Natural and Modified Zeolite—Alginate Composites. Application for Removal of Heavy Metal Cations from Contaminated Water Solutions

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Abstract: In present paper, the influence of the initial pH and concentration of Pb^{2+} on its adsorption by the natural (NZA) and Fe(III)-modified zeolite-alginate beads (FeA) was studied. Results showed that modification of the starting materials have a positive effect on their adsorption capacities (102 and 136 mg/g for the NZA and FeA, respectively). After encapsulation, the mechanism of lead adsorption by both adsorbents was changed and ion exchange dominates. The best adsorption was achieved for initial pH > 3.8. Cation exchange capacity, structural properties, and hydrophobicity of samples were also determined, and the presence of the alginate has no significant influence on investigated properties of samples. Experiments on wastewater from tailings of lead and zinc mine Grot, Serbia, showed that after treatment with both adsorbents, the content of the most abundant heavy metals (Pb, Zn, Hg, and Mn) significantly decreased.

Keywords: lead; ion exchange; alginate; zeolite-alginate composite; isotherms; pH; heavy metals; tailings wastewater

1. Introduction

Lead is one of the prime toxins of heavy metals, which is discharged into the environment by different human activities [1]. When lead is in water solutions, depending of pH, it may be present in different forms [2]. In industrial wastewaters, where pH is usually lower than 6, it exists predominantly in the most dangerous-Pb^{2+} form. Consequently, the removal of Pb^{2+} in an effective manner has become an important issue nowadays. Among the methods that are used for solving this problem, adsorption and ion exchange are the simplest and the most effective, particularly when low-cost, eco-friendly natural materials (such as zeolite-clinoptilolite) are employed [3].

The efficiency of the natural or modified zeolite for removal of Pb^{2+} has already been documented [3–5]. In our previous studies [6,7], the adsorption of Pb^{2+} from water solutions by natural and Fe(III)-modified zeolite (clinoptilolite) with particle size <0.043 mm was investigated. Results showed that after modification, adsorption capacity of the starting material increased from 66 to 133 mg/g. Also, it was shown that due to large adsorption capacity, stability, and simple modification procedure, Fe(III)-modified zeolite could be used as a material for practical application in purification of waters contaminated with Pb^{2+}. However, from a practical standpoint, one of the main limitation is its ultrafine structure which causes difficulties, such as filtration (separation) of solids

from liquids. This problem, in general, could be solved by using material of controlled (higher) particle size or by immobilization into certain form. However, our previous study [7] on these two adsorbents with particle size $-0.8 + 0.6$ mm showed decreasing of adsorption capacities for Pb^{2+} with increasing particle size (62 for the natural and 102 mg/g for Fe(III)modified zeolite), so that the immobilization of the zeolite powder looks like better solution.

Using of polymer matrix for its immobilization-encapsulation could be a useful way for solving this problem. However, in the selection of a polymer it should be taken into account and ensure that applied modification has no negative effect on properties of the starting material, such as adsorption capacity or cation exchange capacity. Also, chelating agents, such as natural polysaccharides, can change hydrophobicity or hydrophilicity of surface of minerals, and, depending on chelating functionalities, improve selectivity and adsorption capacity towards specific metal ions [8]. Since Fe(III)-modified zeolite is used for the removal of Pb^{2+} from water solutions, it is important that applied polymer should not have a negative impact on its hydrophilicity.

Due to its biodegradability, non-toxicity, gelation, etc., using of alginate seems like a very good solution. Also, it is widely used in medical, pharmaceutical, and food applications [9], and shows high affinity for heavy metals, especially for lead [10–12]. The major component of the alginate is alginic acid, (1,4-linked β-D-mannuronic and α-L-guluronic acids), which structural formula is given in Figure 1.
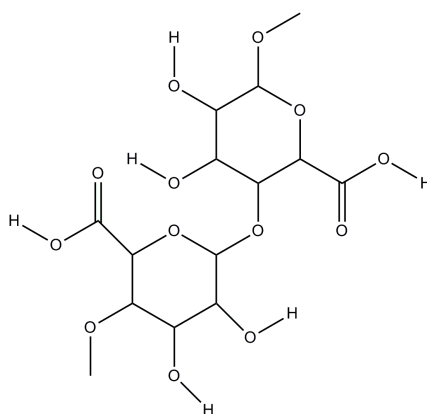

Figure 1. Alginic acid-structural formula.

Alginate is rich in carboxyl and hydroxyl functional groups, which are the main groups included in heavy metal adsorption [13,14]. However, although alginate has high capacity for heavy metals, its effectiveness and applicability in industrial applications has been limited [9]. More often, alginate is used for the encapsulation of different, bio [15], or mineral materials, such as montmorillonite [16], kaolin [17], synthetic zeolite, or active carbon [18], etc., in order to improve their applicability and/or adsorption capacities for different pollutants. However, using natural or Fe(III)-modified zeolite-alginate composites for removal of Pb^{2+} from contaminated water has not yet been studied.

The aim of this study was investigation of the removal of Pb^{2+} from water solutions using natural and Fe(III)-modified zeolite–alginate composite beads as adsorbents. The influence of the initial pH and concentrations on removal of Pb^{2+} from aqueous solution by these adsorbents was investigated. Also, experiments on wastewaters taken from flotation tailing of lead and zinc mine was performed.

2. Materials and Methods

2.1. Samples Preparation

Chemicals that were used in this study were of high purity and supplied from Sigma Aldrich, Darmstadt, Germany.

The natural zeolite-clinoptilolite from Vranjska banja, Serbia with a particle size <0.043 mm (NZ) was used as a starting material. The Fe(III)-modified zeolite (FeZ) was obtained combining the method for the goethite preparation and that for the preparation of Fe-coated zeolite [19,20], and the detailed procedure is given elsewhere [6].

Na-alginate (Table 1) was used for encapsulation of samples.

Table 1. Properties of Na-alginate.

Chemical formula	$(C_6H_8O_6)n$
CAS Number	9005-38-3
MDL	MFCD00081310
Loss on Drying	$\leq$15.5%
Viscosity, c = 1%, Water at 25 °C	5.0–40.0 cps
pH, c = 1%, Water at 25 °C	5–8
Arsenic	$\leq$3 ppm
Cadmium	$\leq$1 ppm
Mercury	$\leq$1 ppm
Lead	$\leq$10 ppm

Natural and Fe(III)-modified zeolite-alginate composites were prepared using a method described by Yuan and Viraraghavan [21]. A 2% polymer solution was prepared by dissolving 2 g of sodium alginate in 100 cm^3 of distillated water and then agitated for 24 h at 300 rpm to make a homogenous polymer solvent mixture. Then, 10 g of the natural or Fe(III)-modified zeolite was blended with 100 cm^3 of 2% w/v sodium alginate solution for 2 h, in order to make beads with zeolite loadings of 10%. Spherical beads were prepared by dropping the mixed solution into 0.1 mol/dm^3 $CaCl_2$ solution cooled to the temperature 4–8 °C. Beads that were 3–5 mm in diameter were formed by drop-wise extrusion through a pipette tip. The beads were hardened by placing them in 2% solution of $CaCl_2$ for 24 h at temperature 4–8 °C. Those that floated on the surface were discarded. The remaining beads were washed in distilled water by agitation at 100 rpm in 250 cm^3 conical flasks for 30 min, discarding the solution and then repeating the process five times. After the removal of residual water with paper towels, the beads were dried gradually at room temperature to constant weight. Finally natural zeolite-alginate beads (NZA) and Fe(III)-modified zeolite beads (FeA) were obtained (Figure 2) and then used for the characterization and adsorption experiments.

(**a**)   (**b**)
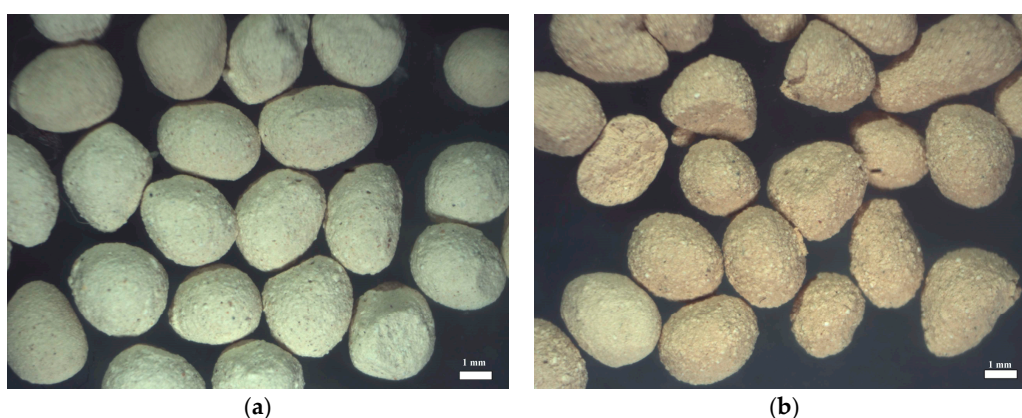
Figure 2. Microscopic images of the natural zeolite-alginate beads (NZA) (**a**) and Fe(III)-modified zeolite bead (FeA) (**b**).

2.2. Samples Characterization

The content and type of exchanged cations and total cation exchange capacity (CEC) of the NZA and FeA were determined by treating 1 g of each sample with 100 cm^3 of 1 mol/dm^3 NH_4Cl [22].

Suspensions were left at room temperature for 24 h with periodic shaking. After 24 h, suspensions were centrifuged and concentrations of the Ca^{2+}, Na^+, K^+, and Mg^{2+} in the supernatants were determined on atomic absorption spectrophotometer (AAS) "Analytic Jena Spekol 300" (Analytic Jena, Jena, Germany). Cation exchange capacity (CEC) for every sample was calculated as the sum of concentrations of the released cations, and is expressed in meq/100 g.

Fourier transform infrared (FTIR) spectroscopic analyses of NZ and FeZ before and after alginate loadings, as well as pure alginate were performed using a Thermo Scientific "Nicolet IS50" spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) in transmission mode. Spectrum of the KBr was used as background. The spectra were recorded between 400 and 4000 cm^{-1} wavelength range, at resolution of 2 cm^{-1} and 64 scans. After recording the spectra, two corrections were performed: automatic correction of the base line and atmospheric suppression.

Diffuse reflectance infrared Fourier transform (DRIFT) (Thermo Fisher Scientific, Waltham, MA, USA) analyses were performed on the same instrument and were recorded in the same range of wavenumber, scans, and resolution as in transmission mode, using the Smart Diffuse Reflectance accessory, at room temperature. The spectra of NZ and FeZ before and after alginate loadings were collected. Samples were prepared by mixing the samples with the KBr, while the KBr spectrum was used as background. These conditions allowed for obtaining spectral absorbance in the range for the application of the Kubelka–Munk transformation [23]. Within each sample, the most intense absorption band, observed at ~1060 cm^{-1} was used for normalization of the band intensities. After the recording of the spectra, the same corrections were performed as for transmission mode.

2.3. Pb^{2+} Adsorption Experiments

Stability of NZA and FeA in distilled water was tested and compared with the immutability of NZ and FeZ. For each sample, experiments were performed under following conditions: 0.5000 g of sample was mixed with 50 cm^3 of distilled water. The initial pH was adjusted to 4.2 by adding negligible amounts of 0.1 mol/dm^3 of HNO_3. Suspensions were mixed at 350 rpm for 24 h. After 24 h, suspensions were centrifuged and concentrations of the Ca^{2+}, Na^+, K^+ and Mg^{2+}, iron, silica and aluminium in the supernatants were determined on atomic absorption spectrophotometer (AAS) "Analytic Jena Spekol 300".

Influence of pH on Pb^{2+} adsorption on NZA and FeA was investigated at different initial pH (pH_i) values. The pH_i was adjusted between 2.5 and 5.2 by adding negligible amounts of 0.1 mol/dm^3 HNO_3 or 0.1 mol/dm^3 KOH. Experiments were performed by shaking at 350 rpm 0.5000 g of NZA or FeA with 50 cm^3 of aqueous lead solution ($C_0 = 1400$ mg/dm^3), at 25 °C for 24 h. The suspensions were centrifuged and concentration of Pb^{2+}, Ca^{2+}, Mg^{2+}, Na^+, and K^+ were determined by AAS.

Influence of the initial Pb^{2+} concentrations on its adsorption was investigated by mixing at 350 rpm and 25 °C 0.5000 g of the NZA or FeA with 50 cm^{-3} of aqueous solutions, containing various initial concentrations of Pb^{2+} (180–3200 mg/dm^3 (18–320 mg/g)) for 24 h. Initial pH was adjusted to 4.2. After 24 h, suspensions were centrifuged and the amounts of Pb^{2+}, Ca^{2+}, Na^+, K^+, Mg^{2+}, Fe^{3+}, Si^{4+}, and Al^{3+} were determined by AAS.

In all of the experiments, the final pH was also measured.

The wastewater sample have been taken from the hydrocyclone overflow on the flotation facility of mining Grot, Serbia, in accordance with standard procedure (ISO 5667-10:1992). Collected sample was kept in the capped container and left at room temperature in order to separate liquid from solid phase. After few days, liquid phase was decanted and filtered through qualitative filter paper in order to remove large particles and impurities. Adsorption experiments were carried out by shaking 0.5 g of NZA or FeA with 50 cm^3 of wastewater at 25 °C for 24 h. Then, suspensions were centrifuged and the initial and non-adsorbed concentrations of heavy metals in the supernatants were determined by using inductively coupled plasma optical emission spectrometry.

3. Results and Discussion

3.1. Determination of Cation Exchange Capacity of the NZA and FeA

Since our previous study [7] showed that ion exchange is one of the main mechanisms that are responsible for removal of Pb^{2+} from water solutions by NZ and FeZ, the determination of the amount and type of exchangeable cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) and total cation exchange capacity (CEC) of NZA and FeA, was very important. For that purpose, standard method with 1 mol/dm³ NH_4Cl was applied and results are shown in Table 2.

Table 2. Determination of the cation exchange capacity (CEC) for NZA and FeA.

Sample	Na$^+$ (meq/100 g)	K$^+$ (meq/100 g)	Ca^{2+} (meq/100 g)	Mg^{2+} (meq/100 g)	Total CEC (meq/100 g)
NZ	23.3	15.5	85.0	22.5	146.5
NZA	15.3	11.1	112.5	10.7	149.6
FeZ	17.9	93.0	48.7	21.7	181.2
FeA	8.5	52.5	112.5	7.2	180.7

As can be seen from Table 2, the CEC of the NZ was ~146, while for FeZ ~181 meq/100 g. Much higher CEC of the FeZ and higher amount of exchanged K^+ than from NZ can be explained by modification procedure for obtaining FeZ in solution of 0.1 mol/dm³ of KOH. Also, presented results showed that the modification procedure used for synthesis of NZA and FeA had no significant impact on total CEC of the NZ and FeZ. After modification with alginate, CEC was ~150 meq/100 g for NZA and ~181 meq/100 g for FeA. However, the amounts of Na^+, K^+, and Mg^{2+} released from encapsulated samples were lower than from starting samples ($\Delta_{NZ-NZA}(Na^+ + K^+ + Mg^{2+}) \approx 25$ meq/100 g and $\Delta_{FeZ-FeA}(Na^+ + K^+ + Mg^{2+}) \approx 64$ meq/100 g), whereas the amount of Ca^{2+} released from NZA and FeA was higher than that from NZ and FeZ ($\Delta_{NZA-NZ}(Ca^{2+}) \approx 27$ meq/100 g and $\Delta_{FeA-FeZ}(Ca^{2+}) \approx 64$ meq/100 g). These results indicate that during modification, ion exchange between Ca^{2+} from $CaCl_2$ solution and Na^+, K^+, and Mg^{2+} from NZ and FeZ occurred, i.e., modification with alginate caused a change in the content of the exchanged cations, but had no influence on a total cation exchange capacity.

3.2. FTIR Spectroscopic Analyses of the NZA and FeA

In order to determine whether encapsulation of the NZ and FeZ causes a change in their structural properties, FTIR analyses of samples before and after alginate loadings, as well as pure alginate were performed, and the results are given in Figure 3.
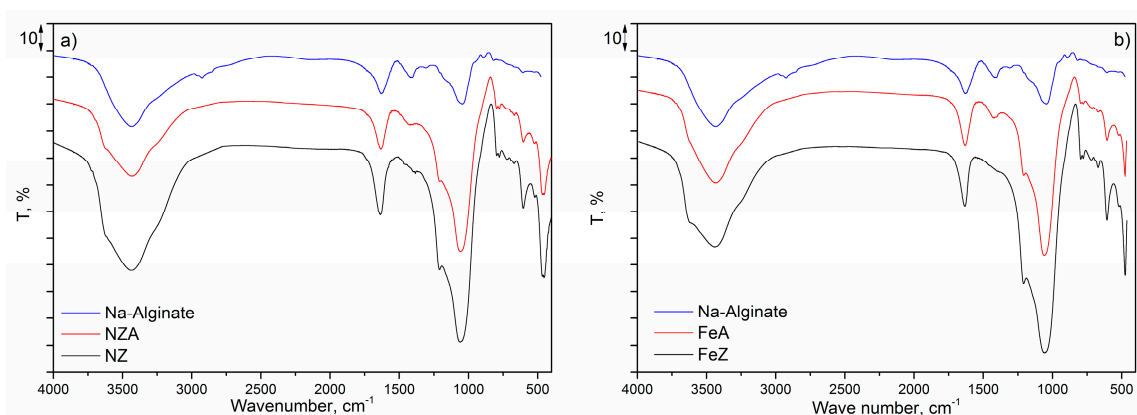
Figure 3. Fourier transform infrared (FTIR) spectra of the Na-alginate and: (**a**) NZ and NZA; and (**b**) FeZ and FeA.

In FTIR spectra of the NZ (Figure 3a) and FeZ (Figure 3b), bands that are characteristic for the natural zeolite (clinoptilolite) are observed, indicating that iron(III) modification had no impact on structural properties of the zeolite. Our published results [6] showed an increase of the iron content in FeZ for 1.25% when compared to the NZ, while transmission electron microscopy [7] showed for FeZ that iron is mainly concentrated in form of amorphous aggregates, which are most probably in the form of iron oxy-hydroxides, and in lower extent in the form of spherical nanoclusters, which could be made by iron oxides. Finally, even though the method for pure goethite preparation was applied, there is an absence of the characteristic FTIR bands for iron oxide. The reason for that could be small increase of the iron amount in the FeZ in comparison with NZ, and consequently, an overlapping of spectral bands characteristic for goethite with those characteristic for starting zeolite, or its mainly presence in form of amorphous aggregates. In NZ and FeZ, vibration peaks are obtained at 456, 605, 775, 800, 1058, 1640, 3438, and 3622 cm^{-1}. In the region of 1200–950 cm^{-1} the strongest vibration band was observed, and is assigned to asymmetric Si–O–Si and Si–O–Al stretching vibrations. In the region from 400 to 600 cm^{-1} are bands that are assigned to Si–O and Al–O bending vibration modes. Bands in the 600–800 cm^{-1} region originate from pseudo-lattice vibrations in zeolite. Bands at 775 and 800 cm^{-1} are due to symmetric Si–O–Si and Al–O–Al vibrations. Bands that are characteristic for vibrations of the hydroxyl group are at 3440 cm^{-1} (hydrogen-bonded OH to oxygen ions), the band typical for isolated OH stretching vibration at 3633 cm^{-1}, and the bending vibration of zeolite water at 1640 cm^{-1} [24–26].

Spectral bands of the Na-alginate are lower in intensities than those that were obtained for the NZ or FeZ. In FTIR spectrum of the Na-alginate, vibration peaks are observed at 3437, 2926, 2853, 1629, 1410, 1300, 1049, 887, and 824 cm^{-1}. The band at 3437 cm^{-1} corresponds to the stretching vibration of the hydroxyl group. Bands at 2923 and 2853 cm^{-1} are assigned to asymmetric and symmetric CH stretching vibrations, respectively. Band at 1629 cm^{-1} corresponds to asymmetric stretching of the C=O group, while bands at 1410 and 1300 cm^{-1} is assigned to stretching symmetric and asymmetric vibrations of –OH and C–OH in carboxyl group, respectively. Band at 1049 cm^{-1} is due to vibration in ether bridge [27], and bands at 887 and 824 cm^{-1} correspond to the bending of the OH^{-} group of carboxylic functional group [28].

The intensities and positions of bands in the spectra of NZA and FeA are very similar to each other, indicating that the presence of iron on surface of FeZ had no influence on structural properties of FeA, and on interaction between starting zeolite and Na-alginate. The spectra of NZA and FeA are mix of the spectra of alginate and NZ or FeZ. All of the bands characteristic for starting NZ or FeZ are registered at the same position (<3 cm^{-1}), but due to presence of the alginate with reduced intensity. The most intense bands characteristic for alginate (3437 and 1049 cm^{-1}) are not visible due to overlapping with the characteristic bands of NZ and FeZ, and only band at 1410 cm^{-1} is visible at the same position in spectrum of NZA and FeA. Spectral band at ~1635 cm^{-1} for encapsulated samples is resulting band of alginate (1629 cm^{-1}) and band of starting materials (1640 cm^{-1}). Also, the other bands for Na-alginate are not visible due to low amount of alginate in NZA and FeA. The absence of new spectral bands and significant changes in the position of the existing peaks could indicate that, with applied modification procedure, only mixed systems of Na-alginate and NZ or FeZ were formed.

3.3. Determination of the Hydrophobicity of the NZA and FeA

As it was mentioned, properties such as hydrophobicity (hydrophilicity) of adsorbents, may affect on selectivity and adsorption capacity towards specific metal ions. Also, since higher hydrophilicity is a prerequisite for high wettability of adsorbents, and better contact between surface of adsorbent and heavy metals dissolved in water solutions, it was of interest to determine whether the encapsulation of NZ and FeZ with Na-alginate has an impact on the hydrophilicity of the starting materials.

The hydrophobicity degree of porous materials could be assess by various proposals, and some of them are related to the adsorption of water in mesoporous silica and related materials [29]. On the other side, diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy provides information about the outer 6–8 μm layer of a sample, meaning that it has a potential for the investigation of

surface of sample [30]. From that point, the detection and identification of the hydrophobic and hydrophilic functional groups on the surface of sample and finding their ratio can be alternative way for the quantification of sample hydrophobicity degree [31]. However, to the best of our knowledge, the information about hydrophobicity degree obtained for a given set of materials from adsorption isotherms or DRIFT experiments were not yet studied.

Hydrophobicity of NZ, FeZ, NZA, and FeA were determined only by using the DRIFT technique. In DRIFT, spectra of samples surfaces (results are not shown) of all spectral bands that are described in Figure 3 were registered on same wavenumbers for each sample, indicating almost homogenous arrangement of the functional groups in all samples. From DRIFT spectra, groups that are particularly relevant in the context of determination of hydrophobicity are those with spectral bands, which are not related to the vibration of water molecule and are located in region below 1500 cm^{-1}, and they are given in Table 3.

The ratio between sum of the bands areas of the hydrophilic groups and areas of all the groups in a sample that is relevant for the determination of hydrophobicity could be an indication of the degree of the hydrophilicity of the material. It is usually expressed in %A. The higher value of the %A corresponds to a material with higher affinity to water and vice versa [23]. To calculate the areas of bands, a deconvolution of the normalized DRIFT spectra was made by fitting Gaussian functions. For that purpose, software Origin Lab 9.0 (OriginLab, Northampton, US) was used. The deconvolution fittings for all the samples are given in Figure 4, while the absorption maxima and relative areas of each group are given in Table 3. Finally, the hydrophilicity degree for samples was calculated using Equation (1) [31], and results are given in Table 4.

Table 3. Maximum absorption wavenumber $\widetilde{\nu}$ (cm^{-1}) and relative area (%A$_{rel}$) obtained by deconvolution of the bands in spectral region 1500–400 cm^{-1}.

Group	Wave Number	NZ	NZA	FeZ	FeA
R–COOH	$\widetilde{\nu}$ (cm^{-1})	-	1425	-	1426
	%A$_{rel}$	-	0.6	-	1.3
Al–O–SI	$\widetilde{\nu}$ (cm^{-1})	1172	1178	1176	1179
	%A$_{rel}$	22.3	18.6	21.3	20.2
	$\widetilde{\nu}$ (cm^{-1})	1057	1060	1056	1059
	%A$_{rel}$	67.6	70.5	68.7	68.4
Al–O (Si–O)	$\widetilde{\nu}$ (cm^{-1})	605	604	607	607
	%A$_{rel}$	1.4	1.3	1.9	1.0
	$\widetilde{\nu}$ (cm^{-1})	521	521	-	-
	%A$_{rel}$	0.7	0.6	-	-
	$\widetilde{\nu}$ (cm^{-1})	462	472	477	468
	%A	8.1	5.1	2.7	5.7
	$\widetilde{\nu}$ (cm^{-1})	-	449	455	445
	%A$_{rel}$	-	2.6	6.0	1.9
	$\widetilde{\nu}$ (cm^{-1})	-	419	-	418
	%A$_{rel}$	-	0.6	-	0.6

$$\%A = \frac{\%A\left(\widetilde{\nu}(\text{R}-\text{COOH}) + \widetilde{\nu}(\text{Al}-\text{O}) + \widetilde{\nu}(\text{Si}-\text{O})\right)}{\%A\left(\widetilde{\nu}(\text{R}-\text{COOH}) + \widetilde{\nu}(\text{Al}-\text{O}) + \widetilde{\nu}(\text{Si}-\text{O}) + \widetilde{\nu}(\text{Al}-\text{O}-\text{Si})\right)} \times 100 \qquad (1)$$

Table 4. %A for NZ, NZA, FeZ, FeA.

Degree of the Hydrophilicity	NZ	NZA	FeZ	FeA
%A	9.3	10.8	10.5	10.7

Due to presence of the hydrophilic [32] goethite and iron oxy-hydroxides on the surface of FeZ [7], after modification of the NZ with Fe(III) ions, its degree of the hydrophilicity slightly increased from

9.3 to 10.5. After encapsulation of the NZ and FeZ with Na-alginate, the degree of the hydrophilicity also slightly increased to 10.8 for NZA and 10.7 for FeA, meaning that there is no negative impact of the modification on hydrophilicity of the starting samples.
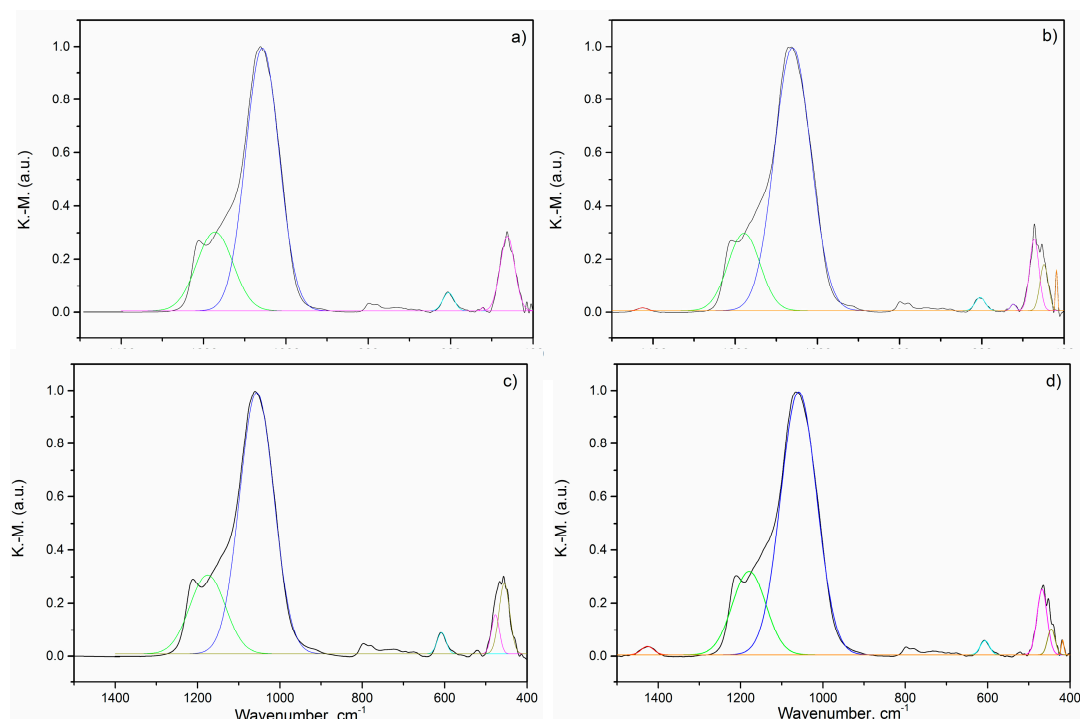
Figure 4. Deconvolution of spectral region between 1500 and 400 cm^{-1}: (**a**) NZ; (**b**) NZA; (**c**) FeZ; and, (**d**) FeA.

3.4. Pb^{2+} Adsorption Experiments

3.4.1. Influence of the Initial Pb^{2+} Concentration

Since it is well known that natural zeolite may interact with the hydrogen or hydroxyl ions from water solutions [33], checking of the immutability of all the adsorbents has been of interest. For that purpose, the stability of the NZA and FeA in distilled water was tested and compared to stabilities of NZ and FeZ, and the results are shown in Table 5.

Table 5. Concentrations of the released cations from adsorbents after contact with water.

Sample	Concentration of the Released Cations, meq/100 g
	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	$\Sigma_{cations}$ *	Fe^{3+}	Al^{3+}, Si^{4+}
H$_2$O	0.03	0.66	4.20	0.02	4.91	0.01	<0.03
NZ	6.20	0.40	3.50	1.80	11.90	0.06	<0.03
NZA	4.31	0.30	5.00	0.57	10.18	0.05	<0.03
FeZ	0.70	3.60	1.30	0.90	6.50	0.13	<0.03
FeA	3.67	2.35	<0.10	0.46	<6.58	0.11	<0.03

* $\Sigma_{cations}$ = sum of the released cations K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}.

Results given in Table 5 showed much lower amounts of the released cations (K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}) than those obtained by determination of the CEC, for all the adsorbents. That means that all of the samples have high stabilities in water solution. However, the stability of the FeZ is slightly higher than NZ, while modification with Na-alginate had no significant influence on stability of NZA and

FZA. Also, the amounts of released iron, aluminium, and silica were very low, supporting the previous conclusion that all of the samples are very stable in water.

Further, Pb^{2+} adsorption on NZA and FeA at different initial concentrations (18–320 mg Pb^{2+}/g) was investigated. During these experiments increase of pH of all the suspensions was observed, and the final pH for both adsorbents was between ~6.1 (for 18 mg Pb^{2+}/g) and 4.5 (for 320 mg Pb^{2+}/g), meaning that lead was predominantly in cationic-Pb^{2+} form [2]. The obtained results are shown in Figure 5.

From Figure 5 it can be seen that, for both adsorbents, adsorption of Pb^{2+} increased with increasing its initial concentration. However, a significantly higher adsorption was achieved for FeA. For the highest initial concentration, maximum adsorbed amounts of Pb^{2+} were: 102 mg/g for NZA and 136 mg/g for FeA, respectively. Our previous studies [7] showed adsorption capacities of 66 for NZ and 133 mg/g for FeZ. By comparing results for NZ and NZA, or FeZ and FeA, it can be concluded that modification with Na-alginate, in addition to encapsulation, also have a positive effect on adsorption capacities of both adsorbents. However, a higher positive effect on adsorption capacity was obtained for the NZ. That could be indication that the adsorption properties of the starting materials (NZ and FeZ) are also important for the removal of Pb^{2+} by NZA and FeA.
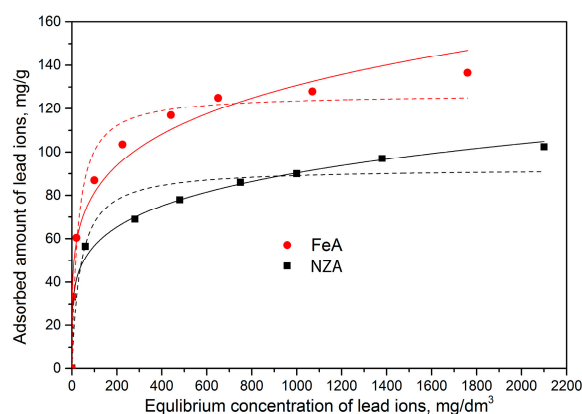
Figure 5. Pb^{2+} adsorption isotherms for the NZA and FeA. Solid lines (Freundlich model) and dashed lines (Langmuir model).

The experimental results were fitted to two the most commonly used adsorption models: Langmuir (Equation (2)) and Freundlich (Equation (3)) [10]:

$$q_e = \frac{b q_{max} C_e}{1 + b C_e} \tag{2}$$

$$q_e = K_F C_e^n \tag{3}$$

where q_{max} is maximal adsorption capacity, (mg/g); b is Langmuir constant that is related to heat of the adsorption (dm^3/mg); C_e is equilibrium concentration of Pb^{2+} (mg/dm^3) and q_e (mg/g) is adsorbed amount of Pb^{2+}, K_F (dm^3/mg); and, n are Freundlich constant related to the adsorption capacity and factor of heterogeneity of surface, respectively. The characteristic parameters of these two models are given in Table 6.

Table 6. Characteristic parameters of the Freundlich and Langmuir isotherms.

Sample	Freundlich Model			Langmuir Model		
	K_F, dm^3/mg	n	R^2	q_{max}, mg/g	b, dm^3/mg	R^2
NZA	22.50	0.20	0.9656	93	0.027	0.8522
FeA	31.47	0.21	0.9562	127	0.038	0.9342

From Table 6 it can be seen that, for both adsorbents, due to the higher values of R^2, Freundlich isotherm better fits the experimental data. That means, that adsorption of Pb^{2+} on both adsorbents takes place over complex mechanism, and/or surfaces of the adsorbents are heterogeneous and/or adsorption is not limited only to monolayer [34]. For both of the adsorbents, Freundlich parameter, *n*, was <1, indicating that adsorption intensity was good (or favourable) over the entire range of studied concentrations [35]. Mahmoud and Mohamed (2012) [36] also found the best fitting of the experimental results with Freundlich model for removal of Pb^{2+} from water solutions by using sodium alginate/itaconic acid hydrogel. However, the obtained value of the *n* parameter was >1, meaning that the adsorption intensity was favourable at a high concentration, but much less at lower concentrations. On the other side, Stewart et al. (2009) [37] found that Langmuir model better describes the adsorption of Pb^{2+} from water solutions on Ca-alginate. Cheraghali et al. (2013) [38] also found the best fit of the experimental data with Langmuir model for the removal of Pb^{2+} from water solutions by alginate-nanoporous silica composite.

For a better explanation of differences in adsorption capacities between NZ and NZA, FeZ and FeA, or NZA and FeA, and understanding of the adsorption mechanism, the concentrations of Ca^{2+}, Mg^{2+}, Na^+, and K^+ released from NZA and FeA, were measured, and their sum, for each initial concentration, when compared to the amounts of Pb^{2+} removed from solutions. The obtained results are shown in Figure 6.
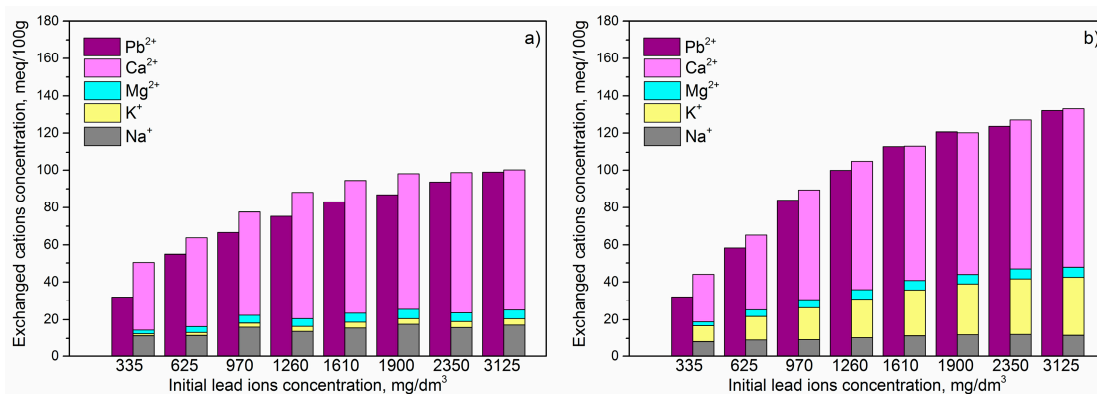
Figure 6. The amounts of Pb^{2+} adsorbed and cations released for different initial Pb^{2+} concentrations for NZA (**a**) and FeA (**b**).

Results that are given in Figure 6 showed, for both adsorbents, increase of the adsorbed amount of Pb^{2+}, as well as the total amount of released cations with increasing of the initial Pb^{2+} concentration. For NZA and FeA, the ratio between released and adsorbed equivalents of positive charges were stoichiometric for higher initial concentrations, while for lower initial concentrations, the total amount of exchanged cations was higher than the amount of adsorbed Pb^{2+}. These results suggest that ion exchange was the only mechanism included in the removal of Pb^{2+} by NZA and FeA. Also, we observed a direct correlation between the amount of Pb^{2+} adsorbed and amounts of exchangeable cations released. For NZA, Pb^{2+} were mainly exchanged with calcium, then sodium, while the contribution of potassium and magnesium was considerably lower. For FeA, Pb^{2+} were also mainly exchanged with calcium and potassium, while the ion exchange with sodium and magnesium was significantly smaller. The largest accessibility of calcium for ion exchange can be explained with the modification procedure by using $CaCl_2$ for preparation of composite samples. On the other side, releasing of the potassium and magnesium during the adsorption process indicate that ion exchange with Pb^{2+}, beside cations from alginate, also includes cations from the surface of NZ in NZA or FeZ in FeA. These results are considerable different in comparison with results for NZ and FeZ [6], where adsorption process beside ion exchange include chemisorption. Additionally, due to the presence of iron, much higher amount of Pb^{2+} was chemisorbed on the surface of FeZ than NZ. Changed

adsorption mechanism after encapsulation could be explained with trapping and unavailability of the active centres where chemisorption occurs due to the presence of big polysaccharide molecule in NZA and FeA. Finally, because a higher number of active centres for chemisorption were trapped in FeA, after encapsulation, a much lower increase of adsorption capacity was obtained than for NZA (Figure 5).

3.4.2. Influence of the Initial pH

Solution pH is a critical factor significantly affecting the metal ions adsorption [39]. At different pH values, lead can be in different forms in water solutions [2], and also, pH can influence the ionization of chemically active sites on the adsorbent surface. It was therefore of interest to investigate the effect of solution pH on the Pb^{2+} adsorption on NZA and FeA. Since the primary goal of this study was the removal of Pb^{2+} from solutions, experiments were carried out for initial pH (pH_i) from 2.5 to 5.2, and the results are shown in Figure 7a.

As it is shown in Figure 7a, the removal of Pb^{2+} from solutions slightly increased (from ~55% to ~61% for the NZA and from ~72% to ~79% for FeA) with an increasing of the pH_i from 2.5 to 3.8. Further increase of the pH_i from 3.8 to 5.2, for both of the adsorbents, had no significant influence on the removal of Pb^{2+}, and adsorption reached a maximum (~63% for NZA and ~80% for FeA). Increasing of the adsorbed amount of Pb^{2+} for ~8%, for both adsorbents, when pH_i increased from 2.5 to 5.2, indicated that initial pH does not have a significant influence on the adsorption capacities of adsorbents. However, slightly higher removal of Pb^{2+} was obtained for pH_i higher than 3.8, for NZA and FeA. These results are in accordance with our previous results [40], where it was shown that initial pH had no significant influence on the removal of Pb^{2+} by NZ and FeZ, and the highest removal is achieved for initial pH > 4.0.
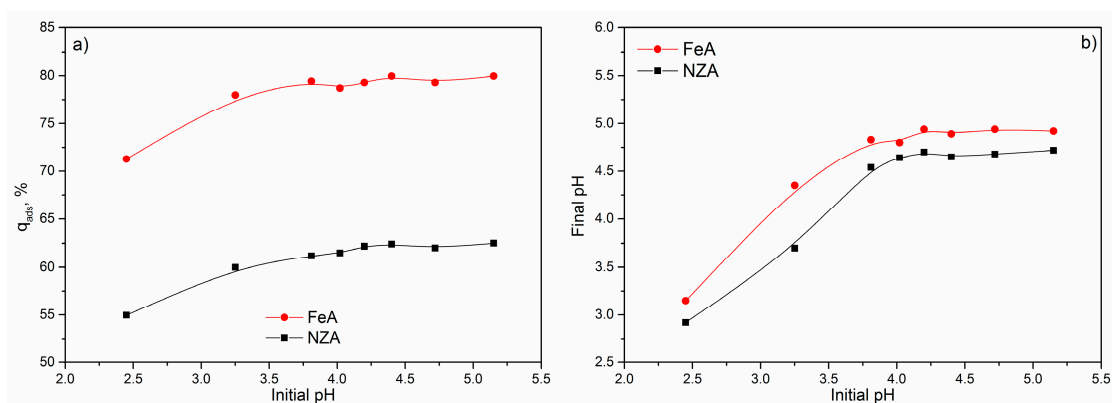

Figure 7. (**a**) Adsorbed amount of Pb^{2+} as a function of pH_i; and, (**b**) pH_f = f(pH_i).

During these experiments, final pH values (pH_f) were also measured and results are shown at Figure 7b. For both adsorbents, an increase of pH_i from 2.5 to 3.8 increased pH_f. After that, curves pH_f = f(pH_i) reached equilibrium, and a further increase of pH_i up to 5.2 had no significant influence on pH_f. Also, for $2.5 \leq pH_i \leq 4.7$, pH_f values were higher, while for $pH_i > 4.7$, the pH_f values were lower than pH_i.

Higher values of pH_f than pH_i obtained for $2.5 \leq pH_i \leq 4.7$ can be explained by the competitive removal of H^+ from solution caused by a high concentration of H^+ in solution. Higher pH_f values obtained for FeA than NZA for same pH_i indicated that a higher amount of H^+ were removed by the FeA. Competitive bounding of the H^+ leads to a decrease in the amount of Pb^{2+} immobilized onto NZA and FeA [39]. Furthermore, at lower initial pHs, the alkaline groups at surface of the adsorbents were protonated, thus electrostatic repulsion of Pb^{2+} caused decrease of Pb^{2+} adsorption capacity [33]. After increase of pH_i, due to decrease of H^+ concentration, the competition of Pb^{2+} and H^+ becomes weak, resulting in more Pb^{2+} and lower H^+ immobilization onto two adsorbents. Consequently, a

lower increase of the pH_f was observed. For the highest pH_i, pH of solutions decreased, as the result of removal of protons from surface Brønsted acidic sites, or from zeolitic water that coordinate exchangeable cations in adsorbents [33].

In order to confirm competitive bounding of the H^+, for all of the initial pH, amounts of released cations were measured and compared with amounts of removed Pb^{2+} from solutions, and results are shown at Figure 8.
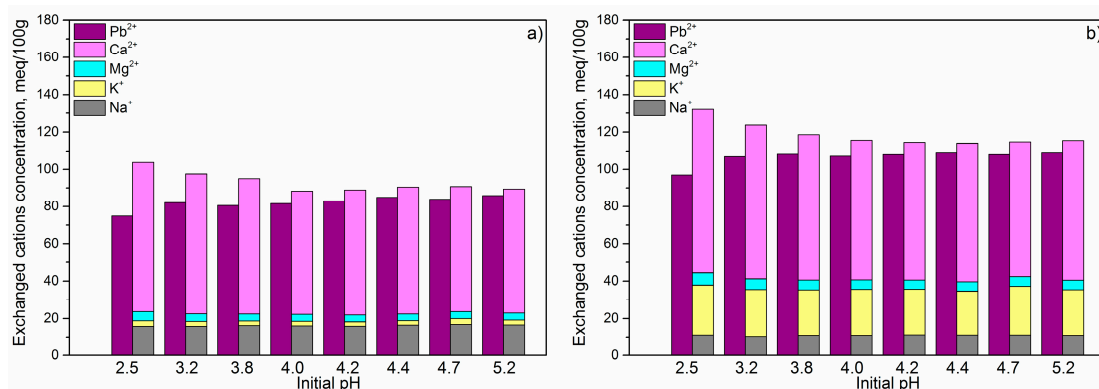
Figure 8. The amounts of Pb^{2+} adsorbed and cations released for different pH_i. (**a**) NZA; and, (**b**) FeA.

Results from Figure 8 showed that, for all the initial pHs, the total amounts of exchanged cations was higher than the amount of removed Pb^{2+}. That means that pH had no influence on the adsorption mechanism, and ion exchange was the only mechanism included in removal of the Pb^{2+} for all initial pHs. For both the adsorbents, for the $pH_i = 2.5$, the total amount of the released cations was much higher than removed Pb^{2+} concentration, confirming that H^+ together with Pb^{2+} from solutions participate in ion exchange with exchangeable cations. Due to decrease of H^+ concentration, and therefore their competitiveness, increasing of the pH_i up to 4.0 decreased the difference between amounts of the total exchanged cations and removed Pb^{2+}. For the $pH_i > 4.0$ concentration of H^+ was lower than 0.1 mmol/dm^3, which is much lower than concentration of the Pb^{2+} in solution (~7 mmol/dm^3), and consequently, their competitiveness was negligible. For that reason, almost stoichiometric ratio of the total concentration of the exchanged cations and removed Pb^{2+} was observed. Also, for all the initial pHs, for both of the adsorbents, the contribution of each individual exchangeable cation in ion exchange with Pb^{2+} (Figure 8) was the same as it was described in Figure 6, indicating that pH_i had no influence on the accessibility of individual exchangeable cations.

Good removals obtained by NZA and FeA, for applied experimental conditions, which are presented in this study, indicated that both alginate composites may be used as potential purifiers of waters contaminated with lead. Possible application may be in mining industry, as materials for collector filters on tailings. Namely, according to the Environmental Protection Agency (2005), in the "Report of the State of the Environment in Republic of Serbia", it is estimated that there are around 700 million tons of flotation and separation tailings, between 1.4 and 1.7 billion tons of tailing wastes from opening pits and around 170 million tons of ashes from thermal power plants on deposit spots and landfills in Serbia [41]. From that reason, experiments on real samples were done. For that purpose, preliminary experiments on removal of heavy metals from wastewater from facility of lead and zinc mine were performed, and the obtained results are shown in Table 7.

Table 7. Preliminary investigations of using NZA and FeA as cleaner of mining wastewaters.

Element, ppm	Wastewater	After Treatment with NZA	After Treatment with FeA
Pb	0.611	<0.1	<0.1
Zn	0.338	0.087	0.110
Hg	2.568	1.864	1.605
Mn	3.069	1.761	1.020
Cd	<0.045	<0.045	<0.045
Fe	0.075	0.068	0.222
Ba	<0.007	<0.007	<0.007
Be	<0.004	<0.004	<0.004
Cu	<0.017	<0.017	<0.017
Al	0.065	<0.01	0.046
Mg	8.105	8.788	8.781
Ca	98.859	116.387	111.554
Si	3.221	11.020	6.061

As can be seen, different elements are presented in investigated water, whereby the concentration of some of them is very high and dangerous to human health. For example, the concentration of lead was ~60, mercury ~2500 or manganese ~615 times higher than the maximum allowed concentration in drinking water. On the other side, concentration of cadmium, barium, beryllium, and copper was very low and below the detection limit of the instrument.

After treatment of wastewater with NZA and FeA, the content of all heavy metal cations was reduced. For both adsorbents, after treatment, the concentration of lead in wastewater was lower than the detection limit of the instrument. On the other side, NZA showed a better removal of zinc and alumina, while FeA better adsorbed manganese and mercury. Higher amounts of Mg, Ca, and Si after the treatment process may be a consequence of ion exchange (Ca and Mg) or very small dissolution of natural or Fe(III)-modified zeolite from NZA or FeA, respectively (Si). However, concentrations of all three elements, as well as Fe, were lower than the maximum allowed amounts for drinking waters, and therefore do not pose a risk to human health and nature in general. From these results, it may be concluded that both samples, and especially FeA, could be used for the production of collector filters for tailings. However, for practical applications, additional investigations must be done, and that will be the aim of our further research.

4. Conclusions

From the results presented in this study, it can be concluded that encapsulation of the NZ and FeZ with alginate, besides solving problems with water turbidity, also have a positive effect on their adsorption capacities. After the encapsulation adsorption capacity increased from 66 to 102 for natural zeolite and from 134 to 136 mg/g for Fe(III)-modified zeolite.. Encapsulation with alginate significantly changed adsorption mechanism in comparison with starting materials, and only ion exchange was included in the removal of Pb^{2+} from solutions, while for starting materials beside ion exchange adsorption ocuurs. Adsorption of lead on NZA and FeA may be described by using Freundlich model ($R^2 > 0.95$). At the same time, modification with alginate had no significant influence on CEC, and after encapsulation, the CEC was almost unchanged (~147 for NZ, ~150 for NZA and ~181 for FeZ and FeA). Stability in water solution was also unchanged for both, natural and Fe(III)-modified sample after encapsulation. Results of the FTIR analysis indicated that there was not significant changes in the structural properties, while DRIFT analysis showed that there is no negative impact of the modification on the hydrophilicity of the starting samples, and %A changed from 9.3 to 10.8 for natural zeolite and from 10.5 to 10.7 for Fe(III)-modified zeolite. Results also showed that initial pH had no influence on adsorption mechanism for Pb^{2+} removal and adsorption capacities of NZA and FeA. The highest removal is achieved for initial pH > 4.0 for both of the samples, and ion exchange was the only mechanism that was included in the removal of lead ions from water solution. Lead ions were

mainly exchanged with calcium, then sodium, while the contribution of potassium and magnesium was considerably lower in experiments on the removal of heavy metals from wastewater from flotation tail showed that after treatment of wastewater with NZA and FeA, the content of all heavy metal cations was reduced, and indicated that zeolite-alginate composites could be suitable for potential practical application.

Author Contributions: Milan Kragović conceived and designed the experiments, wrote the paper and contributed in analyzing of the obtained results. Marija Marković and Marija Petrović and Miloš Momčilović performed the experiments, Blagoje Nedeljković provided sample from flotation tailing and contributed in analyzing of the obtained results. The contribution of Marija Stojmenović and Snežana Pašalić was in explaining of the experimental results.

Conflicts of Interest: The authors declare no conflict of interest.

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