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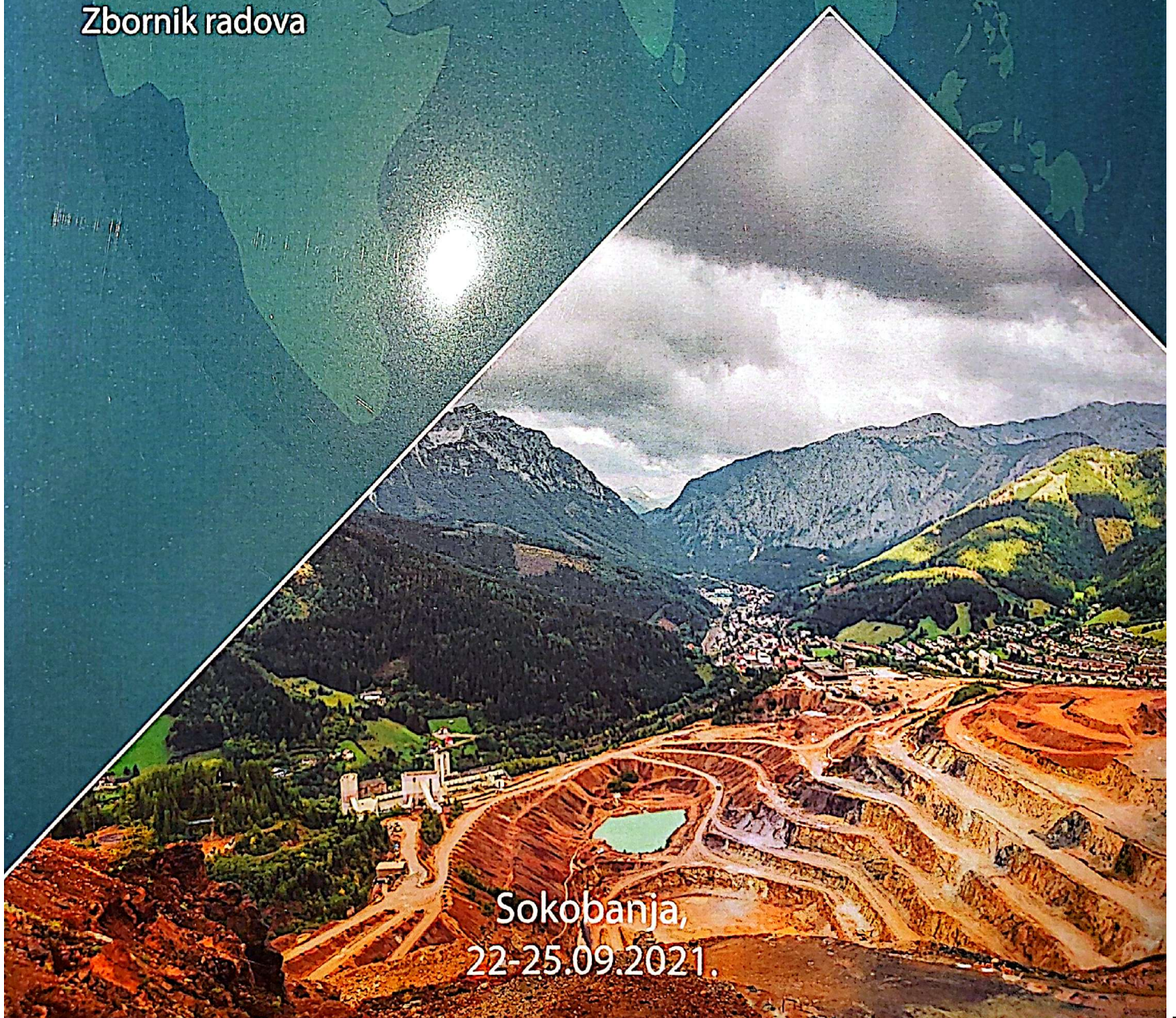
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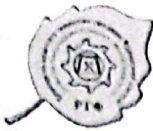
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COMPARATIVE ANALYSIS OF Pb(II) REMOVAL KINETICS IMMOBILIZED BIOWASTE MATERIALS

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Abstract: Growing industrial activities generate huge amounts of waste biomass worldwide annually most often, improperly disposed, representing resource lost and secondary pollution sources investigations have shown that this kind of biomass material can be reused as high quality sorbent modifications which would improve separation process. Having this in mind, we have investigated two biowaste materials-lignocellulosic waste of peach stones (Prunus Persica L) – IPS and invasive (Myriophyllum spicatum) - MsA, both immobilized in sodium alginate, as lead sorbents. For kinetic both sorbents were used to remove Pb^{2+} ions from synthetic solutions (batch reaction system with defined operational parameters. Obtained data were modelled using nonlinear form of three most models.

Keywords: waste biomass, immobilization, sorption kinetics, lead

1. INTRODUCTION

Industrial activities outspread a huge amounts of different pollutants into environment. Mining processing industries are targeted as the ones which often release huge amount of toxic metals lead, cadmium, and copper, whose serious toxicity to animals, plants, and microorganisms major pollution concern. Industrial wastewaters with high concentrations of heavy metals treated by different techniques, among which chemical precipitation, coagulation, membrane or ion exchange are often used [1]. However, if the concentrations of the metals are too low techniques might be ineffective, either in environmental (produced hazardous waste treatment), or economic disadvantage (high operational cost).

Comparing with other techniques for heavy metals removal from contaminated water waste biomass (often called "biosorption") has several advantages: low operation cost availability, easy application using existent operational units, and effectiveness concentrations [2]. Huge amounts of different waste biomass are generated all over the world literature, there might be found many plant-derived biomass wastes that have been used heavy metals, such as Pb, Cd or Cu [3–5]. In opposite, the biosorption might have some such as low sorbent capacity, inadequate mechanical strength, or releasing certain organic which increase total organic content (TOC), or changing chemical oxygen demand (COD) minimize negative effects of biosorbents applications, certain modifications are often used chemical modifications (acid/base or organic agent treatment), thermal modification carbonisation, pyrolysis) or immobilisation into different polymer matrix (such as alginate poly-vinyl alcohol (PVA)).

In this paper we have investigated possible application in Pb(II) removal of two different biomass waste materials: peach stone particles (PS) and waterweed *Myriophyllum spicatum* L (MS). Both native samples were, after mechanical treatment, immobilized in sodium alginate, and obtained beads were further applied in lead removal using batch technique. Obtained experimental results were further modelled using different reaction kinetic equations: pseudo-first, pseudo-second and Elovich model

2. MATERIAL AND METHODS

2.1 Sorbent preparation

Lignocellulosic waste - peach stone biomass was obtained from local fruit processing factory. Collected peach stones were washed with water and dried at room condition. After drying, the stones were grinded into powder by ultra-centrifugal mill "Retsch ZM-1" (Retsch, Gemini BV, Netherland), and screened through the series of wire sieves. For the purpose of this experiment, particles with diameter less than 0.1 mm were used. Before immobilization, milled sorbent particles were dried to constant mass at 60 °C and stored (sample PS).

Samples of freshly harvested *M. spicatum* were taken from the artificial Sava Lake, Belgrade, Serbia. The fresh plant used for study has been harvested with a mechanical underwater harvester by the public company "Ada Ciganlija" (Belgrade, Serbia). Fresh plant material was first washed with tap water and then with distilled water. After washing, *M. spicatum* was dried at 35 °C until constant mass. Dried plant was milled and sieved to particle size less than 0.2 mm (sample MS).

Both samples of PS and Ms were immobilized according to procedure described in Milojković et al [6]. In brief, 2% polymer solution was made dissolving Na-alginate (low viscosity, p.a., Sigma-Aldrich) in distilled water, followed by stirring for 24 h to form homogenous solution. Biomasses powders were then blended with 100 ml of 2 % w/v alginate solution (in biomass/alginate mass ratio 2:1) to obtain desired immobilized beads. After homogenization, obtained suspensions were drop wise extruded using syringe into a cross-linker solution of 0.1 M $CaCl_2$ forming spherical beads, which were left in 2% $CaCl_2$ solution for 24 hours, when the washing process was performed. Beads were dried at the room temperature to constant weight, marked as IPS and MsA, and then used for experiments.

2.2 Sorbents Characterization

Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM-EDX) was used to record surface morphology as well as to confirm lead binding. SEM images were taken for both samples IPS and MsA before and after Pb(II) sorption. SEM analyses were performed with dried sample under vacuum coated with a thin layer of gold and observed using JEOL JSM-6610LV SEM model.

The influence of immobilization process on the release of organic carbon was determined by measuring the TOC content in water samples after biosorption experiments. In all experiments, Pb(II) was removed by raw PS and MS as well as IPS and MsA particles, under defined operational parameters (initial Pb (II) concentration 1 mM, biosorbents dose 2g/L, contact time of 24 hours. TOC concentrations were measured by Analytik Jena, TOC/TN Analyzer (Multi N/C 2100S), using thermo catalytic oxidation, digestion temperature up to 950 °C, Carbon detection - NDIR (coupled with VITA method).

2.3 Sorption Kinetic Experiments

The sorption experiments were carried out with sorbate solutions made from analytical grade $Pb(NO_3)_2$. The initial sorbate (lead ions) concentration was set as 1 mmol/L. In all sorption experiments, the same amount (2 g/L) of both sorbents, IPS and MsA, was used. Experiments were conducted in batch reactor with stirring (200 rpm) at constant room temperature (25 °C). Initial pH values of the system were adjusted to 5 with diluted HNO_3 and NaOH as needed and kept constant during experiment (using Sension MM340 pH meter). At predefined time intervals (ranging from 2 min up to 24 h), samples were taken and the analytical measurement of Pb(II) concentration was conducted using atomic absorption spectrometry (Perking Elmer Analyst 300). All experiments were performed in duplicate, and the average values are presented here.

Lead uptake was calculated from the following expression:

$$q = \frac{V(C_i - C_e)}{m} \tag{1}$$

where q represents the amount of Pb(II) adsorbed by investigated sorbent at any time (mg/L), C_i and C_e are the initial and equilibrium metal concentrations (mg/L), V is the volume of Pb(II) solution (L), and m is the mass of the immobilized sorbent (g). Kinetic models used in this paper are listed in Table 1.

Table 1. Models equations used for evaluation of Pb(II) sorption onto PSA and MsA

Model	Equation	Parameter	Ref.
Pseudo-first order (PS-1)	$q_t = q_e(1 - e^{-k_1 t})$	k_1 (g/mg/min): the pseudo first order rate constant	(Lagergren, 1898)
Pseudo-second order (PS-2)	$q_t = \dfrac{t}{\left(\dfrac{1}{k_2 q_e^2}\right) + \left(\dfrac{t}{q_e}\right)}$	k_2 (g/mg/min): the pseudo second order rate constant	(Ho and McKay, 1999)
Elovich	$q_t = \dfrac{1}{b}\ln(ab) + \dfrac{1}{b}\ln t$	a (mg/g/min): initial Cu(II) sorption rate b (g/mg): extent of surface coverage	(Low, 1960)

*q_e (mg/g): sorption capacity at equilibrium
**q_t (mg/g): sorption capacity at any time t

3. RESULTS AND DISCUSSION

3.1 Sorbents Characterization

SEM images show the sorbent surface texture and its porosity. It is commonly used for examination of the morphological features and surface characteristics of applied sorbents.

SEM images of the samples IPS and MsA before (a and c) and after biosorption of Pb(II) (b and d) are shown in Fig.1. As it can be seen, obtained beads have regular spherical shape, with particle diameter close to 1.5 mm average diameter, with PS and MsA evenly entrapped within the alginate matrix, regularly exposed to highly developed surface. Opposite to the native materials [6, 7], the presence of meso and macro pores is not evident. After Pb(II) sorption, surface of the sorbents has become more smooth, indicating loss of entrapped calcium and swelling process.

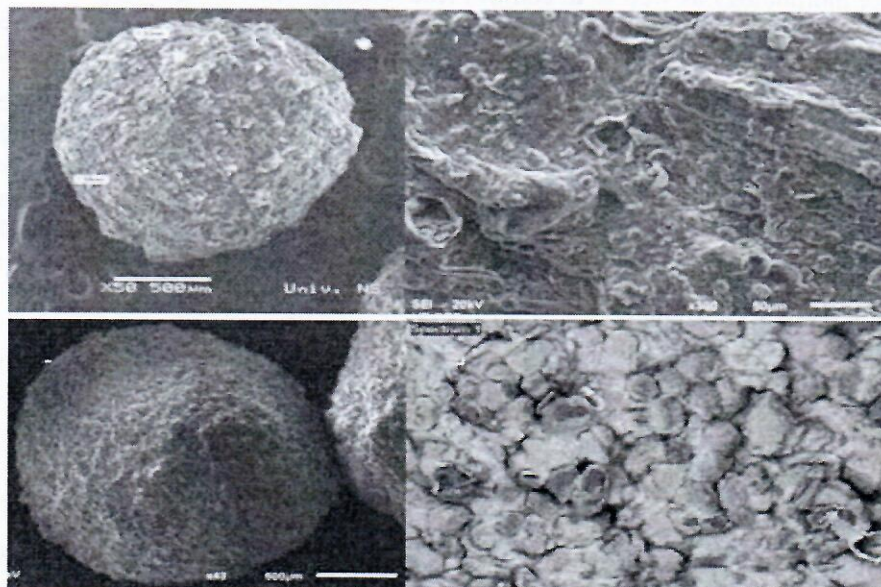*Figure 1.* SEM images of MsA and IPS before (a and c) and after (b and d) Pb (II) sorption

EDS analyses showed typical lignocellulosic composition of the immobilised sorbents, with higher Ca picks than in pure, native materials, as a consequence of Ca immobilisation. After Pb(II) sorption, reduced peaks of Ca as well as a new peak of Pb(II) are observed in EDS spectrum (image not shown). Quantitative

major elements found in both investigated sorbents are presented in Table 2. Beside presented other inorganics such as potassium, silica or aluminum were also recorded in traces.

Table 2. TOC content and weight percent of analysed elements by EDS in samples IPS and MsA

Sample	TOC content, mg/L	Major element (%)			
		C	O	Ca	Pb
raw PS after Pb sorption	10.4	-	-	-	-
raw MS after Pb sorption	32.8	-	-	-	-
IPS before Pb sorption	-	41.62	53.39	3.99	0.00
IPS after Pb sorption	2.79	33.42	43.30	0.66	22.62
MsA before Pb sorption	-	34.92	56.68	7.66	0.00
MsA after Pb sorption	5.90	27.02	37.75	0.93	33.85

analysis indicates that all calcium present in immobilized beads have exchanged with lead, g content of Ca from 3.99% to 0.66% (for IPS) and from 7.66% to 0.93% (for MsA). Also, survey indicates that some inorganic minerals composed of Ca and K on the biomass surface, useful for sorption of Pb through cation exchange [8] For example, Pb can replace Ca or K in and sulfate to form precipitates, indicating one of the possible pathways for sorption of Pb by rich in inorganic minerals. As it is known, the sorption of lead on the sorbent surface is also the surface functional groups of biomass (e.g. oxygen-containing functional groups such as OH, or C–O), which facilitate lead binding through surface functional groups complexation [9].

of carbon and oxygen has also decreased, indicating some changes in the sorbents structure, as also confirmed by TOC analyses, whose results are also given in Table 2. Advantage of ization can been seen in TOC analyses: pure *M. spicatum* releases 32.78 mg/L of total organic while immobilized samples, MsA, only 5.9 mg/L, indicating that immobilization reduced more times TOC in solution after biosorption. Also, IPS sample reduced TOC in solution more than es compared to raw PS. Higher content of TOC after application of raw MS compared to PS can uted to its natural components: PS mainly consist of cellulose, hemicellulose and lignin [6], while his components, MS contains a significant amount of protein [7]. This is very important since mass waste materials have biological origin, so there is a possibility that during the biosorption organic matter is released from materials themselves, although those materials remove pollutants. in mind that the amount of TOC found in drinking water ranges from 0.1 up to 10 mg/L, obtained lues after application of immobilized sorbents are very desirable.

etic Experiments Results

etic profiles (change in sorbents capacity with contact time) are presented at Figure 2. As it can be r both sorbents, IPS and MsA, the initial rapid kinetics into first 90 minutes occurs, thanks to ility of active sites on sorbents surfaces. This can have significant practical importance as it nsure process efficiency and economy at the same time, allowing the smaller reactor dimensions. increase of contact time leads to slower Pb(II) uptake, indicating change in removal kinetic nena, and possible mass transfer resistance which might occurs.

al kinetics were further characterized by applying the following models to the experimental data: first (PS-1) and pseudo-second-order (PS-2) kinetic models as well as Elovich model. Table 3. rizes data for experimental sorption capacity at equilibrium (q_e) and the values of the kinetic ters, together with the corresponding determination coefficients (R^2) and χ^2 values.
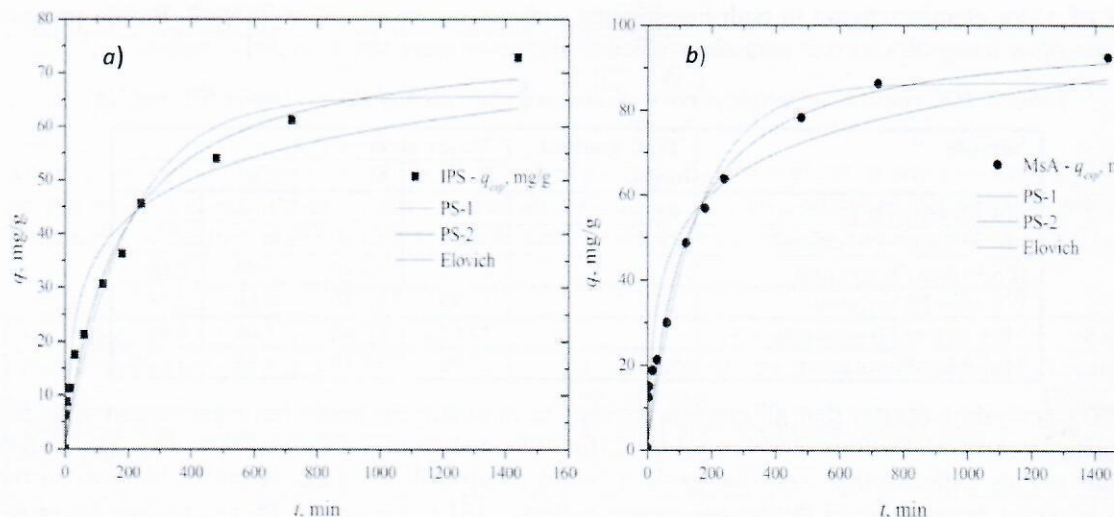
Figure 2. *Kinetic of Pb(II) removal by IPS (a) and MsA (b) 25°C (Ci=1mM, M/V=2g/L, 250 rpm, pH*

As can be seen from Table 3. Lagergren pseudo-first order equation cannot be used to predict the kinetic of lead by IPS and MsA: although R^2 are not considerably low, calculated q_m values no differ from experimental q_{exp} values, which is also confirmed by high χ^2 values. Thus, good lin the Lagergren plots does not insure that interactions between sorbate and solid phase follow fi kinetics, which was also confirmed by Gupta and Bhattacharyya [9]. It was also observed from La plots, that the pseudo-first order equation can be applied to kinetic data only in the initial perio rapid sorption of lead ions occurs.

Table 3. *Kinetic parameters calculated for Pb(II) sorption*

Model	Parameter	Sorbent	
		IPS	MsA
	q_{exp} (mg/g)	74.85	92.45
PS-1	q_e (mg/g)	65.68	86.37
	k_1 (1/min)	0.005	0.007
	R^2	0.9445	0.9488
	χ^2	31.31	50.99
PS-2	q_e (mg/g)	76.79	96.84
	k_2 (g/mg/min)	7.808E-5	8.455E-5
	R^2	0.9695	0.9681
	χ^2	17.09	31.75
	h^* (mg/g/min)	0.4605	0.8222
Elovich	q_e (mg/g)	63.38	87.32
	a (mg/g/min)	3.262	5.644
	b (g/mg)	0.0965	0.0732
	R_E^{**}	0.1635	0.1564
	R^2	0.9144	0.9168
	χ^2	48.00	82.85

* Initial sorption rate: $h=k_2{}^*q_e{}^2$
**Dimensionless equilibrium approach factor: $R_E=1/(b^*q_e)$

Also, results presented in Table 3 show a lowest compliance with the Elovich model, resultin correlation coefficients (0.9144 and 0.9168, for IPS and MsA respectively) and highest error func both samples. It can also be observed (Table 3) that the rate of chemisorption a, is higher for the MsA than in IPS, while the case for the constant related to surface coverage (b) has opposite tr values of approaching equilibrium factor, R_E, are falling in the range from 0.1 to 0.3, bellowin region of mild adsorption, which is faster for the sample MsA. However, the pseudo-second-ord showed the best fit to the experimental data related to the sorption of Pb(II) onto IPS and MsA, highest squared correlation coefficients (0.9695 and 0.9681, respectively). In addition, as shown 2, the pseudo-second-order model predicted capacity, q_e values were in best agreement

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experimental data. Initial speed, h, for MsA was almost twice as the one for IPS, which indicate higher amount of surface functional groups of MsA sorbent. These results suggest that the pseudo-second order model, based on the assumption that the rate-limiting step might be the chemical sorption, provides the best correlation of the kinetic data. Having in mind all previously described, the lead removal onto both IPS and MsA probably takes place via surface exchange reactions until the surface functional sites are fully occupied; after this, lead ions are diffusing into the pores, slowing the overall sorption process. In order to estimate which is the rate-limiting step involved in lead sorption by IPS and MsA, as well as to distinguish the sorption mechanism between them, the kinetic data should be further analysed using some of the intraparticle diffusion models (e.g. Boyd, Weber Morris etc.).

4. CONCLUSION

According to the data presented in this paper, alginate immobilized beads of IPS and MsA might be successfully applied in purification of waters contaminated with lead, which is often found in mining waste streams. This composite sorbents have some advantages comparing to native materials: higher sorption capacity, easy application and separation, sphere shape allowing lower mass resistance and reduced amount of total organic carbon released during the biosorption process. *M. spicatum* immobilized in alginate – MsA demonstrated to be better sorbent of lead compared to IPS, having in mind achieved sorption capacity and initial kinetic under defined kinetic experiments. The sorption mechanism of both sorbents included ion exchange along with chemisorption, but the overall kinetic should be further examined using several intraparticle diffusion models, since the lead removal highly depends on it.

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