The structure of electrical double layer formed on the kaolinite surface in the mixed system of cationic polyacrylamide and lead(II) ions

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Abstract: The bioavailability of toxic heavy metals for organisms depends mainly on the soil physicochemical properties, i.e. type and granulometric composition, pH value, redox potential, individual fractions content and microorganisms presence. The addition of artificial fertilizers rich in humic substances or polyacrylamide soil flocculants may also affect the content of easily absorbed heavy metal forms. Due to their chelating properties, the added substances can bind metal ions in the form of complexes characterized by low mobility in soil environment. As a consequence, the immobilization process takes place, which is a desirable phenomenon for organism health. The aim of the study was to determine the structure of electrical double layer formed on the kaolinite surface in the mixed system of cationic polyacrylamide and lead(II) cations. The influence of cationic PAM presence on the Pb(II) ions sorption on the kaolinite surface as well as heavy metal ion addition on the polymer adsorbed amount on the same clay mineral were studied. The adsorption and electrokinetic properties of studied kaolinite/CT PAM/Pb(II) systems were determined based on the spectrophotometric study, zeta potential measurements as well as potentiometric titration.

Keywords: kaolinite, cationic PAM, Pb(II) ions, electrical double layer, adsorption

1. Introduction

Due to development of industry and technology, a rapid increase in heavy metal content in nature is currently observed. These elements are considered as a dangerous for environment and harmful for living organisms. Increased heavy metals concentration may adversely affect the biological soil properties, have a toxic effect on plants and animals as well as contaminate ground water (Bai et al., 2015; Olayiwola et al., 2017; Rieuwerts et al., 1998). After exceeding the permissible level, heavy metals reduce soil fertility, inhibit the soil enzymatic activity and change the state of soil acidification. But, it must be emphasized that most of heavy metals have a toxic effect on organisms already in a minimal amount (Effron et al., 2004; de Mora et al., 2005; Kunito et al., 2001; Lorenz et al., 2006).

One of the elements belonging to heavy metals group is lead (Pb). In case of plants, this metal causes disturbances in photosynthesis and cell division. What is more, it contributes to numerous mistakes in nitrogen metabolism and water management. In case of humans and other animals, Pb(II) causes changes in protein synthesis and disrupts the enzymes activity. It is characterized by strong mutagenic, carcinogenic and embryotoxic effects even at low concentrations. Lead poisoning can cause disorders in neurological, psychological and reproductive functions (Shahat et al., 2018; Karye and Rajgor, 2007; Chooto et al., 2010).

The accessibility of heavy metals in environment mainly depends on the soil physicochemical properties, which are: granulometric composition and soil type, pH, redox potential, the inherence of microorganisms (Blake and Goulding, 2002; Kabata-Pendias and Pendias, 1999; Tyler and Olsson, 2001; Hao and Chang, 2002; Majewska and Kurek, 2002). Organic matter presence (e.g. humic substances) or

addition of organic and mineral fertilizers to the soil may limit the concentration of heavy metal forms that are easily absorbed by living organisms (Curyło and Jasiewicz, 1998; Gawęda, 1995; Gębski, 1998; Mercik and Kubik, 1995).

In order to reduce the heavy metal bioaccumulation and biomagnification in the environment and prevent their harmful effects on the living organisms, the immobilization process is used (Marecik et al., 2006; LeDuc and Terry, 2005). It involves the toxic metal immobilization in the forms characterized by low assimilation by animals and plants as well as low mobility in soil solution. As a result, the toxic ions infiltration into the ground (or groundwater) and their inclusion in the trophic chain are limited. The immobilization techniques include: bioremediation, phytostabilization or chemical immobilization (i.e. chelation) (Marmiroli and McCutcheon, 2003; Hamby, 1996). The addition of synthetic and organic chelating compounds (e.g. natural, organic, organic-mineral fertilizers or soil flocculants) to the soil, which form complexes with the toxic metal ions, may contribute to reduction in heavy metal amount available to organisms (Adriano, 2001; Sharma and Pandey, 2014).

The aim of the study was to determine the structure of electrical double layer formed on the kaolinite surface in the mixed system of cationic polyacrylamide and lead(II) cations. The influences of cationic flocculant on the Pb(II) ions sorption on the kaolinite surface as well as heavy metal ion addition on the polymer adsorbed amount on the same clay mineral were studied. The adsorption and electrokinetic properties of studied kaolinite/CT PAM/Pb(II) systems were determined based on the spectrophotometric study, zeta potential measurements as well as potentiometric titration.

2.   Materials and methods

2.1. Materials

The adsorbent used in the study was kaolinite (*Sigma-Aldrich*) – a soil mineral which is an 1:1 aluminosilicate. Using the nitrogen adsorption/desorption method (Micromeritics ASAP 2020 analyzer) and XRF technique (*Panalytical* ED-XRF type Epsilon 3 spectrometer) the textural properties and elemental composition of this mineral were determined. Specific surface area (SBET) of kaolinite equals 8.02 m²/g, while pore size was 14.3 nm. The elemental composition of this aluminosilicate was as follows: Si (22.2 wt.%), Al (19.6 wt.%), K (1.5 wt.%), Fe (0.337 wt.%), P (0.189 wt.%) and elements such as Na, Mg, Cr, Rb or Zn with trace content.

A cationic polyacrylamide (PAM, *Korona*) with different content of cationic groups was applied as adsorbate in the study. Two samples marked as CT PAM 35% and CT PAM 80% (number refers to the dissociable quaternary amine groups content in PAM chains) were characterized by weight average molecular weight (M_w) equal to 7 000 kDa. Using potentiometric titration method, the pK_b parameters of polyacrylamides were determined and ionization degrees (α) were calculated. The pK_b values were equal to 9.3 for CT PAM 35% and 9.5 for CT PAM 80%, whereas the degree of cationic groups dissociation was as follows: at pH 3 - 99.9%, pH 5 - 99.9%, pH 7 - 99.4-99.6%, pH 9 - 64-76%.

2.2. Methods

All adsorption measurements were conducted by a static method at 25°C, pH 5 and 0.001 mol/L NaCl as a supporting electrolyte. The range of tested cationic polyacrylamide and lead(II) ions concentrations was as follows: 100 ppm for CT PAM (this is the concentration at which the adsorption equilibrium is established) and 1, 10, 100 ppm for Pb(II) ions. The lowest permissible content of lead(II) in sewage and groundwater is in the range of 0.1-0.5 mgPb/L, thus this range of concentrations is close and significantly exceeding the permissible concentration, which may take place in an environment near industrial areas or roads and highways. Cationic polymer or lead ions concentration was estimated using a UV–Vis spectrometer (Carry 1000, *Varian*). The adsorbed amount on the kaolinite surface (Γ) was determined from the difference between the polyacrylamide or heavy metal ion concentration in the solution before and after its adsorption process using the following equation:

$$\Gamma = \frac{(c_0 - c_a) \cdot V}{m} \qquad (1)$$

where: c_0 – concentration before adsorption process (mg/L), c_a – concentration after adsorption process (mg/L), V (mL) - volume of the solution, m (g) – weight of kaolinite used in the adsorption process.

The studied probes were prepared by adding 0.1 g of clay mineral to 10 mL of solution containing supporting electrolyte, CT PAM 35% or 80% and/or Pb(II) ions. After adjusting the pH value of each sample with a pH-meter (Beckman Instruments), the suspensions were shaken in water bath (OLS 200, *Grant*) for 24 h in order to obtain the polymer adsorption equilibrium. Then, the solids were centrifuged (*MPW Med. Instruments*) and 5 mL of the clear solution was taken for the spectrophotometric analysis. For the cationic polyacrylamide concentration determination, the brilliant yellow as indicator was used. After adjusting pH to 9, the cationic polymer probe in volume of 0.5 mL was added to 4.5 mL of the indicator, and absorbance was measured at 495 nm. To determine the concentration of Pb(II) ions, the PAR method was used (Dagnall et al., 1965). This method is based on Pb(II) reaction with 4-(2-pyridylazo)-rezorcinol (PAR) in an ammonium buffer which results in a red coloured PAR-Pb chelate complex. The content of heavy metal ions was determined spectrophotometrically at 520 nm. A single result of adsorption measurements was the average of three repetitions. The measurement error did not exceed 5%.

In order to determine the kaolinite surface charge (σ_0) and point of zero charge (pH_{pzc}) the potentiometric titration method was applied. For this purpose the mineral suspensions were prepared using 2.5 g of kaolinite and 100 ppm of cationic polyacrylamide or 1 ppm of lead(II) ions. Next the each sample was titrated with NaOH (c=0.1 mol/L) in the pH range of 3-7± 0.1 at 25°C. The measuring set consisted of: thermostated Teflon vessel (thermostat RE 204, *Lauda*), glass and calomel electrodes (*Beckman Instruments*), pH-meter PHM 240 (*Radiometer*), automatic microburette (Dosimat 765, *Methrom*), printer and computer. The solid surface charge density was calculated with the special program Titr_v3 (authored by Janusz) (Janusz, 1994) using the following equation:

$$\sigma_0 = \frac{\Delta V \cdot c \cdot F}{m \cdot S} \tag{2}$$

where: ΔV (mL) – the difference in the base volume added to a suspension and a supporting electrolyte solution that leads to the specific pH value, c (mol/L)– the base concentration, F (C/mol) – the Faraday constant, m (g) – the metal oxide mass in the suspension, S (g/m²) – the solid surface area.

The kaolinite zeta potential (ζ) was established using a Zetasizer Nano ZS (*Malvern Instruments*) with the universal dip cell. These measurements were carried out in systems with and without the CT PAM and/or Pb(II) ions presence, in the narrow pH range from 3 to 7 at 25°C (lead hydroxide can be precipitated from the aqueous solution above pH 7). The mineral suspensions in the supporting electrolyte solution were prepared by adding 0.1 g of kaolinite to 100 mL of the appropriate solution. Each of soil mineral suspension was sonicated for 3 minutes using an ultrasonicator XL 2020 (*Misonix*) and separated into several parts, where different pH value (3-7) was adjusted. By means of Henry equation (Hunter, 1981), the zeta potential value was calculated form solid particles electrophoretic mobility in the liquid medium:

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

where: U_e – the electrophoretic mobility ($\mu m cm/V \cdot s$), ε – the dielectric constant, ε_0 (C²/J · m) – the electric permeability of vacuum, ζ – the zeta potential (mV), η – the viscosity (kg/m · s), $f(\kappa a)$ – the Henry function. The electrochemical method was widely applied in many systems to obtain the structure of interfacial layer (Nosal-Wiercińska, et al., 2018; 2019).

The changes in the kaolinite suspension stability with/without the cationic polyacrylamide and heavy metal ions were monitored using a spectrophotometry method. The examined suspensions were prepared by adding 0.1 g of kaolinite to the 10 mL of supporting electrolyte solution with or without cationic PAM/Pb(II) ions. Then the system pH value was adjusted (pH=5) and the absorbance of kaolinite suspension was measured in function of time at wavelength 500 nm (spectrophotometer Carry 1000, *Varian*).

3.   Results and discussion

3.1. Electrokinetic properties of kaolinite particles dispersed in supporting electrolyte solution

Using microelectrophoresis and potentiometric titration methods, the electrokinetic properties of the kaolinite suspension were determined. Fig. 1 presents the surface charge density (σ_0) and zeta potential (ζ) of kaolinite particles in supporting electrolyte. Kaolinite has layered structure in which one

tetrahedral silica sheet (SiO$_4$) and octahedral alumina sheet (Al(OH)$_6$) are strongly held by shared oxygen and hydrogen bond. The charge formation of mineral particles results from broken bonds or hydroxyl groups protonation/deprotonation (Brady et al., 1996).
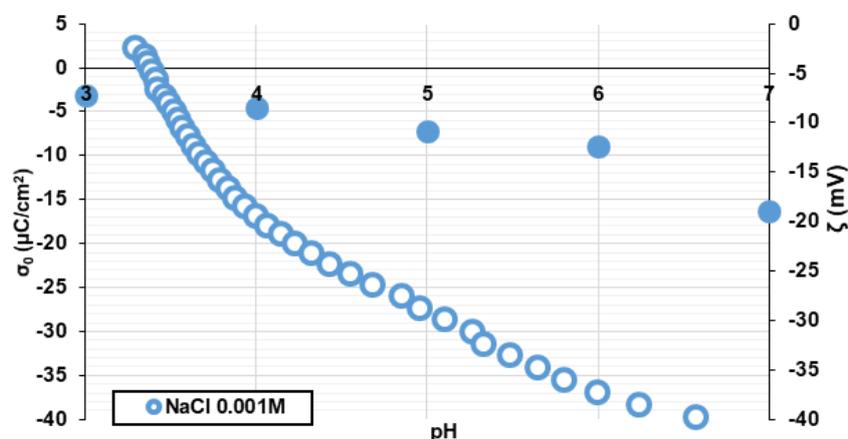
Fig. 1. Surface charge density (open points) and zeta potential (solid points) of kaolinite as a function of solution pH

Considering the change in the absolute values of σ$_0$ parameter the kaolinite surface, charge density increases with increasing pH value (it has a negative sign). What is more, the obtained data indicated that pH$_{pzc}$ (PZC - point of zero charge) of kaolinite equals 3.37. This value is consistent with the literature reports (Tschapek et al., 1974; Yukselen and Kaya, 2003). The pH$_{pzc}$ parameter characterizes the solid electric double layer (EDL) and refers to zero surface charge. At this pH the concentrations of positively (-SiOH$_2^+$) and negatively charged (-SiO$^-$) surface groups are identical. At the pH below pH$_{pzc}$, the mineral surface assumes a positive charge, whereas at pH higher than pH$_{pzc}$ its surface is negatively charged. In the system without any additives, the electrokinetic potential of kaolinite particles becomes more negative when the pH value increases. This parameter assumes only negative values in the whole studied pH range so it can be stated that the pH$_{iep}$ (IEP – isoelectric point) of this clay mineral is lower than 3. This result is consistent with the literature – kaolinite isoelectric point is in the range of 2.8-4 (Min et al., 2013; Ndlovu et al., 2015).

3.2. Structure of electrical double layer on the kaolinite surface in the cationic polyacrylamide presence

The adsorption isotherms of 35% and 80% cationic polyacrylamides on the kaolinite surface at pH 5 are presented in Fig. 2. At pH 5 the surface of mineral particles is negatively charged due to high content of dissociated kaolinite hydroxyl groups. Moreover, as a result of electrostatic repulsion between CT PAM functional groups, polymer chain development takes place. Under these conditions, the dissociation degree of both cationic polymers is equal to 99.9% so most of polymer segments are positively charged. Polymer macromolecules containing –N(CH$_3$)$_3^+$ groups in their chains have a strong affinity for the surface of the clay mineral. The electrostatic attraction between dissociated quaternary amine groups of PAM and hydroxyl groups of the mineral as well as hydrogen bridges formation are important mechanisms in polyacrylamide adsorption. In other words, polymer-kaolinite particles adsorption results from solid charge neutralization or compensation as well as solid-polymer complex formation (Lee et al., 1991; Laird et al., 1997; Mpofu et al., 2003; Deng et al., 2006). Stronger affinity to the kaolinite surface is noted for CT PAM with greater amount of ionizable groups so the adsorbed amount noted for this polymer is higher.

The zeta potential measurements and potentiometric titration provided electrokinetic properties of the kaolinite/supporting electrolyte system without and with cationic polyacrylamide (Fig. 3). The cationic polyacrylamide addition to the clay mineral suspension cause changes in both σ$_0$ and ζ parameters. The absolute values of solid surface charge density is slightly lower, whereas electrokinetic potential assume only positive values in the entire pH range when CT PAM is present in the system.

These effects are induced by the presence of positively charged moieties in 'tail' and 'loop' structures of adsorbed polyacrylamide chains which are placed in the by-surface layer. The polymer with a higher content of dissociable amine groups (CT PAM 80%) has a stronger impact on σ_0 and ζ values resulting in a larger increase in these parameters (Wiśniewska et al., 2014).
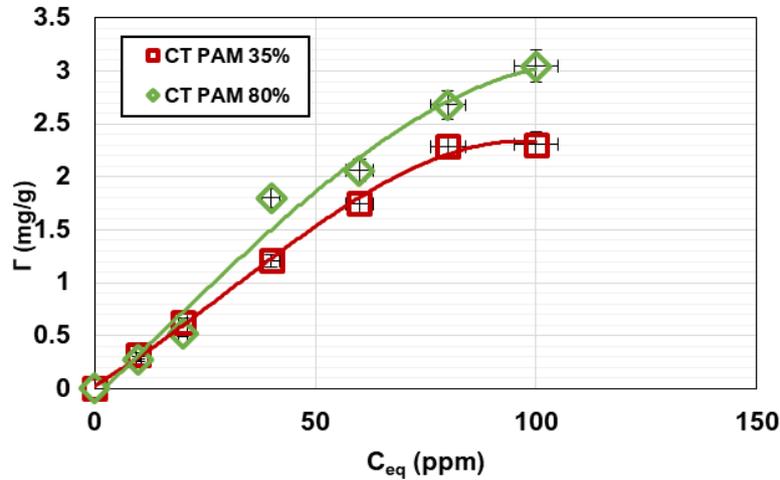
Fig. 2. Adsorption isotherms of CT PAM with different ionic group content on the kaolinite surface at pH 5
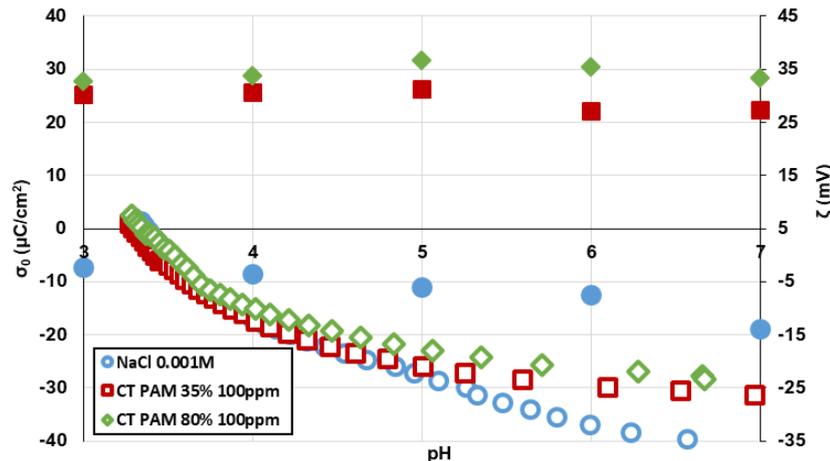
Fig. 3. Surface charge density (open points) and zeta potential (solid points) of kaolinite with and without CT PAM as a function of solution pH

The changes in the kaolinite suspension stability after cationic PAM addition at pH 5 are presented in Fig. 4. In case of kaolinite system without polymer the absorbance remains at relatively high level for 100 minutes. Due to high negative surface charge and electrostatic repulsion between negatively charged particles the electrostatic stabilization may occur in the system. The presence of both cationic polyacrylamides affects the stability of clay mineral suspension. In case of system with CT PAM 35% and 80%, after 5 minutes the absorbance value is over 3 times smaller than that of kaolinite suspension without any additive. The CT PAM adsorption on the kaolinite surface contributes to polymer bridging and formation of easily sedimenting flocs (large aggregates of mineral particles covered with the cationic PAM layers). Therefore, cationic polyacrylamide exhibits flocculating ability relative to the selected aluminosilicate particles.

3.3. Structure of electrical double layer on the kaolinite surface in the lead(II) cations presence

Fig. 5 presents the amount of lead(II) ions adsorbed on the kaolinite surface at pH 5. Similarly to cationic polyacrylamide, lead(II) cations have a strong affinity for the kaolinite surface. For the initial lead(II)
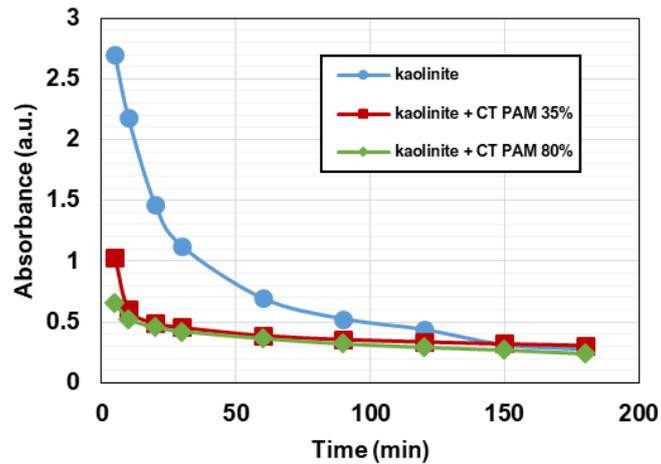
Fig. 4. Influence of cationic PAM addition on the kaolinite suspension stability at pH 5

ions concentrations: 1, 10 and 100 ppm, their adsorbed amount on the clay mineral surface is equal to 0.1, 0.7 and 7.1 mg/g, respectively. Thus, when heavy metal ions concentration increases, there is a growth in the Pb(II) adsorbed amount associated with increasing driving force of lead ions towards the kaolinite active sites (Jiang et al., 2010; Adebowale et al., 2006). The Pb(II) adsorption on mineral surface is mainly caused by electrostatic attraction between the positively charged lead cations and the negatively charged surface of the mineral.
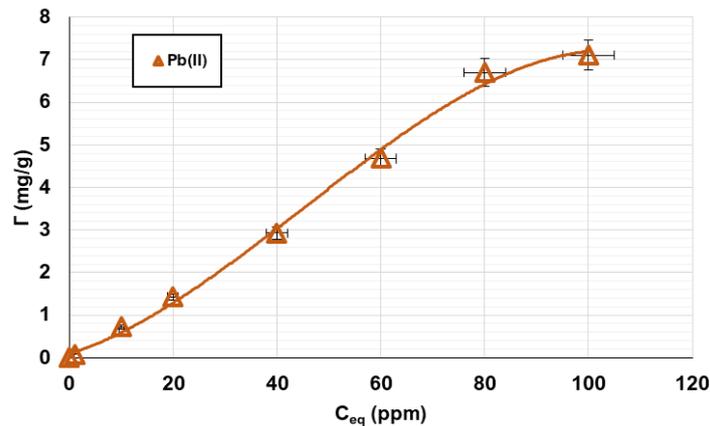
Fig. 5. Adsorption isotherm of Pb(II) ions on the kaolinite surface at pH 5

The changes in surface charge density and zeta potential of kaolinite particles after Pb(II) ions addition are presented in Fig. 6.

The surface charge density of kaolinite in the Pb(II) ions presence is slightly higher than that observed without heavy metal ions considering the absolute values of this parameter. According to the site-binding model (Wiśniewska et al., 2017), the interaction of lead cations and surface hydroxyl groups of kaolinite occurs with following reactions:

$$\equiv SiOH + Ct^{2+} \leftrightarrow \equiv SiO^- Ct^{2+} + H^+ \tag{4}$$

$$2(\equiv SiOH) + Ct^{2+} \leftrightarrow (\equiv SiO)_2 Ct^{2+} + 2H^+ \tag{5}$$

$$\equiv SiOH + Ct^{2+} + H_2O \leftrightarrow \equiv SiO^- CtOH^+ + 2H^+ \tag{6}$$
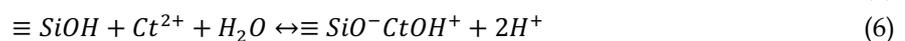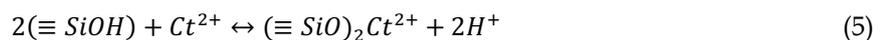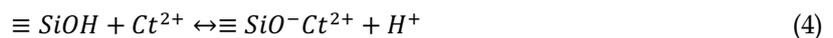
Thus, the Pb(II) adsorption contributes to creation of additional negatively charged sites on the kaolinite surface (Skwarek and Janusz, 2019). In case of electrokinetic potential, the presence of lead(II) cations in the system induces a reduction in kaolinite zeta potential. Adsorption of this heavy metal ions affects accumulation of positive charge on kaolinite particles surface, which is neutralized by negative moieties located in the slipping plane area.
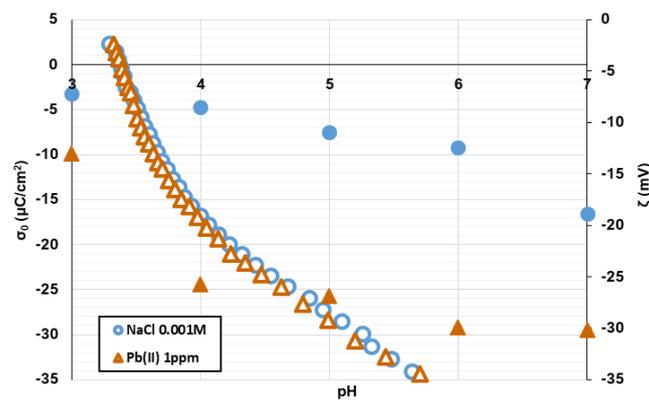
Fig. 6. Surface charge density (open points) and zeta potential (solid points) of kaolinite with and without lead(II) ions as a function of solution pH

3.4. Electrokinetic properties of kaolinite particles dispersed in mixed system of cationic polyacrylamide and lead(II) cations

The effect of the individual adsorbates on the adsorption of the cationic polyacrylamide or lead(II) ions on the kaolinite surface at pH 5 is presented in Figs 7-8. Both, cationic polymer and heavy metal ions are the source of the positive charge and thus have a high affinity for the kaolinite surface at pH 5. Lead(II) ions, despite the occurrence of repulsive interaction between the mono-charged adsorbates, contributes to increase in the polyacrylamide adsorbed amount (Fig. 7).
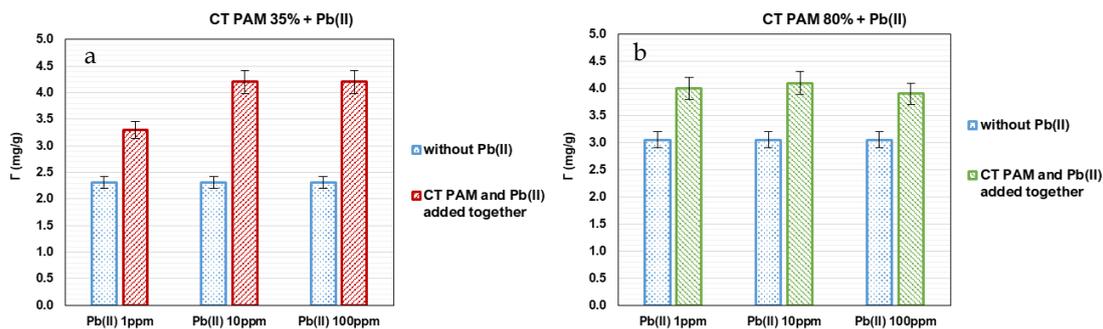
Fig. 7. Influence of Pb(II) ions with different concentration on the: a) CT PAM 35% and b) CT PAM 80% adsorbed amount on the kaolinite surface at pH 5

Some researchers (Gu et al. 2018; Zhao et al. 2009; Zhou et al. 2011; Li et al. 2005) explained this phenomenon as a result of polymer-metal complexes creation. In PAM chains, beside quaternary amine groups, the neutral amide moieties are present. The free electron pairs, located on the nitrogen atoms of these groups, and lead(II) cations form covalent bonds. For CT PAM 35%, due to higher content of neutral amide groups, the observed adsorption level in the Pb(II) ions presence is much greater than that noted for CT PAM 80%. Due to the fact that Pb(II) ions are divalent, they interact simultaneously with two amide groups and make the polymer structure more packed. During adsorption, the formed metal-polymer complexes occupy a smaller part of the surface than the macromolecules without additives and, consequently, in the heavy metal presence, the polymer adsorbed amount on the kaolinite surface is greater. Furthermore, the formed complexes have a larger positive charge than PAM macromolecules without Pb(II) ions and the attraction between them and negative kaolinite surface is stronger. On the other hand, the polymer addition contributes to slight reduction in lead(II) ions adsorbed amount. Fig. 8 shows the influence of CT PAM 35% and 80% on the Pb(II) adsorption on the kaolinite surface at pH 5. Probably in this case, repulsive interaction occurring between Pb(II) and polymer has a great impact on heavy metal adsorbed amount. The described small decrease in lead(II) adsorbed amount is observed for both polymer samples and all tested Pb(II) ions concentrations.

The electrokinetic properties of kaolinite particles dispersed in the mixed system containing cationic polyacrylamide and lead(II) cations are presented in Figure 9. The σ_0 and ζ parameters of kaolinite in the CTPAM/Pb(II) presence assumes higher values in comparison to the system containing only supporting electrolyte. This indicates that the positively charged amine groups, which are not involved in the formation of polymer-heavy metal ions complexes, are present in non-adsorbed polymer segments ('loops' or 'tails'). These moieties interact with the slipping plane area (making the ζ parameter higher) and simultaneously induce positive charge on the kaolinite surface (Wiśniewska et al., 2019).
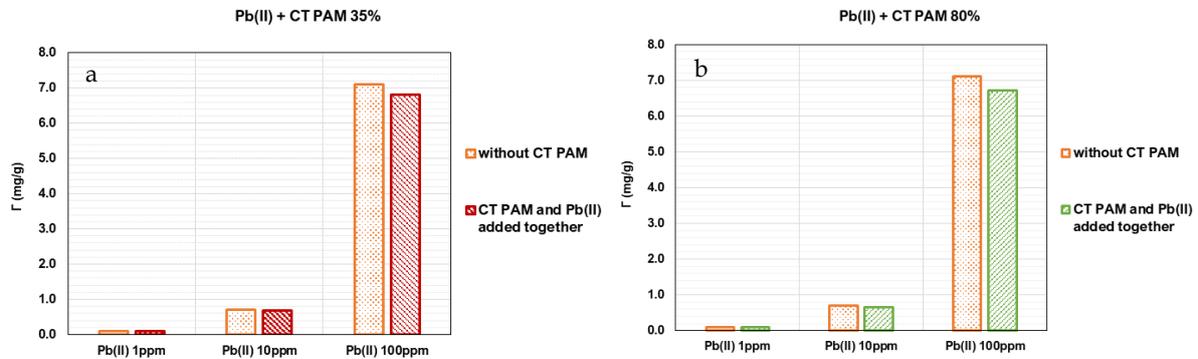
Fig. 8. Influence of: a) CT PAM 35% and b) CT PAM 80% on the Pb(II) adsorbed amount on the kaolinite surface at pH 5

The stability changes in the studied kaolinite suspension in the polyacrylamide/heavy metal ions presence are illustrated in Fig. 10. The simultaneous addition of cationic polyacrylamide and Pb(II) ions to the kaolinite suspension causes noticeable stability reduction manifested by the absorbance decrease (for both polyacrylamide types). This is probably associated with polymer bridging and flocculation process that occurs in the examined systems. The polymers used retain their ability to form large aggregates of mineral particles even if heavy metal ions are present in the system.
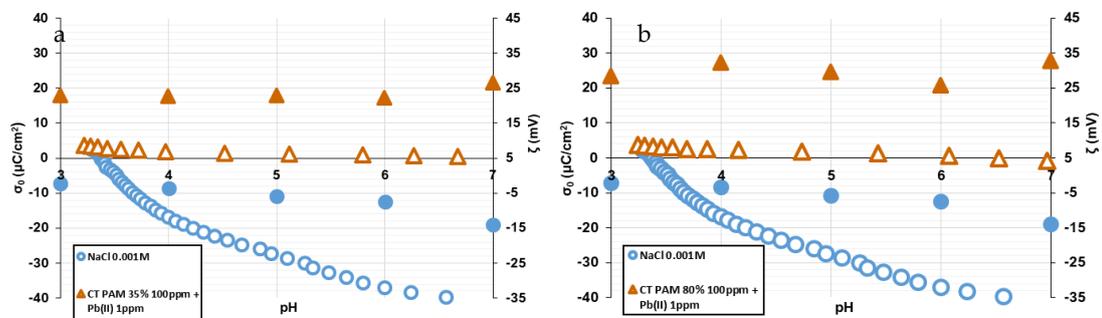
Fig. 9. Surface charge density (open points) and zeta potential (solid points) of kaolinite with and without: a) CT PAM 35%/ Pb(II) ions, b) CT PAM 80%/ Pb(II) ions as a function of solution pH
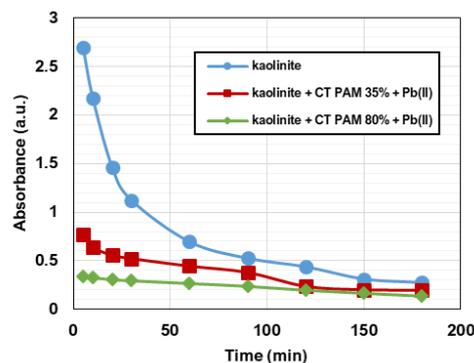
Fig. 10. Influence of cationic PAM/ Pb(II) addition on the kaolinite suspension stability at pH 5

4. Conclusions

Obtained results of adsorption, electrokinetic and stability measurements allowed formulate following conclusions:

- Adsorption of cationic polyacrylamide as well as Pb(II) ions affects the EDL structure of the mineral particles which is manifested by changes in kaolinite surface charge density and zeta potential.
- A stronger affinity for the kaolinite surface and thus greater adsorption is observed for cationic polyacrylamide with higher content of quaternary amine groups.
- The cationic PAM presence causes a slight decrease in Pb(II) adsorbed amount due to occurrence of repulsive interaction between the mono-charged adsorbates.
- Despite electrostatic repulsion between positively charged ($-N(CH_3)_3^+$) of polyacrylamide and Pb(II) cations, the accumulation of Pb(II) occurs in the PAM presence. There is a formation of covalent bond between amide polymer groups and lead(II) ions.
- Cationic PAM has flocculating properties relative to kaolinite particles, even in the Pb(II) ion presence.

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