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Ionic Polyacrylamides as Stability-Modifying Substances of Soil Mineral Suspensions Containing Heavy Metal Impurities

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Abstract: The accumulation of heavy metal in soils is a serious environmental problem. The aim of this paper was to compare the adsorption mechanism of ionic polyacrylamides (PAMs)—anionic and cationic with different contents of functional groups, on the surface of clay minerals—montmorillonite (type 2:1) and kaolinite (type 1:1), without and with the presence of heavy metal ions (Cr(VI) or Pb(II)). The dependence of solution pH, structure of mineral, type of PAM, ionic form of heavy metal, as well as order of adsorbates addition on the adsorption efficiency and stability of the clay mineral-polymer-heavy metal system was determined. In addition to adsorption and stability studies, electrokinetic and potentiometric titration measurements were performed. It was shown that the mixed PAM+heavy metal adsorption layers modify the surface properties of clay minerals significantly, which in many cases leads to the effective destabilization of the solid suspension and its separation from the liquid phase. Moreover, the most important factor, which influences the adsorbed amount of ionic polyacrylamide, turned out to be the internal structure of layered aluminosilicates and the presence of inter-package spaces capable of adsorbate molecules accumulating. For this reason the obtained adsorption capacity of montmorillonite is about 100 times higher in comparison to kaolinite.

Keywords: ionic polyacrylamide; layered aluminosilicates; heavy metal; solid aggregation; lead(II) and chromium(VI) separation; flocculation; adsorption removal

1. Introduction

Highly-dispersed suspensions, including clay minerals, are used in many industrial processes, e.g., in production of ceramics, paper coatings, cosmetics, paints, rubbers and other plastics. These suspensions are usually very concentrated and for this reason it is extremely difficult to maintain the high stability of the solid particles in the liquid phase over a long period of time. Thus, the effective control of colloidal properties and dispersion stability is extremely important [1,2]. The addition of high-molecular compounds (linear water-soluble polymers) affect the stability of colloidal suspensions and its rheological properties very efficiently. Depending on the conditions, the presence of polymer in the dispersed system can increase or decrease its aggregation abilities. A polymer often used for this purpose is ionic polyacrylamide (PAM). Polyacrylamide is a water-soluble synthetic polymer, which consists of repeating units with amide functional groups (forming a chain structure and possessing hydrophilic character). The amide groups are non-ionic and, therefore, do not dissociate. In order to give PAM macromolecules a charge, groups of anionic or cationic nature are introduced into them, which leads to the formation of ionic forms of this polymer [3,4]. Both nonionic and ionic PAMs are widely used in many

industries, including mineral processing; wastewater treatment; production of paints, inks, varnishes, plastics, paper, cosmetics and ceramics; pharmaceuticals; food industry [5–8] and agriculture, as polymeric additives controlling the soil erosion process [9,10].

There are numerous literature reports on the adsorption of polymers and heavy metal ions on the surface of soil minerals, however, this problem has not been fully and systematically investigated so far [11,12]. Very often, experiments are carried out only in simple systems, not mixed ones (containing at least two types of adsorbates) [13]. Many scientific reports determine the influence of the polymer presence on the binding efficiency of heavy metals and the stability of soil mineral suspension, but without explaining the mechanism of its adsorption on the surface of a selected solid [14,15]. Moreover, the adsorption experiments on the surface of natural clay minerals or those modified with polymer macromolecules usually refer to heavy metal cations, even though some of the toxic elements are present in the environment in the form of anions [16,17]. It is also worth noting that in order to increase the adsorption efficiency of aluminosilicates in the solid/heavy metal system, only polymers that, due to the dissociation of their functional groups, have a charge opposite to that shown by the captured heavy metal ion are used [18–20].

Therefore, the aim of the present study was to compare the adsorption mechanism of polyacrylamide (PAM) flocculants of various ionic nature in the presence of heavy metal ions (i.e., Cr(VI) and Pb(II)) on the surface of selected soil minerals—montmorillonite and kaolinite. These adsorbents belong to the group of layered aluminosilicates, however, they have a different internal structure, which affects their sorption capacity. Ionic polyacrylamide flocculants were characterized by a different ionic character, i.e., in their macromolecules there were groups with a negative (anionic PAM) or positive (cationic PAM) charge, as well as a different average molecular weight, which significantly influences their binding mechanism on the solid surface. Two heavy metal ions were selected—they have an adverse effect on living organisms but differ in the form in which they occur in the aqueous solution—the lead(II) cations and the chromium(VI) anions. The performed research focused on determination of the effects of: the solution pH, the aluminosilicate type, the ionic nature of the polymer, the ionic form of heavy metal and the order of adsorbates addition. The collective analysis of the obtained adsorption, electrokinetic and stability results allowed for a comprehensive and systematic characterization of the mechanism of adsorption of both heavy metal ions and polyacrylamide structure-forming compounds on the surface of soil minerals, and the determination of the influence of these substances on the accumulation and immobilization of ionic forms of heavy metals in the soil environment.

Both chromium(VI) and lead(II) are elements that, in a minimal amount, have definitely adverse effects on animals and plants [21]. Cr(VI) occurring as a chromate or dichromate anions in aqueous solutions is a very strong oxidant with high bioavailability and solubility in a wide pH range. Thus, it penetrates biological membranes readily and oxidizes unsaturated bonds in fatty acids, nucleic acids and proteins (it damages the gastrointestinal tract and skin). Both examined metals shows mutagenic, teratogenic and carcinogenic effects relative to humans and animals. In plant organisms, they may damage the photosynthetic apparatus [22].

2. Materials and Methods

2.1. Clay Mineral and Adsorbates Characterization

Two clay minerals belonging to the group of layered aluminosilicates were used as adsorbents: kaolinite (type 1:1) and montmorillonite (type 2:1) [23], both delivered by Sigma-Aldrich (purity 99.9%). The specific surface area of adsorbents was determined using the low-temperature nitrogen adsorption–desorption method (Micromeritics ASAP 2405 analyzer). The average size, volume and distribution of pores of the clay minerals were determined on the basis of the BJH method (developed by Barret, Joyner and Halenda) [24].

Several varieties of ionic polyacrylamide PAM (Korona JV) with different contents of ionizable functional groups and weigh average molecular weights were used in the

research, i.e., two varieties of anionic polymer with high molecular weight—13,000 and 14,000 kDa and the content of carboxyl groups 5% and 30%, as well as two 7000 kDa cationic polyacrylamides containing 35% or 80% of quaternary amine groups.

The pK values of polymeric samples were determined using potentiometric titration method [25]. On the basis of the obtained results of the polymer samples titration, curves showing the dependence of changes in the pH of the tested PAM solution as a function of the volume of added titrant were prepared. The anionic PAM was titrated with a HCl solution with a concentration of 0.1 mol/L, and in the case of cationic PAM, a NaOH solution with a concentration of 0.1 mol/L was applied. Using the Hahn method [26], the pK_a (for AnPAM) or pK_b (for CtPAM) points were determined, which define the pH value at which half of the functional groups present in the polyacrylamide chain exist in a dissociated form. Based on the determined pK points of polymers, the degree of ionization (α) of macromolecular compounds at a given pH was calculated using the Henderson–Hasselbalch equations [27]:

$$\alpha_{AnPAM} = \frac{100}{1 + 10^{(pK_a - pH)}} \tag{1}$$

$$\alpha_{CtPAM} = \frac{100}{1 + 10^{(pH - pK_b)}} \tag{2}$$

Two heavy metals with strong toxic properties towards living organisms were used for the research, differing in the ionic form in which they occur in the aqueous solution, i.e., lead(II) forming Pb^{2+} cations and chromium(VI) occurring mainly in the form of CrO_4^{2-} and $HCrO_4^{-}$ anions. Metal ion solutions were prepared by dilution of stock solutions of $Pb(NO_3)_3$ or $K_2Cr_2O_7$ salts with a concentration of 1000 mg/dm^3. All adsorption and stability measurements for systems containing Cr(VI) were carried out at pH 5 and 7, whereas for those containing Pb(II) it was only at pH 5, due to the precipitation of these ions in the form of lead hydroxides at pH close to 7.

2.2. Adsorption Studies

The adsorbed amount (Γ) of ionic polyacrylamide and Pb(II) and Cr(VI) ions on the surface of layered aluminosilicates was determined based on the difference in their concentration in the solution before and after the adsorption process. The adsorption measurements were carried out at the pH values of 5 (Pb(II) ions) or 5 and 7 (Cr(VI) ions and PAM polyelectrolyte), at the temperature of 25 °C, in the presence of the supporting electrolyte—NaCl with a concentration of 0.001 mol/L. In the case of lead(II) and chromium(VI) ions, the initial concentration range was 1–100 mg/L, and for polyacrylamide: 1–150 mg/L. In the first step the calibration curves for all adsorbates were prepared. The concentration of individual adsorbates was determined spectrophotometrically by measuring the absorbance of the color solution formed after adding the appropriate indicator. For this purpose, the following reactions were used: reaction with Hyamine in the case of AnPAM [28], reaction with brilliant yellow in alkaline medium at pH 9 for CtPAM [29], whereas for Pb(II) ions, their reaction with 4- (2-pyridylase)—resorcinol with the addition of a buffer at pH 10 [30], and Cr(VI) ions—with diphenyl carbazide [31]. The concentration of polymer and heavy metal ions was determined using the Carry 1000 spectrophotometer (Varian, Crawley, UK) at wavelengths: 500 nm (AnPAM), 495 nm (CtPAM), 520 nm (Pb(II)) and 546 nm (Cr(VI)). The adsorption tests were repeated 3 times and the final result was the mean value of these 3 measurements. The measuring error did not exceed 5%.

2.3. Electrokinetic and Stability Studies

Using the potentiometric titration method, the surface charge density of the examined clay minerals was determined without and in the presence of individual adsorbates as a function of the solution pH. The pH_{pzc} (pzc—point of zero charge) values were also obtained. The surface charge densities (σ_0) of the examined minerals were determined using the special set containing burette Dosimat 665 (Methrom), thermostat RE204 (Lauda),

pH meter 71 (Beckman), computer with the specialist program "Titr_v3" by Professor W. Janusz [32] and printer. For this purpose the following equation was used:

$$\sigma_0 = \frac{\Delta V \cdot c \cdot F}{m \cdot S} \tag{3}$$

where: ΔV—the difference in the base volume added to a suspension and a supporting electrolyte solution that leads to the specific pH value, c—the base concentration, F—the Faraday constant, m—the solid mass in the suspension, S—the solid surface area.

The suspensions of the used minerals were titrated with a NaOH solution with the concentration of 0.1 mol/L in the range of pH 3–10 (for PAM containing system) and 3–6 (for those with heavy metal ions).

The electrokinetic potential zeta (ζ) of solid particles in the examined systems was determined using the Doppler laser microelectrophoresis method and Zetasizer Nano ZS apparatus (Malvern Instruments). The experiments were carried out in systems without and in the presence of macromolecular compounds (in the range of pH 3–9) and heavy metal ions (in the range of pH 3 to 6). The zeta potential was determined automatically with the use of computer software, converting the measured electrophoretic mobility (U_e) of the aluminosilicate particles into the value of the ζ potential, in accordance with the following Henry equation [33]:

$$U_e = \frac{2\varepsilon_0 \varepsilon \zeta}{3\eta} f(\kappa a) \tag{4}$$

where: ε—the dielectric constant, ε_0—the electric permeability of vacuum, η—the liquid phase viscosity, f(κa)—the Henry function.

The final value of zeta potential for each sample was the average of 5 repetitions. Based on the obtained results, the dependencies of the electrokinetic potential of solid particles without and in the presence of adsorbates as a function of the solution pH were prepared, and the values of pH_{iep} (iep—isoelectric point) were determined.

Changes in the stability of the clay mineral suspension without and in the presence of polyacrylamide and heavy metal ions were determined using the spectrophotometric method (spectrophotometer Carry 1000, Varian) [34]. The absorbance of individual systems was measured as a function of time at a wavelength 500 nm, and the total experiment time was 3 h.

3. Results and Discussion

The successive subsections present selected results concerning the behavior of the examined suspensions as a function of: the solution pH, the type of mineral, the type of ionic polyacrylamide, the nature of the heavy metal ions and the order of adsorbates addition, which present the most important trends and relationships obtained in the course of experimental research.

The textural characteristics of the applied aluminosilicates is presented in Table 1, whereas the characteristics of examined polyacrylamides are placed in Table 2 (physicochemical properties) and Table 3 (dissociation of PAM functional groups).

Table 1. Textural characteristics of the examined aluminosilicates.

Parameter	Montmorillonite	Kaolinite
Specific surface area [m^2/g]	259	8.02
Mean pore diameter [nm]	3.8 and 5.6	14.3
Micropore area [m^2/g]	22.6	1.83
Total pore volume [cm^3/g]	0.38	0.0287
Micropore volume [cm^3/g]	0.008	0.0008
pH_{pzc}	5.02	3.37
pH_{iep}	<3	<3

Table 2. Characteristics of examined polyacrylamides.

Polyacrylamide	Anionic (AnPAM)		Cationic (CtPAM)	
Symbol	AnPAM-5	AnPAM-30	CtPAM-35	CtPAM-80
Weigh average molecular weight [Da]	13,000,000	14,000,000	7,000,000	7,000,000
Content of ionizable groups [%]	5	30	35	80
Molecular structure				

Table 3. Characteristics of dissociation of the examined polyacrylamides as a function of the solution pH.

Polyacrylamide	pK	α [%]			
		pH 3	pH 5	pH 7	pH 9
AnPAM-5	3.3	33.38	98.04	99.98	99.99
AnPAM-30	3.2	38.7	98.4	99.98	99.99
CtPAM-35	9.3	99.99	99.99	99.44	64.00
CtPAM-80	9.5	99.99	99.99	99.68	75.97

3.1. Effect of the Solution pH

Figure 1 shows effect of the solution pH on the adsorbed amount (Γ) of anionic and cationic polyacrylamide with different content of functional groups, as well as heavy metal ions on the montmorillonite surface [35,36].
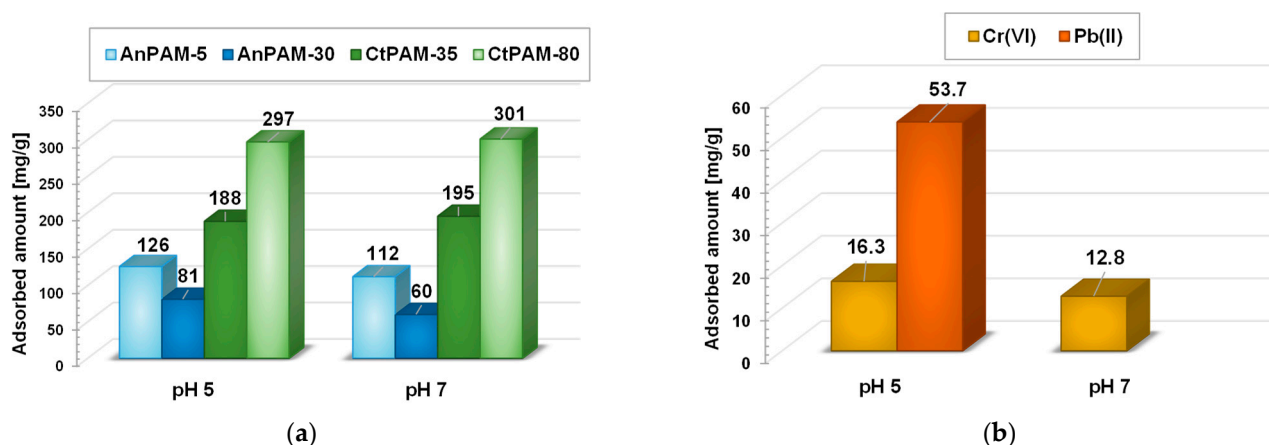
Figure 1. Adsorbed amounts of: (**a**) ionic PAMs; (**b**) heavy metal ions on the montmorillonite surface at pH 5 and 7; initial concentration of adsorbates is 100 mg/L.

Depending on the ionic nature of the polymer, an increase in the pH value causes a decrease or increase in the Γ value—in the case of AnPAM, greater adsorption is observed at pH 5, whereas CtPAM is more effectively bounded with the solid surface at pH 7 [37,38].

The pH value determines both the surface properties of the mineral and the conformation of the adsorbed polymer chains. In solutions with the examined pH values, i.e., 5 and 7, both types of ionic polymers are characterized by a fairly high degree of dissociation, about 98–99% (Table 3). The binding of AnPAM and CtPAM molecules with the mineral surface under these conditions undergoes through the electrostatic interactions and the hydrogen bonds formation (Figure 1a).

The noticeably lower adsorption of the anionic polyacrylamide at pH 7 is due to the unfavorable electrostatic repulsion occurring between the negatively charged macromolecules and the negatively charged surface of the mineral. At a pH of about 5, the point

of zero charge of montmorillonite is observed (the total surface charge is zero) and under such conditions the solid surface is neutral (Table 1). For this reason, more favorable conditions for AnPAM adsorption occur in a system with a lower pH. During the adsorption of the polymer, hydrogen bonds are formed between the hydroxyl groups of the solid and the polymer functional groups—both neutral amide and anionic carboxyl (occurring in undissociated and dissociated form) [37].

The higher CtPAM adsorption is observed in a solution with a higher pH [38]. It results from the strong electrostatic attraction between the negatively charged surface of the mineral and the positively charged polymer macromolecules. The differences in the adsorbed amounts of the cationic and anionic polyacrylamides are also related to the different conformation of the polymer chains with different content of dissociating groups. Due to the higher content of negatively (AnPAM) or positively (CtPAM) charged groups, the polymer chain develop, thus extending the PAM conformation. Adsorbing macromolecules form mainly loop- and tail-type structures, thanks to which they assume such a developed conformation that the area of interaction with the adsorbent surface is very small. Consequently, a greater number of macromolecules can adsorb on a unit of montmorillonite surface. It is worth noting, that in the case of systems containing an anionic PAM with a higher content of -COOH groups at pH 7, despite the highly developed structure of polymer macromolecules, the PAM adsorption affinity decreases. It is due to the stronger electrostatic repulsion of the adsorbate–adsorbent and the difficult access of AnPAM-30 chains to the active sites on the montmorillonite surface.

Pb(II) ions adsorption measurements were not performed at pH 7 due to the precipitation of lead hydroxide in solutions under such conditions and the initial concentration of lead equal to 100 mg/L (Figure 1b). Under the examined conditions, lead appears as a Pb^{2+} cation, and chromium(VI) ions in the form of CrO_4^{2-} and $HCrO_4^{-}$ anions. The mechanism of heavy metal ion adsorption on the surface of clay minerals is closely related to the interaction with the active centers of aluminosilicate and penetration into the inter-package spaces inside the mineral structure. In the case of lead(II) cations, charge compensation can also be considered, as well as the process of ion exchange with inter-package cations [39,40]. The adsorbed amount of Pb(II) ions on the surface of the mineral at pH 5 is noticeably greater than that of Cr(VI) ions, which is probably related to the smaller size of lead cations compared to chromate anions and the possibility of lead cations exchanging with cations present in the spaces between the aluminum and silica packages. Moreover, as the pH increases, the adsorbed amount of Cr(VI) ions decreases. This is due to the difference in affinity to the montmorillonite surface, which gains a negative charge in the pH range above 5.02 (Table 1).

3.2. Effect of the Mineral Type

Aluminosilicates are characterized by a different arrangement of layered packages in the crystal lattice, thus they have a different internal structure and sorption capacity. The way of connecting octahedral and tetrahedral layers in the structure of a clay mineral and the presence of a negative charge in the network, or the so-called inter-package cations also affects the binding mechanism of metal ions and macromolecular compounds of different ionic nature on the surface of these solids [41–43].

In the pH range 5–7, both the 2:1 and 1:1 type aluminosilicate surfaces are characterized by the presence of negatively charged functional groups (Figure 2b), which promotes the adsorption of CtPAM macromolecules and Pb(II) cations. It should be emphasized that almost 100 times higher polymer adsorption value is observed in the case of montmorillonite, which has a strongly developed specific surface area (Figure 2a). The significant difference in the amount of adsorbed PAM macromolecules results primarily from the differences in the structure of the crystal lattice of layered minerals and the possibility of the displacement of packages inside their structure, resulting from the intercalation of the adsorbate molecules [23,44]. Clay minerals with 2:1 structure can adsorb heavy metal cations both on the mineral surface, at the edges of the aluminum and silica layers, as well

as inside the space between the packets, where interlayer cations are replaced with heavy metal ions [45]. Deprotonated surface groups of clay minerals are mainly responsible for the adsorption of metal cations. In the case of 1:1 type layered aluminosilicates, metal ion adsorption can only take place on the active sites of the mineral surface due to the lack of interlayer space in its internal structure. Moreover, the interaction between the bilayer packages occurs through the formation of hydrogen bonds between the oxide ions of one layer and the hydroxyl groups of the other layer. Consequently, these bonds prevent the packages from being moved apart. The sorption capacity of clay minerals of the 1:1 type is, therefore, limited only to the outer surface, which is confirmed by the very small Γ values of adsorbates on the kaolinite surface [46].
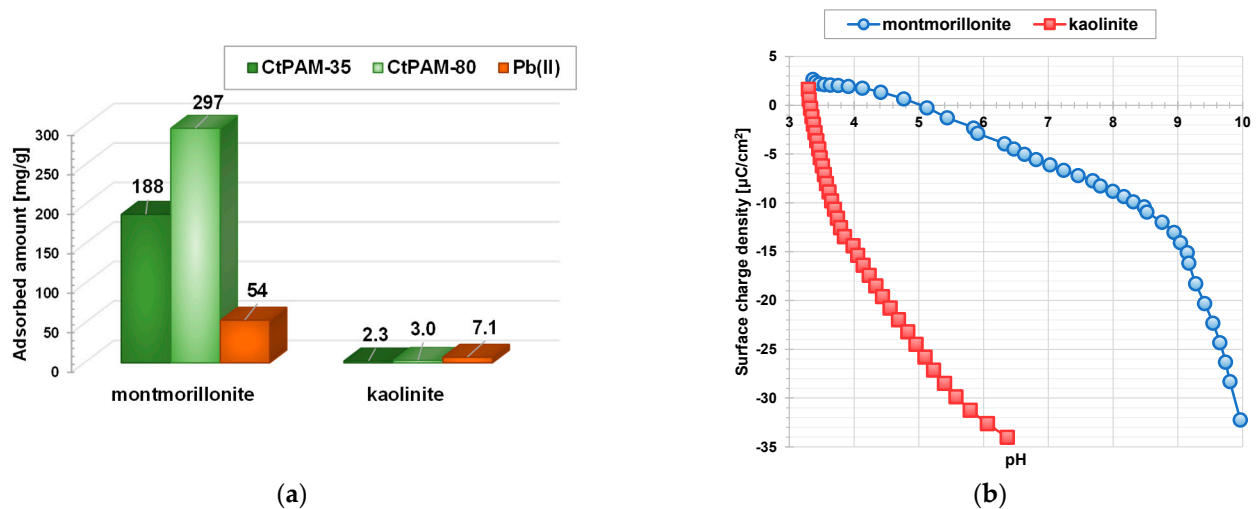

(**a**)　　　　　　　　　　　　　　　　　　　　　　　　(**b**)

Figure 2. (**a**) Adsorbed amounts of cationic PAMs and heavy metal ions on the montmorillonite and kaolinite surface at pH 5; initial concentration of adsorbates is 100 mg/L; (**b**) surface charge density of minerals as a function of solution pH.

Changes in the stability of the layered aluminosilicates suspension with a different internal structure depending on the presence of cationic polyacrylamide and Pb(II) ions at pH 5 are shown in Figure 3.
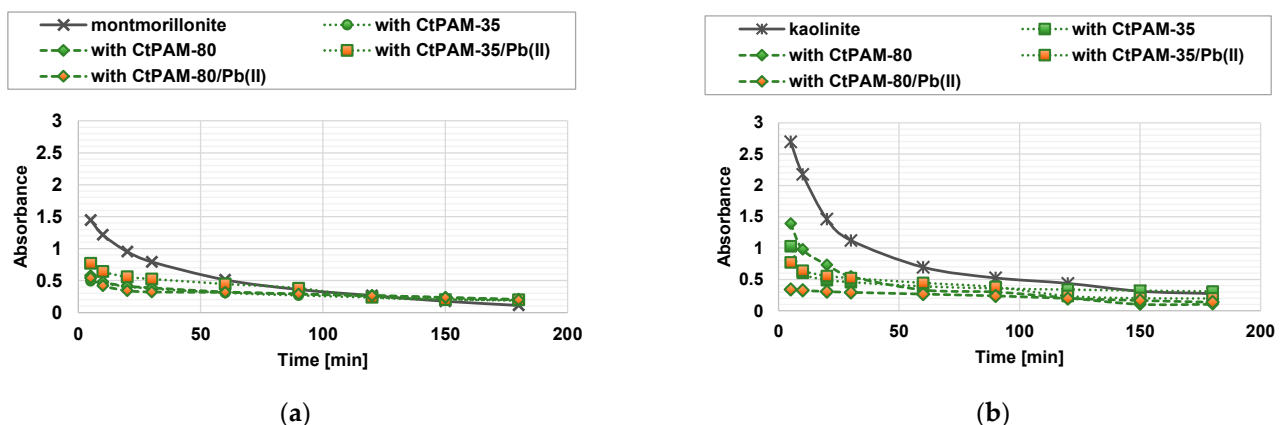

(**a**)　　　　　　　　　　　　　　　　　　　　　　　　(**b**)

Figure 3. The influence of the presence of cationic polyacrylamide with different content of functional groups with initial concentration 100 mg/L) and Pb(II) ions (initial concentration 10 ppm) on the stability of the suspension of: (**a**) montmorillonite; (**b**) kaolinite at pH 5.

The stability of montmorillonite suspension without adsorbates at pH 5 is noticeably lower than kaolinite one. The presence of cationic polyacrylamide and lead ions affects the suspension stability of both montmorillonite and kaolinite. In the systems where CtPAM-

35 and CtPAM-80 were added, the absorbance value decreased significantly after 5 min compared to the system without the polymer. Due to the strong affinity of CtPAM macromolecules and Pb(II) cations to the surface of layered aluminosilicates, the addition of these adsorbates significantly reduces the stability of the clay mineral suspension, regardless of the type of internal structure they exhibit. Polymer macromolecules, by adsorbing on the surface and penetrating into montmorillonite inter-package spaces or by binding with kaolinite surface groups, favor the flocculation process, i.e., the formation of larger aggregates. The simultaneous addition of cationic PAM with a different content of functional groups and Pb(II) ions to the clay mineral suspension causes a noticeable reduction in stability manifested by a decrease in absorbance (for both types of polyacrylamides). Thus, the used polymers retain the ability to form large aggregates of mineral particles with a different structure of layered packages, even in the presence of heavy metal ions in the system.

The schematic representation of the effect of mineral type on the binding mechanisms of both adsorbates (for example, AnPAM-30 and Pb(II)) at pH 5 on the montmorillonite surface is presented in Figure 4.
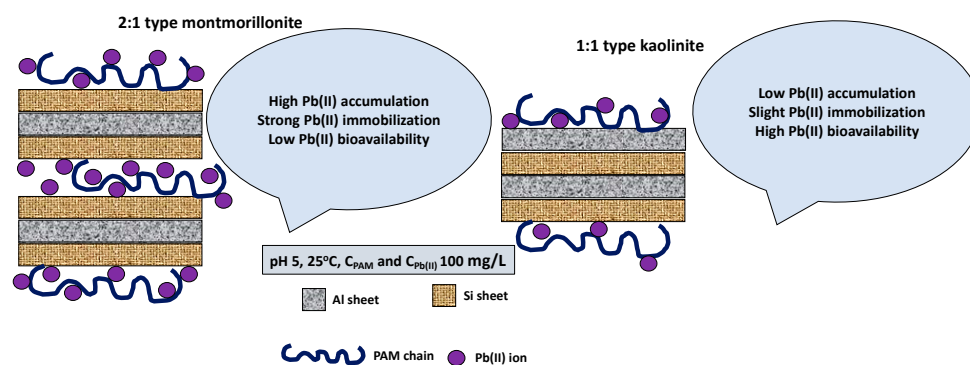

Figure 4. The schematic representation of effect of mineral type on the binding mechanisms of both adsorbates (for example, AnPAM-30 and Pb(II)) on the aluminosilicate surface; pH 5, initial concentration of adsorbates is 100 mg/L.

3.3. Effect of the Polyacrylamide Type

The adsorbed amount of polyacrylamide on the layered aluminosilicates also depends on the ionic nature of the groups present in their structure. The presence of the charge of a different sign in the polymeric chains determines its conformation and affinity to the solid surface, and thus influences the mechanism of its adsorption [41,42,47]. Figure 5 shows the polyacrylamide adsorption on the clay minerals surfaces depending on the type of functional groups present in the polymer macromolecules and their percentage content.
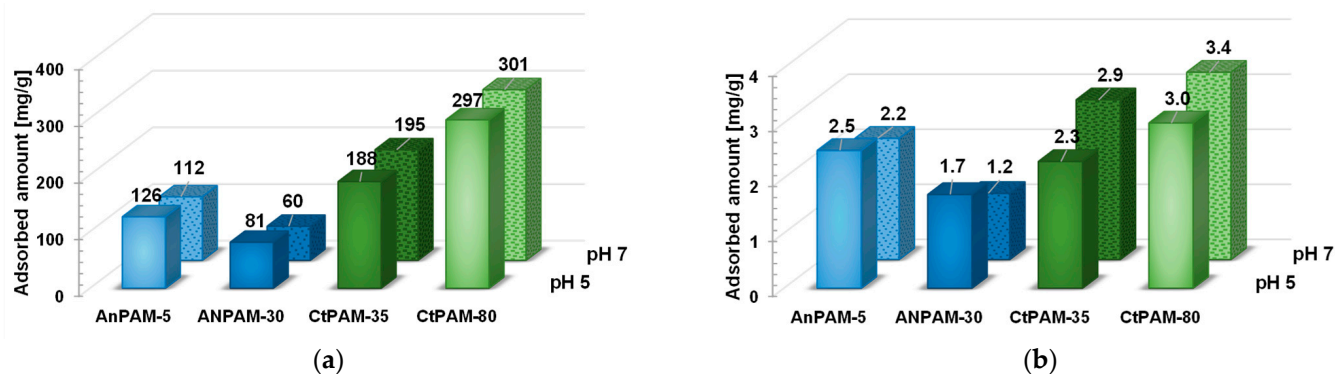

Figure 5. The adsorbed amounts of ionic polyacrylamides on the surface of: (**a**) montmorillonite; (**b**) kaolinite at pH 5 and 7, initial concentration of adsorbates is 100 mg/L.

The analysis of the obtained data shows that the cationic polymer has greater affinity to the clay mineral surface than the anionic one, thus in the examined system its adsorption is clearly higher [16,48]. Under the examined pH conditions, due to the high degree of dissociation, most of the cationic polymer segments acquire a positive charge (the presence of numerous -N(CH$_3$)$^{3+}$ groups). Stronger electrostatic attraction between the mineral surface and the cationic PAM chains occurs in a solution with pH 7 and in a system containing polymer with a higher content of functional groups, which translates into a higher value of Γ. Anionic polyacrylamide, due to the presence of a negative charge in its structure, binds much less effectively with the surface of the examined minerals. The lower adsorption of AnPAM is due to the electrostatic repulsion between the ionized -COO$^-$ groups present in the macromolecules and the negatively charged surface of the solid particles. Despite the unfavorable electrostatic conditions and low affinity, the anionic polymer binds on the surface of montmorillonite and kaolinite. As was mentioned previously, the adsorption process undertakes the formation of hydrogen bonds.

In the case of the AnPAM/montmorillonite system, the polymer adsorption causes a slight changes in the zeta potential value compared to the suspension without the polymer (Figure 6). The increase in the pH of the solution results in complete dissociation of the adsorbed PAM macromolecules, and the presence of their -COO$^-$ groups in the area of the slipping plane causes a noticeable decrease in the zeta potential value. The addition of the cationic form of PAM causes an increase in the electrokinetic potential of the solid compared to the system without the polymer. This is mainly due to the presence of positively charged functional groups belonging to the adsorbed polymer chains in the area of the slipping plane.
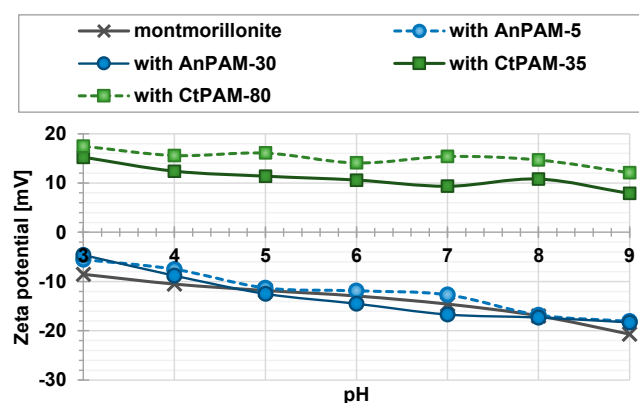

Figure 6. Influence of the presence of ionic polyacrylamide with different content of functional groups on the electrokinetic potential of montmorillonite particles as a function of solution pH, initial concentration of adsorbates is 100 mg/L.

3.4. Effect of the Ionic form of Heavy Metal

The mechanism of adsorption of polyacrylamide on the soil mineral particles also depends on the presence of heavy metals in the system. These elements, both in the form of a cation and an anion, show a high affinity for the surface of the solid. In a solution with pH 5, corresponding to the natural pH of clay soils, the surface of kaolinite is negatively charged, and in the case of montmorillonite, the surface charge is close to zero. On the other hand, the electrokinetic potential of solid particles of both examined minerals is negative. Such a slipping plane potential definitely favors the contact of the aluminosilicate surface groups with positive Pb(II) cations and hinders the interaction with Cr(VI) anions [43,44,47]. A comparison of the heavy metal ions adsorption on the surface of 2:1 layered aluminosilicate in the presence of both ionic forms of polyacrylamide is presented in Figure 7a.
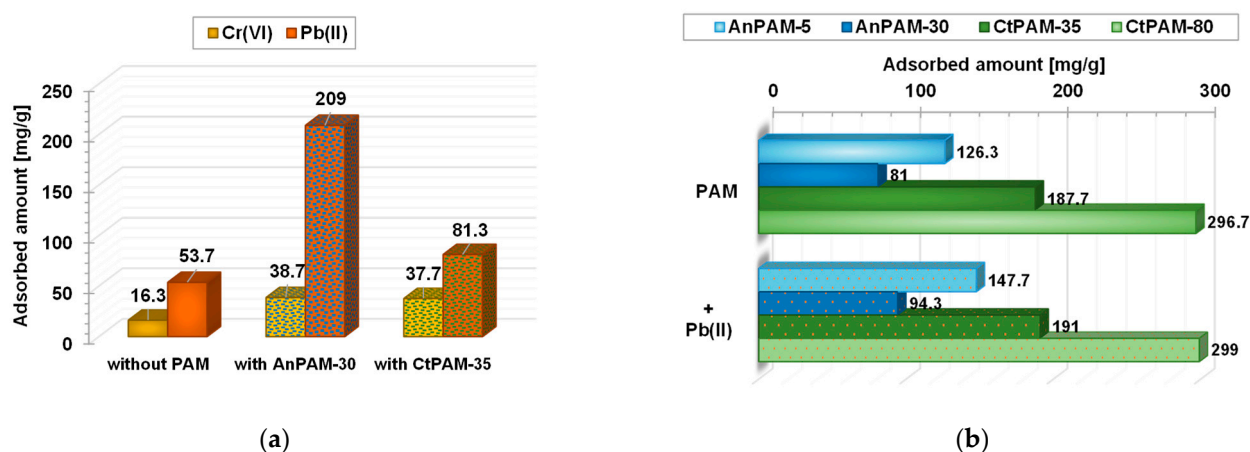
(a)

(b)

Figure 7. Influence of: (**a**) the presence of ionic polyacrylamide on the adsorbed amounts of heavy metal ions; (**b**) the presence of Pb(II) cations on the adsorbed amount ionic polyacrylamide on the surface of montmorillonite at pH 5, initial concentration of adsorbates is 100 mg/L.

The presence of ionic polyacrylamide in the system increases the accumulation of heavy metal ions on the surface of layered aluminosilicate. The introduction of the cationic polymer into the system increases the adsorption of chromium(VI) ions. On the other hand, when anionic PAM is added, an increase in the amount of bounded lead(II) ions on the solid is observed. The reason for this behavior is the formation of complexes of heavy metals with polymer macromolecules under certain conditions. Polymer chains efficiently trap inorganic ions from an aqueous solution, regardless of whether the two adsorbates are identically or oppositely charged to each other. The formation of the Pb(II)–AnPAM complex is dictated by the electrostatic attraction between the metal cation and dissociated carboxyl groups in polymer macromolecules, whereas in the case of cationic PAM—by the creation of covalent bonds [34,44,45]. Neutral amide groups present in CtPAM macromolecules, namely free electron pairs on nitrogen atoms of these groups, are responsible for the formation of these chemical bonds. In turn, the formation of the Cr(VI)–CtPAM complex is associated with the electrostatic interaction between negative chromate ions and positive polymer segments containing quaternary amine groups. Another possible mechanism responsible for the binding of Cr(VI) by polymer macromolecules can be the formation of hydrogen bonds between the amide groups of PAM and the chromium(VI) anions [41,45].

Heavy metal cations, apart from a stronger affinity to the surface of layered aluminosilicates, especially of the 2:1 type, show the ability to modify some of the internal structure of the mineral, mainly by ion exchange processes. The effect of the presence of a heavy metal cation on the adsorbed amount of ionic polyacrylamide on the montmorillonite surface at pH 5 is shown in Figure 7b. The sizes of the anionic polymer macromolecules with a highly developed conformation are much larger than the dimensions of lead(II) ions, which significantly limits their penetration into the internal structure of montmorillonite, and consequently also their adsorption. Contrary to the polymer, lead(II) ions are characterized by a relatively small size, which allows them to freely penetrate the montmorillonite pores with an average size of 5.9 nm. Moreover, due to the ion exchange phenomenon and the intercalation process, these ions can increase the interlayer spaces in the 2:1 clay mineral, which can lead to an increase in the adsorption of other adsorbates. Nevertheless, due to the electrostatic attraction between negatively charged carboxyl groups in AnPAM macromolecules and positively charged lead(II) cations, the formation of polymer–metal complexes both of intra- and inter-molecular nature occurs. As a consequence, an increase in the adsorption of anionic polyacrylamide in the presence of Pb(II) cations is observed. Nevertheless, this increase is not significant, suggesting that the metal–polymer complexes are rather intramolecular character (many divalent Pb ions are bounded in one PAM macromolecule). The formation of intermolecular complexes is also possible, but

the obtained adsorption results indicate that they contribute negligibly to increase in the anionic polymer adsorption.

In the case of the system containing cationic polyacrylamide and Pb(II) ions, despite the presence of electrostatic repulsion between positively charged polymer chains and lead cations, a slight increase in the amount of bounded PAM in the mixed adsorbate system is observed. The increase in Γ is caused by the interaction between the adsorbates of the same charge through covalent bonding, as well as the penetration of the developed CtPAM chains into interpackage spaces of the mineral.

3.5. Effect of the Order of Adsorbates Addition

The mechanism of adsorption of polyacrylamides also depends on the order in which adsorbates are added to the system, as shown by the results presented in Figure 8 [42,49,50]. Polymer samples with an initial concentration of 100 mg/L and chromate anions with concentrations of 1, 10 and 100 mg/L were added to the test systems simultaneously or 1 h apart.
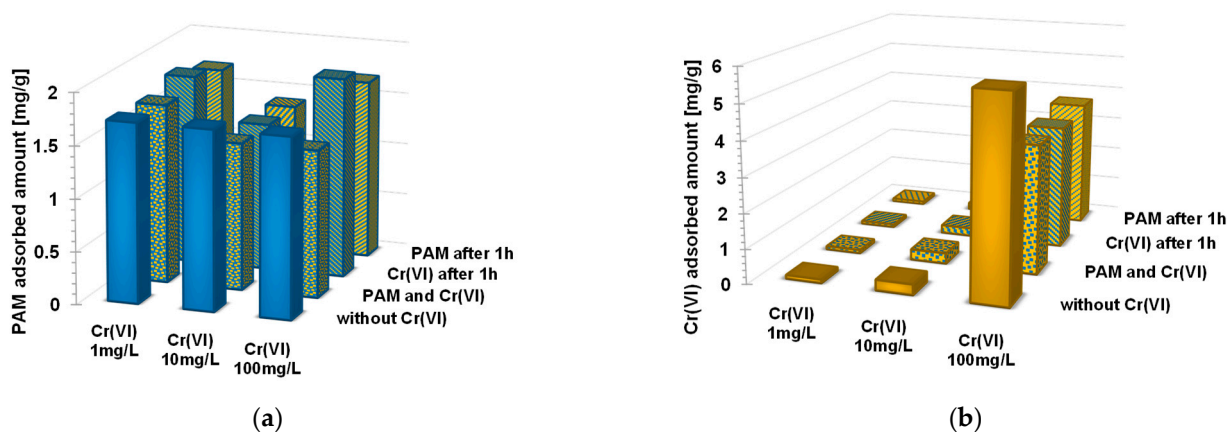

Figure 8. The effect of the order of adsorbate addition (AnPAM-30 and Cr (VI) with different concentrations) on the adsorbed amounts of: (**a**) anionic polymer; (**b**) chromium anions adsorption on the kaolinite surface at pH 5, initial concentration of polyacrylamide is 100 mg/L.

The presence of individual adsorbates generally causes a slight decrease in their adsorption in mixed AnPAM/Cr(VI)/clay mineral systems at pH 5. Comparing the obtained results for mixed adsorbate systems, chromium(VI) binds most effectively to the surface of kaolinite when it was added first to the system, and the polymer after 1 h. At pH 5, the lowest adsorbed amount was observed when the chromate ions were added last. Taking into account the amount of adsorbed anionic polyacrylamide, the opposite tendency occurs—the greatest amount of polymer is adsorbed when inorganic ions are added 1 h apart. These differences are due to changes in the affinity to the mineral surface modified by adsorbed polymer chains or heavy metal ions [51,52].

Both anionic polyacrylamide and chromate anions show rather low affinity for kaolinite particles, and the presence of one of the adsorbates in the system causes a noticeable decrease in the adsorption of the other. It is due to the unfavorable electrostatic interaction between polymer macromolecules and metal ions and the competition between two negatively charged compounds of active sites on the solid surface. A slight increase in the adsorbed amount of anionic polyacrylamide in the presence of Cr(VI) anions was observed in the system in which the AnPAM was added first (Figure 8a). This can be due to more favorable conditions for the formation of hydrogen bonds between already adsorbed polymer macromolecules and chromium ions.

The definition of conformation of the adsorbed PAM macromolecules, as well as the structure of the polymer–metal complexes in the surface layer allowed for a detailed characterization of the processes taking place at the clay mineral–solution interface. Soil

flocculants selected for research are widely used in agriculture. The addition of such macromolecular compounds affects the stability of colloidal mineral particle suspensions and their rheological properties. As a result of the flocculation process, the soil cohesion; its structure; and the infiltration of rainwater are improved. The use of polymer-containing structure-binding agents reduces the transport of sediments, and thus slows down the soil erosion process. On the other hand, the use of polyacrylamide flocculants changes the bioavailability of heavy metal ions present in soil to living organisms. The conducted research may contribute to a more conscious use of polyacrylamide flocculants in agriculture and will allow predictions of the mechanisms of the immobilization process and the bioavailability of heavy metal ions for plants.

4. Conclusions

The analysis of the obtained data confirmed the influence of the solution pH, the type of mineral, the type of ionic polyacrylamide, the nature of the heavy metal ions and the order of adsorbates addition on the adsorption mechanism of PAM ionic flocculants. More favorable electrostatic conditions for the adsorption of anionic PAM occur at a lower pH values, whereas the cationic polyacrylamide binds more effectively to the solid at a higher pH values. The binding mechanism of AnPAM and CtPAM under these conditions is based on electrostatic interactions and the formation of hydrogen bonds between the polymer chains and the solid surface. Montmorillonite, due to the presence of interpackage spaces in its internal structure, shows considerably better adsorption capacity compared to kaolinite. Significantly higher adsorption of both polymer and heavy metal ions is observed in the case of systems containing 2:1 type clay mineral. The adsorbed polyacrylamide macromolecules modify the surface properties of aluminosilicates, which leads to an increase in the efficiency of heavy metals adsorption on their surfaces. The order of adsorbates addition to the system is also important factor due to their competition for the solid active sites. Adsorbed polyacrylamide chains can capture heavy metal ions by the formation of metal–polymer complexes through chemical bonds, which increases the adsorption of polyacrylamide by adsorption multi-layer creation. The addition of ionic polyacrylamide influences the stability of aluminosilictaes suspension in various ways—adsorption of cationic PAM causes flocculation and promotes the formation of large aggregates, whereas the anionic polymer enhances the stability of the mineral suspension. The adsorbed anionic polyacrylamide strongly immobilizes the toxic Pb(II) ions on the montmorillonite surface and thus significantly reduces their bioavailability to living organisms.

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