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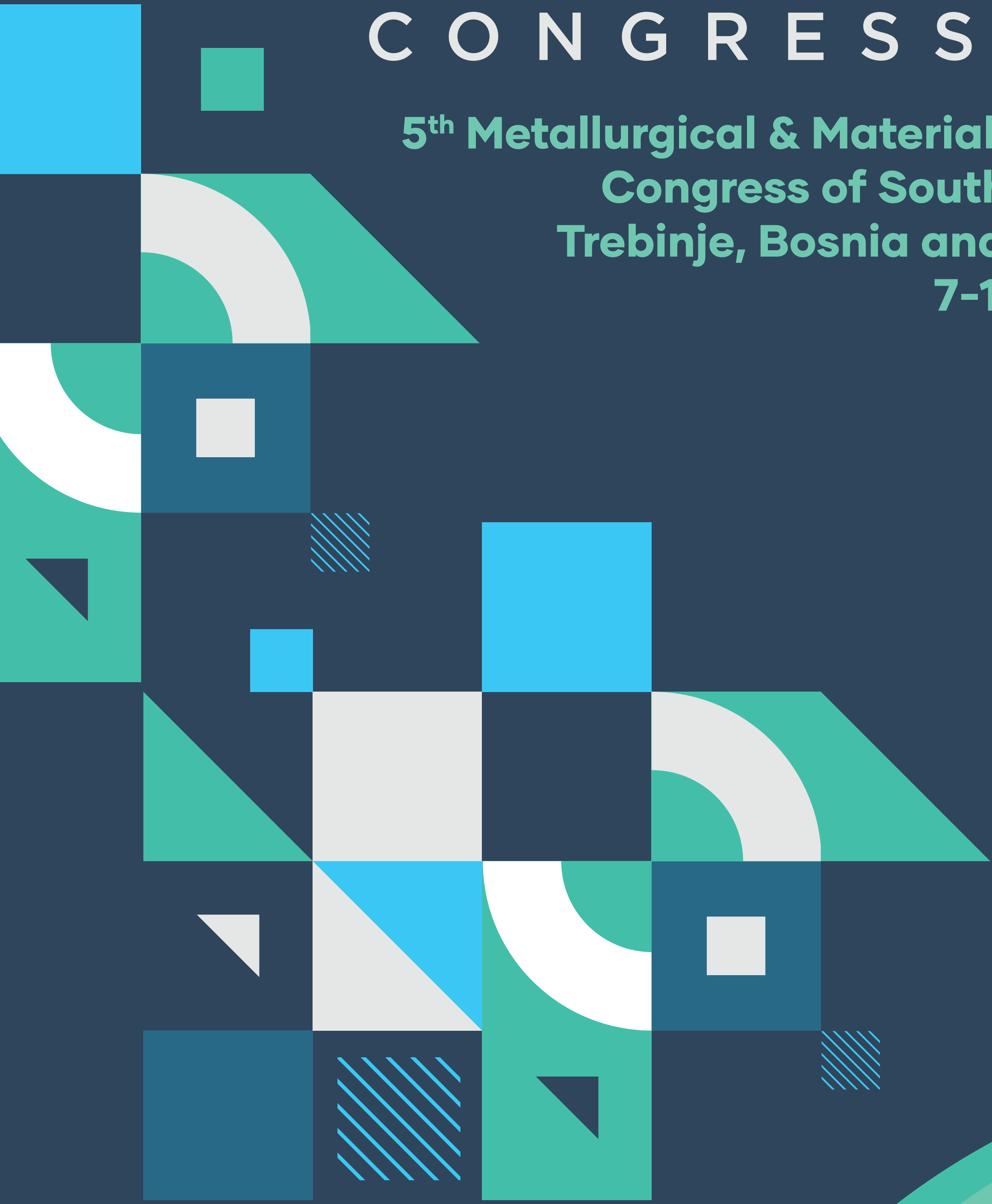
CONGRESS 2023

**5th Metallurgical & Materials Engineering
Congress of South-East Europe
Trebinje, Bosnia and Herzegovina
7-10th June 2023**



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PROCEEDINGS

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5th Metallurgical & Materials Engineering Congress of South-East Europe

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THE ADSORPTION OF ARSENIC(V) IONS FROM AQUEOUS SOLUTIONS BY COMPOSITE OF NATURAL POLYMER AND METAL OXIDE

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The presence of arsenic in drinking water above the permissible limits is one of the current problems facing modern engineers in the field of separations and it has not yet been satisfactorily resolved, because the permissible concentrations of arsenic in drinking water are constantly reduced by the World Health Organization (WHO). Among the various processes for arsenic removal, adsorption has a special place as one of the most efficient and cheap process. Many natural and artificial materials are tested for adsorption processes, and adsorption on metal powders is particularly interesting because they represent adsorbents with fast kinetics and relatively high adsorption capacities. However, the application of powder adsorbents is difficult due to their separation from the mixture after adsorption. In order to solve that problem, metal powders may be immobilized into particles obtained by gelling natural polymers. In this way, it is easier to separate the adsorbent from the mixture, however this must be achieved without losing the adsorption capacity and rate compared to pure metal powders.

In this study, the use of metal oxide (iron oxide nanoparticles) immobilized within the alginate gel showed good potential for arsenic (V) ions removal. The obtained results showed that arsenic adsorption by obtained composite has fast kinetic, following pseudo-second-order model, and that it is conducted in several steps, according to the Weber-Morris model. It was suggested that external diffusion is the dominant mechanism at the beginning of the arsenic adsorption, followed by intraparticle diffusion. The obtained results confirmed that gelling with alginate did not significantly affect the adsorption process, that is, it does not interfere with the adsorption capacity of metal oxide~~s~~, which is a very important factor. Arsenic (V) removal was successfully performed using the investigated composite.

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

Introduction

Water pollution either due to naturally present toxic species or caused by human activities is grooving problem in modern world and represents one of the most important ecological issues nowadays. Among toxic contaminants, heavy metals and metalloids represent especially dangerous group of pollutants because they are toxic even at low concentrations, non-biodegradable and highly bio cumulative (Gorelick and Zhang, 2015). In most cases these pollutants have very destructive health effects, which even if are not immediate, due to low concentrations, certainly are obvious after continued exposure. Arsenic, is one of the most dangerous and toxic metalloids, since it is present even in natural waters, usually due to the dissolution of rocks, minerals and ores, with incorporated arsenic compounds and some biological processes. In addition, there are numerous anthropogenic sources such as mining, use of pesticides etc., which may further increase arsenic concentrations in ground waters. Problems associated with arsenic present in ground waters are especially expressed in Serbian districts of Banat and Bačka.

Arsenic, brittle, steel-gray, toxic, and non-degradable metalloid, may be present in nature in different oxidation states, but the most abundant inorganic species are arsenite (As(III)), and arsenate (As(V)) (Kanel et al., 2005). Although arsenite is more poisonous and is dominant form in underground waters, it is easily oxidized and therefore the most dominant form of arsenic in the surface waters is arsenate (Rajakovic and Rajakovic-Ognjanovic, 2018).

Furthermore, since arsenate is generally more efficiently removed from water, either by conventional or nonconventional methods than arsenite, some kind of pretreatment (commonly preoxidation of As(III) to As(V)) is needed in order to improve removal efficacy (Issa et al., 2011).

Many studies have shown that high arsenic concentrations in drinking water can cause different lung, skin, bladder, liver, and vascular diseases and disorders, and have teratogenic, mutagenic, and carcinogenic effects and therefore when detected they must be lowered to the acceptable levels (Vujović et al., 2019). In order to prevent mentioned health problems, the World Health Organization (WHO), United States Environmental Protection Agency (US EPA), European Commission drinking water directive and Serbian water potability regulations ~~has~~ recommended a maximum permitted concentration of arsenic in drinking water ~~to~~ of 10 μg/L.

The methods that may be used for successful removal of arsenite from drinking and waste waters can be divided into traditional methods (adsorption, chemical coagulation) and relatively new, but expensive methods (electrocoagulation, ion exchange, membrane techniques). Each of these methods has its own advantages and drawbacks but adsorption as highly effective and efficient low-cost technology certainly is the most useful. The main aim of researches focused on improving adsorption capabilities is finding new and/or improving existing adsorbent materials used for arsenic removal.

Materials and Methods

Adsorption materials

Many different natural and artificial materials have been tested for arsenite adsorption, but adsorption on metal powders is particularly interesting because of their fast kinetics and relatively high adsorption capacities (Chiban et al. 2015, Hao et al., 2018). These adsorbents are especially effective if they are nano-sized since they can be up to 5-10 times more efficient for arsenic removal compared to their micron size equivalents (Ponder et al., 2001). One of the main reasons for this behavior is their highly expanded surface area but with size reduction there emerge a serious problem connected to separation of adsorbent in the fine powder form from the mixture after adsorption process (Živanić, 2019). Challenges connected to the use of nano-particles can be overcome by using different materials for their immobilization. In this work the iron oxide nanoparticles were used as adsorbent while alginate beads were used as immobilization agent. Iron compounds are recommended as good candidates for arsenic removal since they are non-toxic, low cost, easily accessible in large quantities, and have lowest leaching of adsorbed arsenic from exhausted adsorbent (Hao et al., 2018, Bugarčić et al., 2021). While there are number of options, selecting the suitable immobilizing material for nanoparticles is very demanding task among other reasons because use of the immobilization agent may reduce kinetic parameters of iron oxide nanoparticles due to intraparticle diffusion limitations. In this work alginic acid was used as immobilization agent while Ca^{2+} cations were used as gelling agent. Alginate gels has promising physical and chemical properties not only as immobilizing agent but also as adsorbents for heavy metals (Milivojevic et al., 2015). Calcium alginate thermally irreversible gels, combined with ferric oxides, produced composite particles which were used in this adsorption experiments.

Preparation of the composite particles

Materials used for the preparation of the composite particles were: 1) 2% Natrium-alginate solution (water + Na-alginate); 2) Calcium-chloride, $CaCl_2*2H_2O$; 3) Iron(II)-sulfate, Fe_2SO_4, and 4) sodium bicarbonate, $NaHCO_3$. Preparation of composite particles was done according to previously determined procedure (Živanić, 2020). Schematic figure of composite preparation and its SEM image is given in Figure 1.

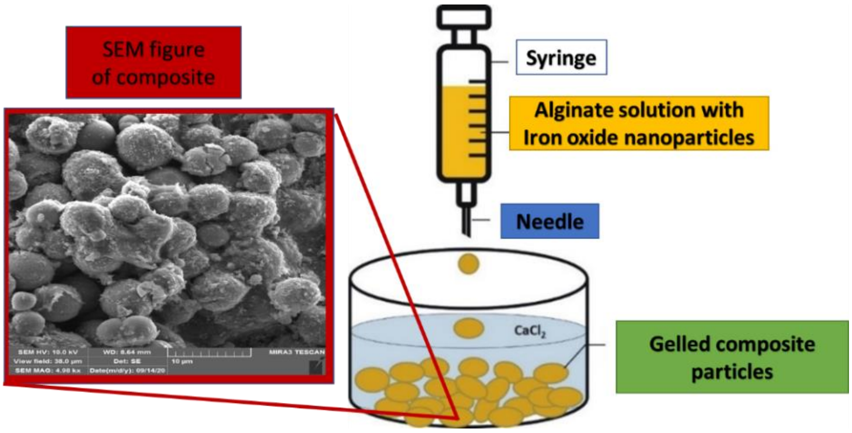

Figure 1 Preparation and structure of composite particles

Adsorption experiments were done by using 50 mL of the initial Arsenate(V) concentration (7.00 mg/L) and 0.0125 g of composite in time interval from 0 to 120 min. After each specified reaction time (1, 3, 5, 10, 15, 30, 45, 60, 90, and 120 min), solution and composite were separated and supernatants were collected for analysis. The initial and non adsorbed arsenate concentrations were determined by AAS.

Adsorption kinetics

The main goal of experiments was to examine whether the kinetic of such composite~~s~~ is still satisfying and if adsorption rate is not significantly diminished by immobilization. Adsorption kinetics along with adsorption capacity of adsorbent are two key parameters for designing and optimizing of 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.

The PFO, or Lagergren model, describes adsorption rate based on the adsorption capacity and links adsorption rate to the number of free active spaces on the surface of adsorbent. It may be presented by following linearized equation:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 * t \tag{1}$$

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.

The PSO model is based on the assumption that adsorption can be presented as the second order chemisorption and it assumes that adsorption rate is proportional to the number of available active sites on adsorbent surface. It may be described with following linearized equation:

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

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

Elovich kinetic model neglects desorption and it is good for describing chemisorption but for systems where kinetics is far from equilibrium (desorption is negligibly small due to low surface coverage).

Linearized form of this model is given by following equation:

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

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

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

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

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.

Results and Discussion

According to experimental results obtained adsorption capacity, qt (mg/g) and adsorption efficiency, R (%), are presented in Figure 2.

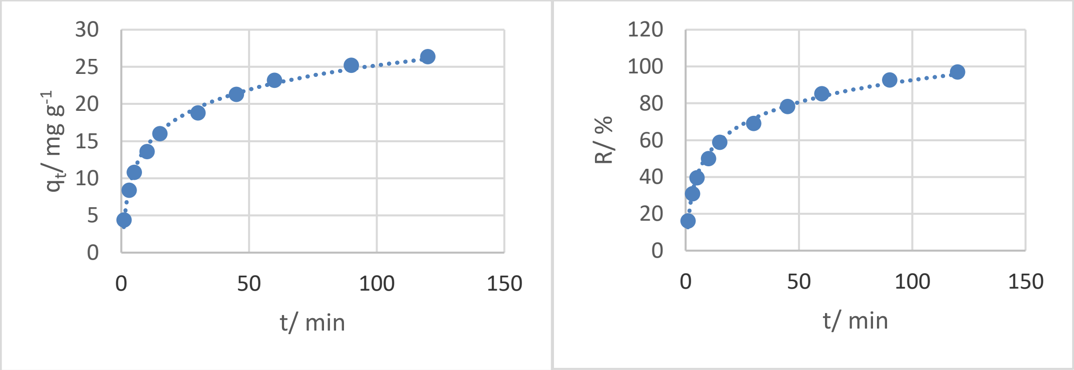

Figure 2 Adsorption capacity qt (mg/g) and adsorption efficiency, R (%)

As it can be seen from Figure 2, composite adsorption capacity for arsenate removal is higher than 26 mg/g after 120 min, while adsorption efficiency is very high (over 97%).

Adsorption kinetics was investigated by PFO, PSO and Elovich models. Data analysis showed that the best fitting of the experimental data was obtained by PSO and Elovich models. Good fitting of the data with these models suggests that chemisorption is dominant mechanism relevant for arsenate adsorption by composite. Obtained kinetic data for PFO, PSO and Elovich models are summarized in Table 1, while graphs for PSO and Elovich model are given in Figure 3.

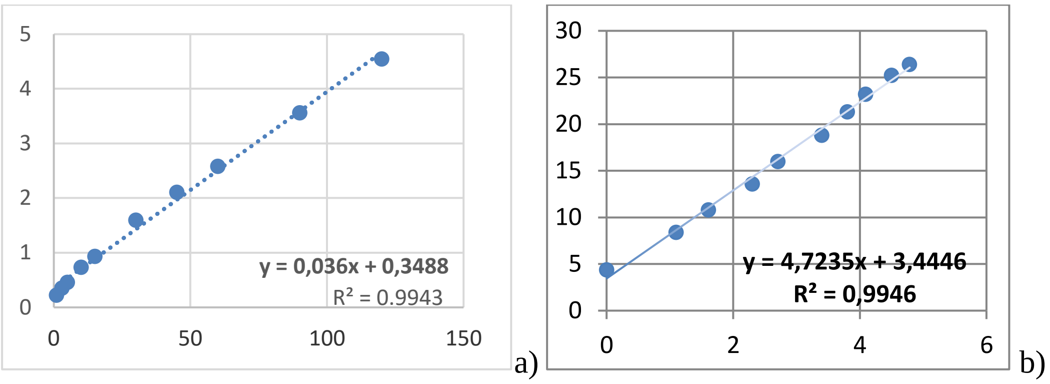

Figure 3 a) PSO model (t/q_t – t), b) Elovich model (qt – ln(t))

Experimental results fitted by IPD are given in Figure 4.

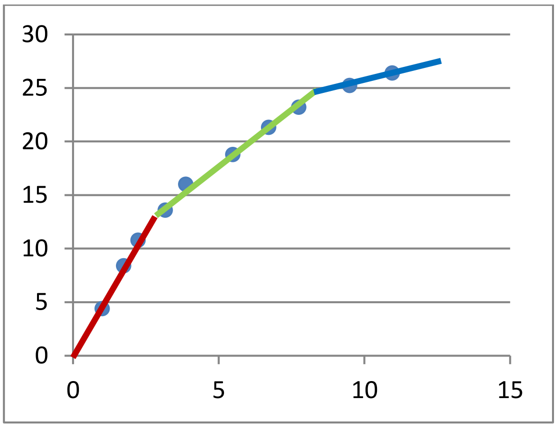

Figure 4 IPD model (q_t – sqrt(t))

As it can be seen from Figure 4. the multiple linear sections with different slopes and intercepts are present for examined process. There are three distinct linear sections: 1) initial section (external) surface diffusion which is the fastest process; 2) macropore diffusion, slower than initial process, and 3) micropore diffusion, which is the slowest process. The calculated diffusion coefficients are given in Table 1.

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		
		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

Conclusions

The obtained results suggested that adsorption kinetics of As (V) onto tested adsorbent is best represented by the PSO and Elovich kinetic models which indicate that the rate-limiting step is the chemical reaction (chemical process). Adsorbent has good mass transfer properties, (it has easily available surface for adsorption) and therefore investigated composite has good adsorption kinetics. For applied adsorbate concentration and adsorbent amount preferable adsorption capacities and efficiencies are obtained. Further investigations are needed in order to determine other important adsorption parameters of investigated material.

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