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Application of natural polymer and metal oxide composite for removal of arsenic(V) ions from aqueous solutions

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ABSTRACT

In this study, iron oxide nanoparticles immobilized within alginate gel exhibited promising potential for the removal of arsenic (V) ions. The preparation of the polymer-oxide composite was achieved by the ionic crosslinking of an alginate/iron oxide solution with a calcium (II) ions solution. The maximum amount of arsenic adsorbed by the investigated composite under the experimental conditions was slightly above 26 mg/g in 120 min. The results indicated that arsenic adsorption by this composite material follows a fast kinetic profile, adhering to a pseudo-second-order model. The adsorption process occurs in multiple stages, as suggested by the Weber-Morris model, with external diffusion dominating initially, followed by intraparticle diffusion. Importantly, the results confirmed that the use of alginate gel does not significantly impact the adsorption process, preserving the adsorption capacity of the metal oxides. Overall, the investigated composite successfully removed arsenic (V) from the solution, addressing a critical issue in water treatment.

Keywords: arsenic (V) removal, alginate, goethite, nanoparticles, composite.

1. Introduction

Water pollution, arising from naturally occurring toxic substances or as a result of human activities, is a growing concern in the modern world and represents one of the most actual ecological issues today. Among the various hazardous pollutants, heavy metals and metalloids form an especially dangerous category due to their toxicity at low concentrations, resistance to biodegradation, and high potential for bioaccumulation (Gorelick and Zhang, 2015). In many cases, these pollutants have profoundly detrimental health effects. While these effects may not be immediately apparent due to their low concentrations, they become increasingly evident with prolonged exposure. Arsenic, in particular, is one of the most hazardous and toxic metalloids. It occurs naturally in water, primarily from the dissolution of rocks, minerals, and ores that contain arsenic compounds, as well as from certain biological processes. Moreover, human activities such as mining and the use of pesticides contribute to elevated arsenic levels in groundwater. The issues related to arsenic contamination in groundwater are especially pronounced in the Serbian regions of Banat and Bačka (Božo Dalmacija, 2023).

Arsenic, a brittle, steel-gray metalloid, is a toxic and non-degradable element that exists in various oxidation states. The most common inorganic forms are arsenite (As(III)) and arsenate (As(V)) (Kanel et al., 2005). While arsenite is more toxic and frequently found in underground water sources, it readily oxidizes. As a result, arsenate predominates in surface waters (Rajakovic and Rajakovic-Ognjanovic, 2018). Since arsenate can be removed more effectively from water using both conventional and unconventional methods compared to arsenite, a pre-treatment step, typically involving the oxidation of As(III) to As(V), is often required (Issa et al., 2011).

The challenge of elevated arsenic levels in drinking water, often surpassing permissible limits, presents a significant obstacle for modern engineers specializing in separation processes. This issue persists as the World Health Organization (WHO) continues to reduce the acceptable arsenic concentrations in drinking water. Among various arsenic removal techniques, adsorption is recognized for its efficiency and cost-effectiveness. Researchers have investigated a broad array of natural and synthetic materials for adsorption, showing a particular interest in metal powders for their fast kinetics and relatively high adsorption capacities. Nonetheless, the use of powder adsorbents poses a separation challenge post-adsorption. To overcome this, metal powders can be immobilized within particles formed through the gelation of natural polymers like alginate. This method facilitates easier separation while preserving the adsorption capacity and speed akin to that of pure metal powders.

Numerous studies have shown that high concentrations of arsenic in drinking water are linked to various health issues, including diseases of the lung, skin, bladder, liver, and vascular system. Additionally, exposure to arsenic is associated with teratogenic, mutagenic, and

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carcinogenic effects. Consequently, reducing arsenic levels in drinking water to acceptable limits is crucial (Vujović et al., 2019). In response to this concern, the World Health Organization (WHO), the United States Environmental Protection Agency (US EPA), the European Commission's drinking water directive, and Serbian water potability regulations have all set the maximum allowable concentration of arsenic in drinking water at 10 μg/L.

Various methods are available for effectively removing arsenite from drinking water and wastewater. These methods can be divided into traditional approaches, such as adsorption and chemical coagulation, and newer but more expensive techniques, including electrocoagulation, ion exchange, and membrane technologies. Each method comes with its own set of pros and cons. However, adsorption is often considered the most practical option due to its high efficiency and cost-effectiveness. Current research primarily aims at identifying new and improving existing adsorbent materials to enhance arsenic removal capabilities.

Among various materials utilized for arsenite adsorption, metal powders stand out due to their rapid kinetics and relatively high adsorption capacities (Chiban et al., 2015; Hao et al., 2018). These adsorbents are notably more effective in nano form, offering arsenic removal efficiency up to 5-10 times greater than their micro-sized counterparts (Ponder et al., 2001). This enhanced performance is primarily attributed to their significantly increased surface area. However, the reduction in size also introduces significant challenges in separating the adsorbent from the mixture post-adsorption, especially when the adsorbents are fine powders (Živanić, 2019). Such issues are typically addressed by creating composites of metal oxides, immobilizing them within various materials, for instance, polymers like alginate.

The use of iron compounds for arsenic removal is highly recommended due to their low cost and toxicity, abundance, and minimal leaching of adsorbed arsenic from exhausted adsorbents (Hao et al., 2018; Bugarčić et al., 2021). However, selecting the optimal immobilizing material for nanoparticles presents a challenge, as the use of an immobilization agent can slow down inter and intraparticle diffusion, thus diminishing the kinetic parameters of the adsorption process. In this study, alginic acid, gelled by Ca^{2+} cations, was employed as the immobilization agent, given that alginate gels exhibit promising physico-chemical properties not only as immobilizing agents but also as adsorbents for heavy metals, which may further enhance the adsorption capacity of the formed composite (Milivojevic et al., 2015). Therefore, the aim of this work was to investigate the basic adsorption properties of polymer oxide composite for the removal of arsenite from aqueous solutions, primarily drinking water, in order to assess its potential for this application and to justify the need for further, more detailed investigations.

2. Materials and Methods

2.1. Composite preparation

The materials utilized for the preparation of composite particles included: 1) a 2% sodium alginate water solution; 2) calcium chloride, CaCl2*2H2O; 3) iron(II) sulfate, FeSO4; and 4) sodium bicarbonate, NaHCO3. The process for creating composite particles adhered to a method previously outlined (Živanić, 2020). Figure 1 provides a schematic of the composite preparation process, alongside a scanning electron microscope (SEM) image of the resulting composite. Adsorption experiments were carried out with 50 mL of an initial arsenate(V) solution at a concentration of 7.00 mg/L and 12.5 mg of the composite, over periods ranging from 0 to 120 minutes. After each specified reaction time (1, 3, 5, 10, 15, 30, 45, 60, 90, and 120 minutes), the solution and composite were separated, and the supernatants were collected for subsequent analysis. The initial and residual concentrations of arsenate were measured using flame atomic absorption spectroscopy (FAAS) (PerkinElmer 3100).

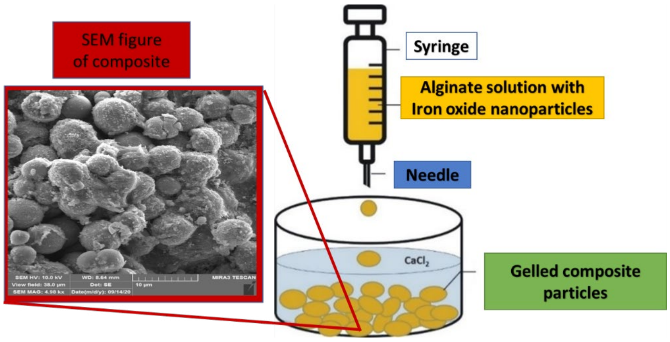


Fig. 1. Preparation procedure and SEM figure of composite particles.

2.2. Adsorption kinetics

The main goal of experiments was to examine is the adsorption rate extensively reduced by immobilization or not. Adsorption kinetics and adsorption capacity are two main parameters for designing and optimizing adsorption processes. Within this work, Pseudo-First-Order (PFO), Pseudo-Second-Order (PSO), and Elovich kinetic models, as well as Intra Particle Diffusion (IPD) model were tested for description of obtained experimental data.

1. **The PFO, or Lagergren model**, defines adsorption rate based on the adsorption capacity and links adsorption rate to the number of free active spaces on the surface of adsorbent. It can be for practical reasons given as linearized equation:

$$ln\left(q_e - q_t\right) = \ln\left(q_e\right) - k_1 * t \qquad 1$$

where q_e (mg/g) is equilibrium adsorption capacity, q_t (mg/g) is adsorption capacity in time t (min) and k_1 (min^{-1}) is the PFO adsorption rate constant.

2. **The PSO, or Ho's model** is based on the assumption that adsorption can be presented as the second order chemisorption and it supposes that adsorption rate is proportional to the number of available active sites on adsorbent surface. It can be also defined by linearized equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad 2$$

where q_e, q_t and t are defined for PFO model, and k_2 (min^{-1}) is the PSO adsorption rate constant.

3. **Elovich kinetic model** neglects desorption and it is good for describing chemisorption for systems in which desorption is negligibly small compared to adsorption due to low surface coverage (kinetics is far from equilibrium). Linearized form of this model is:

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}ln(t) \qquad 3$$

where q_t and t are defined for PFO model, while a is the initial adsorption rate (mg/g min), and b is a desorption constant.

4. **The IPD or Weber-Morris model** is proposed to model adsorption processes where kinetic is limited by diffusion.

$$q_t = k_i t^{\frac{1}{2}} + C \qquad 4$$

where the slope, k_i is the IPD rate constant [mg/(g·$min^{0.5}$)], and intercept, C is the initial adsorption capacity (mg/g).

The k_i usually increases if initial adsorbate concentration is increased while the C is equal to zero if kinetics is controlled only by IPD. However, in most cases plot is multilinear and C commonly is not equal to zero. Higher values of C indicate higher film diffusion resistance.

3. Results and Discussion

The experimental results yielded adsorption capacity (q_t) (mg/g) and adsorption efficiency (R) expressed as a percentage, as illustrated in Figure 2.

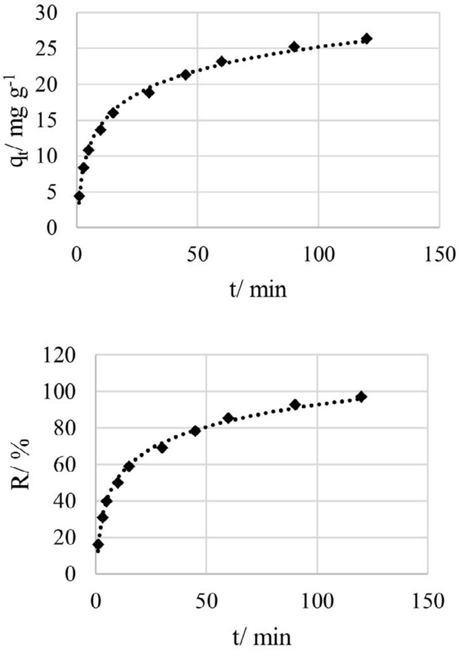


Fig. 2. Adsorption capacity q_t (mg/g) and adsorption efficiency, R (%).

Figure 2 shows that, under the given experimental conditions, the maximum amount of arsenate adsorbed by the composite within 120 minutes was 26 mg/g, representing an exceptionally high adsorption efficiency of 97%.

To investigate the adsorption kinetics, the Pseudo-First-Order (PFO), Pseudo-Second-Order (PSO), and Elovich models were utilized. Analysis of the data indicated that the PSO and Elovich models offered the best fit for the experimental results, implying that chemisorption is the primary mechanism behind arsenate adsorption by the composite material. The kinetic results for the PFO, PSO, and Elovich models are presented in Table 1, and the associated graphs for the PSO and Elovich models are depicted in Figure 3.

Experimental results fitted by IPD are given in Figure 4 while the calculated diffusion coefficients are provided in Table 1. As Figure 4 highlights multiple linear sections with varying slopes and intercepts are present, indicating different stages in the examined process. These stages comprise the initial step, characterized by external surface diffusion, which is the fastest process; followed by macropore diffusion, slower than the initial process; and finally, micropore diffusion, the slowest process.

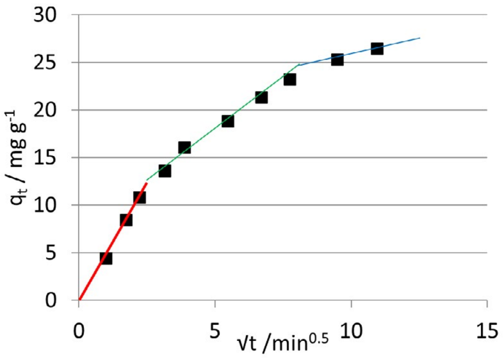
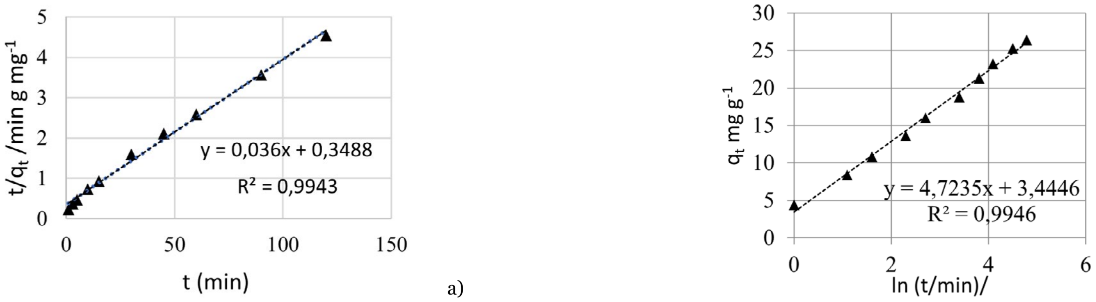


Fig. 4. IPD model (q_t – sqrt(t)).

Table 1. Experimentally obtained parameters for PFO, PSO, Elovich and IPD models.

Kinetic model	PFO	PSO	Elovich	IPD
k_1 (min^{-1})	0.0321			
q_e (mg/g)	20.264			
R^2	0.9819			
k_2 (min^{-1})		0.0371		
q_e (mg/g)		27.793		
R^2		0.9943		
a			0.9795	
b			2.1172	
R^2			0.9946	
k_1 (min^{-1})				0.483
k_2 (min^{-1})				0.22
k_3 (min^{-1})				0.0848

The value of RE = $1/(q_e{*}b) = 0.01$ derived from the Elovich model suggests that the adsorption curve rapidly reaches equilibrium, entering what is referred to as zone IV (when RE < 0.02), indicative of very fast processes (Wu, Feng-Chin et al., 2009). Consequently, the composite demonstrates highly favorable kinetic parameters for arsenic removal via adsorption. Nevertheless, the study recognizes the need for further research to identify additional critical adsorption parameters of the material under investigation. These forthcoming studies will offer a more detailed insight into the material's adsorption characteristics and its potential utility in water treatment processes.



a)

b)

Fig. 3. a) PSO model (t/q_t – t), b) Elovich model (q_t – ln(t)).

4. Conclusions

The findings of this research demonstrate that the adsorption kinetics of As(V) on the examined adsorbent align most precisely with the PSO (Pseudo-Second-Order) and Elovich kinetic models. According to these models, the chemical reaction represents the rate-limiting step in the adsorption process, highlighting the significance of the chemical processes involved in the removal of arsenate.

Moreover, the adsorbent showcases advantageous mass transfer properties, marked by a readily accessible surface for adsorption. This beneficial trait enhances the composite's overall adsorption kinetics, facilitating effective arsenate removal.

In practical terms, given the concentration of the adsorbate applied and the quantity of adsorbent used, the study reveals that favorable adsorption and removal efficiency are attained. This outcome underscores the efficacy of the composite material under investigation for arsenate removal under designated conditions.

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