30 wt.%, practically does not affect adsorption capacity, being 240 mg/g for the AlOOH/FeAl₂ (30%) adsorbent. This may be due to the formation of larger iron entities during the oxidation of Al-30Fe powder with water.



Figure 10. Adsorption isotherms of As(V) specie on the nanostructured composite adsorbents: (a)—AlOOH/FeAl₂ (10%); (b)—AlOOH/FeAl₂ (20%); (c)—AlOOH/FeAl₂ (30%).

The adsorption isotherms were analyzed using Langmuir and Freundlich adsorption models [40–44]. The applicability of adsorption models was evaluated by comparing determination coefficients R^2 [44].

The Langmuir model assumes a sorbate monolayer on a homogeneous adsorbent surface at a constant temperature, the distribution of the sorbate between two phases being characterized by the equilibrium constant K_a . The Langmuir adsorption isotherm equation is:

$$q_e = q_{max} \, \frac{K_a C_e}{1 + K_a C_e} \tag{9}$$

where q_e (mg/g) is the amount of As(V) sorption, C_e (mg/L) is the concentration at the stage of equilibrium, K_a is the Langmuir constant (L/mg), q_{max} is the monolayer Langmuir capacity (mg/g). The linear form for the Langmuir isotherm model is expressed as follows:

$$\frac{1}{q_e} = \left(\frac{1}{K_a q_{max}}\right) \frac{1}{C_e} + \left(\frac{1}{q_{max}}\right) \tag{10}$$

The Freundlich adsorption model assumes the adsorption process occurs on an energetically inhomogeneous surface. The Freundlich adsorption isotherm equation is:

$$q_e = K_f C_e^{1/n} \tag{11}$$

where K_f (L/mg) is an indicator of the adsorption capacity and 1/n is the adsorption intensity, indicating both the relative distribution of energy and the heterogeneity of the adsorbent sites.

The linear equation for the Freundlich isotherm model is expressed as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{12}$$

The fitted values of the adsorption parameters for the Langmuir and Freundlich adsorption models are summarized in Table 3, and these values were used to plot adsorption isotherms.

Table 3. Adsorption model parameters.

Samulas	BET Surface Areas (m²/g)	Langmuir Model			Freundlich Model		
Samples		<i>q_{max}</i> (mg/g)	Ka	R^2	K _f	1/n	R^2
AlOOH/FeAl ₂ (10%)	330	144.2	0.0107	0.9828	5.51	0.54	0.9912
AlOOH/FeAl ₂ (20%)	282	313.6	0.0275	0.9798	17.99	0.57	0.9908
AlOOH/FeAl ₂ (30%)	255	258.9	0,0494	0.9671	27.21	0.46	0.9775

Figure 11 presents the adsorption isotherms in linear form. Based on the values of determination coefficient R^2 , the sorption of As(V) for all types of the nanostructured composite adsorbents is most adequately described by the Freundlich equation. In addition, Freundlich isotherm constant 1/n can be used to evaluate the favorability adsorption level and the degree of heterogeneity of the adsorbent surface. The sorption process is irreversible when 1/n = 0, favorable adsorption is in the case of 0.1 < 1/n < 1, and at 1/n > 1—unfavorable condition [45]. As summarized in Table 3, in all cases, the Freundlich isotherm constant values are in the range of 0.1 to 1.



Figure 11. Linear plots of Langmuir (**a**) and Freundlich (**b**) adsorption isotherms for nanostructures: 1—AlOOH/FeAl₂ (10%); 2—AlOOH/FeAl₂ (20%); 3—AlOOH/FeAl₂ (30%).

Thus, the increase in the Fe content in the initial Al/Fe nanoparticles, of up to 20 wt.%, allowed for more than a 2-fold increase in the sorption capacity of AlOOH/FeAl₂ nanostructured composite adsorbents with respect to As(V) specie. A further increase in Fe content, up to 30 wt.%, did not lead to an increase in adsorption capacity, which may be due to the enlargement of iron-containing nanoparticles in the composite adsorbent and the corresponding reduction of the surface's contribution to the sorption process.

The obtained results on the adsorption of arsenate on the surface of the prepared nanostructures indicate that their adsorption efficiency is mostly determined not by the amount of intermetallide, but by its dispersivity. The increase in iron content, to up to 30 wt.%, leads to the fact that the surface of intermetallide particles in the AlOOH/FeAl₂ nanostructures does not increase, and consequently, there is no increase in the number of sites responsible for the adsorption of As(V).

One should also note the high adsorption capacity of AlOOH/FeAl₂ (20%) nanostructures achieved with respect to arsenate, which exceeds many reported arsenic adsorbents [20–22,28], which makes the above nanostructures very promising in this direction of use. Boehmite in the AlOOH/FeAl₂ nanosheet structures promoting arsenic adsorption [31] is a good adsorbent for anionic dyes, negatively charged nanoparticles, and bacteria and viruses [46]. Its efficient adsorption of As(V) on the surface of nanostructured AlOOH, as well as other negatively charged species, is due to its highly developed surface and positive surface charges, which present over a wide pH range (3–9). The positive surface charge of AlOOH favors the electrostatic attraction of negatively charged entities. Clearly, a treatment of composites after the adsorption of As(V) in weakly alkaline solutions will result in their regeneration due to the change of the adsorbent surface charge. This makes the AlOOH/FeAl₂ nanostructures a universal adsorbent for the purification of contaminated water. Zeta potential measurements suggest that arsenic desorption at a high pH is possible, and the consideration of the regeneration of adsorbents is planned. Also, in the future, we plan to focus on studying the adsorption mechanisms of As compounds and other pollutants by AlOOH/FeAl₂ (20%) composite.

4. Conclusions

The effect of the FeAl₂ content in AlOOH/FeAl₂ composites on their adsorption characteristics towards As(V) was studied for the first time.

The oxidation of bimetallic Al/Fe nanoparticles with iron contents of 10–30% by water at 60 °C has been found to yield nanosheet composite nanostructures of fine crystalline boehmite, on the surface of which FeAl₂ intermetallide particles are distributed. The nanosheet structures so prepared have a positive zeta potential in the acidic and neutral pH ranges and a high specific surface area of 255–330 m²/g due to the mesoporous structure of the composites.

When studying the adsorption characteristics of the prepared composite nanostructures towards As(V), the adsorption process has been found to be best described by the Freundlich model, indicating the inhomogeneity of the surface of the nanostructures as well as possible multilayer adsorption. The arsenic adsorption process obeys pseudo second order kinetics.

The adsorption capacity of nanostructures prepared from Al/Fe nanoparticles containing 10 wt.% Fe was 112 mg/g, containing 20 wt.% Fe—248 mg/g, containing 30 wt.% Fe—240 mg/g. The lack of increase in the sorption capacity with respect to As(V) specie for nanostructures prepared from Al/Fe nanoparticles containing 30 wt.% Fe may be due to the enlargement of FeAl₂ intermetallide particles.

As a result, the optimal ratio of Al and Fe in the Al/Fe nanoparticle composition has been determined to obtain an AlOOH/FeAl₂ composite with a high adsorption capacity towards As(V). The obtained results will be useful for solving environmental problems related to arsenic removal from water.

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References

- Padervand, M.; Gholami, M.R. Removal of toxic heavy metal ions from waste water by functionalized magnetic core-zeolitic shell nanocomposites as adsorbents. *Environ. Sci. Pollut. Res.* 2013, 20, 3900–3909. [CrossRef] [PubMed]
- Chiban, M.; Carja, G.; Lehutu, G.; Sinan, F. Equilibrium and thermodynamic studies for the removal of As(V) ions from aqueous solution using dried plants as adsorbents. *Arab. J. Chem.* 2016, *9*, S988–S999. [CrossRef]
- Abdulkhaleq Alalwan, H.; Alminshid, A.H.; Mustafa Mohammed, M.; Mohammed, M.F.; Hatem Shadhar, M. Reviewing of using nanomaterials for wastewater treatment. *Pollution* 2022, *8*, 995–1013.
- Ren, X.; Feng, H.; Zhao, M.; Zhou, X.; Zhu, X.; Ouyang, X.; Tang, J.; Li, C.; Wang, J.; Tang, W.; et al. Recent Advances in Thallium Removal from Water Environment by Metal Oxide Material. *Int. J. Environ. Res. Public Health* 2023, 20, 3829. [CrossRef] [PubMed]

- Valles-Aragón, M.C.; Olmos-árquez, M.A.; Llorens, E.; Alarcón-Herrera, M.T. Redox potential and pH behavior effect on arsenic removal from water in a constructed wetland mesocosm. *Environ. Prog. Sustain. Energy* 2013, 33, 1332–1339. [CrossRef]
- Zambrano Guisela, B.; De Almeida Ohana, N.; Duarte Dalvani, S.; Velasco Fermin, G.; HM, L.F.; Luis, N.G. Adsorption of arsenic anions in water using modified lignocellulosic absorbents. *Results Eng.* 2022, 13, 100340. [CrossRef]
- Lizama, A.K.; Fletcher, T.D.; Sun, G. Removal processes for arsenic in constructed wetlands. *Chemosphere* 2011, 84, 1032–1043. [CrossRef]
- Yao, S.; Liu, Z.; Shi, Z. Arsenic removal from aqueous solutions by adsorption onto iron oxide/activated carbon magnetic composite. J. Environ. Health Sci. Eng. 2014, 12, 58. [CrossRef]
- Höll, W.; Litter, M.I. Ocurrencia y química del arsénico en aguas. Sumario de tecnologías de remoción de arsénico de aguas. In *Tecnologías Económicas Para El Abatimiento de Arsénico En Aguas*; Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo; Consejo Nacional de Investigaciones Científicas y Técnicas: Buenos Aires, Argentina, 2010; pp. 17–31.
- 10. Baskan, M.B.; Pala, A. A statistical experiment design approach for arsenic removal by coagulation process using aluminum sulfate. *Desalination* **2010**, 254, 42–48. [CrossRef]
- 11. Sarkar, A.; Paul, B. The global menace of arsenic and its conventional remediation—A critical review. *Chemosphere* **2016**, *158*, 37–49. [CrossRef]
- Zemskova, L.A.; Voit, A.V.; Shlyk, D.K.; Barinov, N.N. Carbon fibers modified with molybdenum for sorption of arsenic(V). *Russ. J. Appl. Chem.* 2016, *89*, 592–596. [CrossRef]
- Pillai, P.; Kakadiya, N.; Timaniya, Z.; Dharaskar, S.; Sillanpaa, M. Removal of arsenic using iron oxide amended with rice husk nanoparticles from aqueous solution. *Mater. Today Proc.* 2020, 28, 830–835. [CrossRef]
- 14. Goswami, A.; Raul, P.K.; Purkait, M.K. Arsenic adsorption using copper (II) oxide nanoparticles. *Chem. Eng. Res. Des.* 2012, 90, 1387–1396. [CrossRef]
- 15. Awual, M.R.; Shenashen, M.A.; Yaita, T.; Shiwaku, H.; Jyo, A. Efficient arsenic (V) removal from water by ligand exchange fibrous adsorbent. *Water Res.* **2012**, *46*, 5541–5550. [CrossRef]
- 16. Wan, W.; Pepping, T.J.; Banerji, T.; Chaudhari, S.; Giammar, D.E. Effects of water chemistry on arsenic removal from drinking water by electrocoagulation. *Water Res.* **2011**, *45*, 384–392. [CrossRef]
- 17. Saitua, H.; Gil, R.; Padilla, A.P. Experimental investigation on arsenic removal with a nanofiltration pilot plant from naturally contaminated groundwater. *Desalination* **2011**, 274, 1–6. [CrossRef]
- 18. Zhang, G.; Li, X.; Wu, S.; Gu, P. Effect of source water quality on arsenic (V) removal from drinking water by coagulation/microfiltration. *Environ. Earth Sci.* 2012, *66*, 1269–1277. [CrossRef]
- 19. Yao, R.; Yang, H. An overview of As (V) removal from water by adsorption technology. Ann. Musculoskelet. Med. 2020, 4, 015–020.
- 20. Kim, Y.; Kim, C.; Choi, I.; Rengaraj, S.; Yi, J. Arsenic removal using mesoporous alumina prepared via a templating method. *Environ. Sci. Technol.* **2004**, *38*, 924–931. [CrossRef]
- Pena, M.; Meng, X.G.; Korfiatis, G.P.; Jing, C.Y. Adsorption mechanism of arsenic on nanocrystalline titanium dioxide. *Environ. Sci. Technol.* 2006, 40, 1257–1262. [CrossRef] [PubMed]
- 22. Li, R.; Li, Q.; Gao, S.; Shang, J.K. Exceptional arsenic adsorption performance of hydrous cerium oxide nanoparticles: Part A. Adsorption capacity and mechanism. *Chem. Eng. J.* **2012**, *185*, 127–135. [CrossRef]
- 23. Bae, J.; Kim, S.; Kim, K.S.; Hwang, H.K.; Choi, H. Adsorptive removal of arsenic by mesoporous iron oxide in aquatic systems. *Water* **2020**, *12*, 3147. [CrossRef]
- 24. Banerjee, K.; Amy, G.L.; Prevost, M.; Nour, S.; Jekel, M.; Gallagher, P.M.; Blumenschein, C.D. Kinetic and thermodynamic aspects of adsorption of arsenic onto granular ferric hydroxide (GFH). *Water Res.* **2008**, *42*, 3371–3378. [CrossRef]
- 25. Ruiping, L.; Lihua, S.; Jiuhui, Q.; Guibai, L. Arsenic removal through adsorption, sand filtration and ultrafiltration: In situ precipitated ferric and manganese binary oxides as adsorbents. *Desalination* **2009**, *249*, 1233–1237. [CrossRef]
- Habuda-Stanić, M.; Kalajdžić, B.; Kuleš, M.; Velić, N. Arsenite and arsenate sorption by hydrous ferric oxide/polymeric material. Desalination 2008, 229, 1–9. [CrossRef]
- Alchouron, J.; Navarathna, C.; Chludil, H.D.; Dewage, N.B.; Perez, F.; Pittman, C.U., Jr.; Vega, A.S.; Mlsna, T.E. Assessing South American Guadua chacoensis bamboo biochar and Fe₃O₄ nanoparticle dispersed analogues for aqueous arsenic (V) remediation. *Sci. Total Environ.* 2020, 706, 135943. [CrossRef]
- Ha, H.T.; Phong, P.T.; Minh, T.D. Synthesis of iron oxide nanoparticle functionalized activated carbon and its applications in arsenic adsorption. J. Anal. Methods Chem. 2021, 2021, 6668490. [CrossRef]
- 29. Meez, E.; Tolkou, A.K.; Giannakoudakis, D.A.; Katsoyiannis, I.A.; Kyzas, G.Z. Activated Carbons for Arsenic Removal from Natural Waters and Wastewaters: A Review. *Water* **2021**, *13*, 2982. [CrossRef]
- Svarovskaya, N.; Bakina, O.; Glazkova, E.; Rodkevich, N.; Lerner, M.; Vornakova, E.; Chzhou, V.; Naumova, L. Synthesis of novel hierarchical micro/nanostructures AlOOH/AlFe and their application for As (V) removal. *Environ. Sci. Pollut. Res.* 2022, 29, 1246–1258. [CrossRef]
- 31. Kazantsev, S.O.; Lozhkomoev, A.S.; Rodkevich, N.G. Preparation and adsorption properties of nanostructured composites derived from Al/Fe nanoparticles with respect to arsenic. *Nanomaterials* **2022**, *12*, 3177. [CrossRef]
- Lerner, M.I.; Pervikov, A.V.; Glazkova, E.A.; Svarovskaya, N.V.; Lozhkomoev, A.S.; Psakhie, S.G. Structures of binary metallic nanoparticles produced by electrical explosion of two wires from immiscible elements. *Powder Technol.* 2016, 288, 371–378. [CrossRef]

- 33. Li, X.; Scherf, A.; Heilmaier, M.; Stein, F. The Al-rich part of the Fe-Al phase diagram. *J. Phase Equilibria Diffus.* **2016**, *37*, 162–173. [CrossRef]
- Lozhkomoev, A.S.; Kazantsev, S.O.; Lerner, M.I.; Psakhie, S.G. Acid-base and adsorption properties of the AlOOH 2D nanostructures as factors for regulating parameters of model biological solutions. *Nanotechnol. Russ.* 2016, 11, 506–511. [CrossRef]
- 35. Shefer, K.I.; Cherepanova, S.V.; Moroz, E.M.; Gerasimov, E.Y.; Tsybulya, S.V. Features of the real structure of pseudoboehmites: Violations of the structure and layer packing caused by crystallization water. *J. Struct. Chem.* **2010**, *51*, 132–141. [CrossRef]
- Shields, J.E.; Lowell, S.; Thomas, M.A.; Thommes, M. Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density; Kluwer Academic Publisher: Boston, MA, USA, 2004; pp. 43–45.
- 37. Alothman, Z.A. A review: Fundamental aspects of silicate mesoporous materials. Materials 2012, 5, 2874–2902. [CrossRef]
- 38. Azizian, S. Kinetic models of sorption: A theoretical analysis. J. Colloid Interface Sci. 2004, 276, 47–52. [CrossRef]
- 39. Lin, X.; Wang, L.; Jiang, S.; Cui, L.; Wu, G. Iron-doped chitosan microsphere for As (III) adsorption in aqueous solution: Kinetic, isotherm and thermodynamic studies. *Korean J. Chem. Eng.* **2019**, *36*, 1102–1114. [CrossRef]
- Nagy, B.; Mânzatu, C.; Măicăneanu, A.; Indolean, C.; Barbu-Tudoran, L.; Majdik, C. Linear and nonlinear regression analysis for heavy metals removal using Agaricus bisporus macrofungus. *Arab. J. Chem.* 2017, 10, S3569–S3579. [CrossRef]
- Ayawei, N.; Ebelegi, A.N.; Wankasi, D. Modelling and interpretation of adsorption isotherms. J. Chem. 2017, 2017, 3039817.
 [CrossRef]
- Amrhar, O.; Nassali, H.; Elyoubi, M.S. Application of nonlinear regression analysis to select the optimum absorption isotherm for Methylene Blue adsorption onto Natural Illitic Clay. Bull. De La Société R. Des Sci. De Liège 2015, 84, 116–130.
- 43. Elmorsi, T.M. Equilibrium isotherms and kinetic studies of removal of methylene blue dye by adsorption onto miswak leaves as a natural adsorbent. *J. Environ. Prot.* **2011**, *2*, 817. [CrossRef]
- Ho, Y.S.; Chiu, W.T.; Wang, C.C. Regression analysis for the sorption isotherms of basic dyes on sugarcane dust. *Bioresour. Technol.* 2005, 96, 1285–1291. [CrossRef] [PubMed]
- 45. Erdogan, F.O. Freundlich, Langmuir, Temkin and Harkins-Jura isotherms studies of H2 adsorption on porous adsorbents. *Chemistry* **2019**, *13*, 129–135. [CrossRef]
- Lozhkomoev, A.S.; Lerner, M.I.; Tsukanov, A.A.; Kazantsev, S.O.; Bakina, O.V.; Psakhie, S.G. On the possibility of soft matter nanostructure formation based on mesoporous aluminum hydroxide. Prospects for biomedical applications. *Phys. Mesomech.* 2017, 20, 134–141. [CrossRef]

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