

Synthetic polyacrylamide as a potential flocculent to remove commercial chromium(III) oxide from aqueous suspension

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Abstract The effects of solution pH and cationic group contents in polyacrylamide (PAM) macromolecules on the polymer adsorption mechanism on chromium(III) oxide surface were studied. The structure of PAM adsorption layer was also characterized to explain the changes in solid suspension stability. The following methods were applied: turbidimetry, spectrophotometry, potentiometric titration and microelectrophoresis. Thanks to them, the stability of the Cr₂O₃–polymer systems, polymer-adsorbed amount, surface charge density and zeta potential of solid particles were determined. The experimental results indicate that adsorption of cationic PAM increases with the rising pH. The larger the content of cationic groups in PAM chains is, the higher the adsorption level is observed. The most effective chromium(III) oxide removal is achieved at pH 9 after addition of PAM with the largest content of cationic groups (i.e. 80 %). The neutralization of solid surface negative charge by positively charged polymer chains (assuming more coiled conformation) is responsible for this.

Keywords Cationic group content · Cationic polyacrylamide · Cr₂O₃ removal · Polymer adsorption · Suspension destabilization

Introduction

Polymers belonging to the polyacrylamides group are often used because of their lower sensitivity to temperature and being prone to self-association. Moreover, they can be easily modified using the copolymerization reaction, which provides a wide range of their applications. In many cases, the polyacrylamide (PAM) macromolecules stabilize the colloidal dispersion by the steric effect or form polymeric bridges between the colloidal particles, leading to their destabilization. This polymer is very often used because of its high efficiency, low cost and not large requirements for its quality (Zhang and Miller 1996; Taylor and Nasr-El-Din 1998; Pefferkorn 1999; Nasser and James 2006; Tripathy and De 2006; Sojka et al. 2007).

Recently, various types of water contamination are serious problem from an ecological point of view. This is due to high industrial development. An important issue is the treatment of wastewater, industrial waste (Gupta et al. 2012a; Saleh and Gupta 2012a, b, c, d; Gupta and Saleh 2013; Gupta et al. 2013) and those from minerals processing. Removal of these pollutants requires application of appropriate methods such as adsorption, flocculation, filtration and evaporation (Gupta et al. 2011a; Saleh 2011; Saleh et al. 2011; Gościańska et al. 2012; Kaźmierczak et al. 2013; Nosal-Wiercińska 2012, 2013, 2014; Nowicki et al. 2013, 2015; Saleh 2015a, b). Nevertheless, the flocculation process is one of the most important and most frequently applied methods (Jin et al. 2003; Haydar and Aziz 2009; Wiśniewska et al. 2013).

Polyacrylamide is also used for treatment of drinking water, by simultaneous improvement of its physicochemical properties. Polyacrylamide finds application in production of paper, flotation of minerals and enhanced oil recovery and is used as a fertilizer inhibiting soil erosion.

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PAM is also used as a dispersant, spatial stabilizer and thickener (Sojka and Entry 2000; Entry et al. 2002; Zolfaghari et al. 2006; Xia 2007; Yuan et al. 2011).

The main aim of the present paper is determination of the impact of cationic group content of ionic polyacrylamide (PAM) on the conformation of its macromolecules in adsorption layer formed at Cr_2O_3 /polymer aqueous solution interface. The effect of solution pH was also examined. Explanation of PAM adsorption mechanism enabled clarification and understanding of Cr_2O_3 suspension stability in the polymer presence. The research presented in this paper is continuation of experiments concerning removal of undesirable solids from aqueous solutions. The previous paper focused on separation possibilities of Cr_2O_3 from the aqueous suspension by the use of anionic polyacrylamide (with a different content of cationic groups) (Wiśniewska et al. 2015a, b).

The world literature reports provide information about chromium(III) oxide removal using both synthetic and natural polymer flocculants such as polyacrylic acid, polyamino acids (anionic polyaspartic acid, cationic polylysine), its copolymers with polyethylene glycol, albumins (bovine serum albumin, ovalbumin, human serum albumin) and bacterial polysaccharide *Sinorhizobium meliloti* (Wiśniewska and Szewczuk-Karpisz 2013; Ostolska and Wiśniewska 2014a, b, 2015; Szewczuk-Karpisz and Wiśniewska 2014; Szewczuk-Karpisz et al. 2014). On the other hand, separation of Cr_2O_3 can be accomplished by application of various adsorbents, among other active carbons, mixed adsorbents of activated carbons and metal oxides as well as biosorbents (Gupta and Ali 2004; Gupta et al. 2007, 2011b, c, 2012b, c; Gupta and Rastogi 2009).

Chromium(III) oxide is one of the most frequently used dyes in the industry. It is applied for colouring glass, concrete, ceramic, plastic or leather. It is also used as a catalyst for organic syntheses. Cr_2O_3 is a very popular colourant in the production of banknotes and green ink. It is also used as an ingredient in cosmetics (eyeshadow) and dye in bronzers, lipsticks and cheek rose (Anger et al. 2005).

This compound is so widely applied due to the fact that it is not toxic and is the most stable (resistant to changes in temperature and weather conditions) compared to other green colourants. The pigment maintains the same colour. It may change tint in the cooler with blue tones at a temperature above 1000 °C, which is caused by the increase in the solid particle diameter.

Due to the wide application of chromium oxide (III) in industry, its increased amount can be found in wastewaters. Cr_2O_3 has an intense green colour, and even its low concentrations can inhibit light penetration to greater depths of water. This can lead to oxygen deficiency caused by disruptions in the process of photosynthesis carried out by

aquatic plants and algae (Bielicka et al. 2005; Oliveira 2012; Sarker et al. 2013). Therefore, it is important to look for new ways to remove coloured substances from wastewaters. One of them can be adsorption of macromolecules (i.e. ionic polyacrylamide) on the solid particle surfaces, making their removal much simpler.

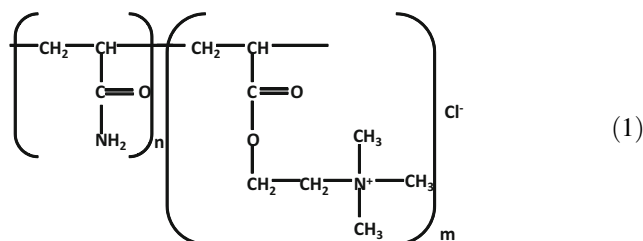
Materials and methods

Adsorbent characteristics

Chromium(III) oxide (POCh) was used as adsorbent in the experiments. The BET-specific surface area of Cr_2O_3 was equal to 7.12 m^2/g (BET method; Micromeritics ASAP 2405 analyzer). The mean grain size of the solid particles in water was 265 nm. The average pore diameter of the solid particle was 6.1 nm. These two parameters were obtained using photon correlation spectroscopy (Zetasizer 3000, Malvern Instruments).

Polymeric samples characteristics

Four samples of cationic polyacrylamide—PAM (Korona)—characterized by different contents of cationic groups were applied (Fig. 1; Table 1). The chemical formula of this polymer is:



This PAM cationic form is obtained by copolymerization reaction of acrylamide with cationic monomer (i.e. containing the quaternary amine group). The pK_b values of PAM solutions were determined by the potentiometric titration technique (Wiśniewska et al. 2015a), and the ionization degrees of cationic groups (α) were calculated (Table 1).

Adsorption measurements

All experiments were carried out at 25 °C in the solution of sodium chloride with the concentration ($1 \times 10^{-2} \text{ mol}/\text{dm}^3$), which played role of supporting electrolyte.

The static method was applied in adsorption measurements. The polymer concentrations were in the range 5–120 ppm. Three pH values were examined: 3, 6 and 9

Table 1 Characteristics of cationic polyacrylamide samples

Symbol	Molecular weight (Da)	Cationic group content (%)	pK _b	α (%)		
				pH 3	pH 6	pH 9
PAM 8.5_20 %	8,500,000	20	10.1	99.9	99.9	92.6
PAM 7.0_35 %	7,000,000	35	10.1	99.9	99.9	92.6
PAM 7.0_50 %	7,000,000	50	9.9	99.9	99.9	88.8
PAM 7.0_80 %	7,000,000	80	9.9	99.9	99.9	88.8

(±0.1). The used solid mass was 0.07 g. Next, suspensions were shaken in a water bath for 24 h. Then, for each of them, the solid was centrifuged and 5 cm³ of supernatant was taken for analysis. The reaction of cationic polyacrylamide with a saturated solution of bromine, sodium formate and starch (in acetate buffer) (Scoggins and Miller 1975) was applied. The formed complex gives blue colour of the solution of different intensity (depending on the polymer concentration). The solution absorbance was measured after 5 min using the UV–Vis spectrophotometer (Carry 1000; Varian) at 585 nm. The amount of the adsorbed polymer was determined from the difference between the PAM concentration in the solution before and after the adsorption process (using the calibration curve prepared earlier).

Surface charge density determination

The potentiometric titrations of Cr₂O₃ suspension without and with PAM (polymer concentrations 1 and 10 ppm) were performed in the thermostated Teflon vessel. The computer program Titr_v3 (author Janusz 1999) was used to the solid surface charge density calculation and pH_{pzc} determination. 1.5 g of chromium(III) oxide was added into the vessel up to 50 cm³ of PAM–NaCl solution (or only to NaCl solution). The suspension was titrated by NaOH of the concentration starting with the pH value about 3.5. The measuring set was composed of the following parts: burette Dosimat 665 (Methrom), thermostat RE204 (Lauda), pH meter PHM 240 (Radiometer), computer and printer.

Zeta potential measurements

Cr₂O₃ suspensions (without and with PAM) were prepared, adding 0.02 g of Cr₂O₃ to 100 cm³ of NaCl solution or PAM–NaCl solution (polymer concentrations 1 and 10 ppm) solutions. After the sonification process, the obtained suspension was divided into 6 parts of the same volume. Then in each of them, the pH value was adjusted to: 3, 4.5, 5.5, 6.5, 8.5 and 10 ± 0.1, respectively. The zeta

potential was measured with the Zetasizer Nano ZS using the universal dip cell and MPT-2 titrator (Malvern Instruments).

Determination of Cr₂O₃ suspension stability without and with polymer

Stability measurements of the Cr₂O₃–NaCl and Cr₂O₃–PAM–NaCl systems were made using Turbiscan Lab^{Expert} with the cooling module TLab Cooler. The suspension of 0.2 g of oxide in 20 cm³ of NaCl solution (or PAM–NaCl, C_{PAM} 100 ppm) was prepared. Each experiment of suspension stability lasted 15 h, and every 15 min the respective data were collected.

As a result, the curves of transmission (and backscattering) intensities of light directed towards the examined suspension as a function of time were obtained. These data enable special parameters calculation (TLab EXPERT 1.13 and Turbiscan Easy Soft programs) which characterize suspension stability. There are: the stability coefficient Turbiscan Stability Index (TSI), the formed sediment thickness, the aggregate (flock) size and the aggregate (flock) migration velocity.

The following dependencies were applied for this purpose:

$$TSI = \sqrt{\frac{\sum_{i=1}^n (x_i - x_{BS})^2}{n - 1}} \quad (2)$$

where x_i is average backscattering for each minute of measurement, x_{BS} average x_1 , and n number of single measurement during the total time of the experiment,

$$V(\phi, d) = \frac{|\rho_p - \rho_c| g d^2}{18 \nu \rho_c} \cdot \frac{[1 - \phi]}{\left[1 + \frac{4.6\phi}{(1-\phi)^3}\right]} \quad (3)$$

where ν is aggregate migration velocity, ρ_c continuous-phase density, ρ_p particle density, d particle mean diameter, ν continuous-phase dynamic viscosity, and ϕ volume fraction of dispersed solid.



Results and discussion

Adsorption mechanism of polyacrylamide on the chromium(III) oxide surface

The exemplary adsorption isotherms of polyacrylamide on the chromium(III) oxide surface, obtained for the polymer samples containing 80 % of cationic groups, are presented in Fig. 1.

The analysis of these dependencies shows that in all examined systems, adsorption of cationic polyacrylamide on the solid surface increases with the increasing pH. This is due to the changes in polymer–surface electrostatic interactions (degree of PAM macromolecules ionization, sign and surface charge density of the metal oxide). The macromolecules of cationic PAM contain two types of functional groups. There are: nonionic amide groups that do not dissociate in aqueous solution and specified amounts (20, 35, 50 and 80 %) of cationic groups (quaternary amine moiety). The latter dissociate over a range of the studied pH (i.e. 3–10), whereby they are a source of positive charge of PAM macromolecules. Total dissociation of all cationic groups takes place at the pH values of 3 and 6 (approximately 99.9 %, Table 1). With the pH rise, the ionization degree of cationic groups decreases slowly and at pH 9 it reaches the value in the range 88.8–92.6 %. At pH equal to the pK_b value ranging 9.9–10.1 for the applied polymer samples, the dissociation degree of the polymer cationic groups is 0.5 (Table 1).

It is obvious that the adsorption affinity of positively charged macromolecules depends on the sign and density of the surface charge of chromium(III) oxide. The used adsorbent is characterized by the pH_{pzc} (pzc—point of zero charge) of 5.9–6.0. At this pH value, the total surface charge of the solid is zero, which means that the concentration of positively charged surface groups is equal to that of negative groups. Thus, in the pH range lower than

5.9, the Cr_2O_3 surface charge is positive, which is the reason for the electrostatic repulsion between the charged polymer chains and adsorbent. It is worth noting that the total charge of adsorbent is dependent on concentrations of the following surface groups: neutral ($=CrOH$) and charged ($=CrO^-$, $=CrOH_2^+$). On the other hand, in the range of pH values above pH_{pzc} of metal oxide, there are attractive electrostatic interactions between the PAM-positive functional groups and negatively charged solid surface. However, the occurrence of the cationic polymer adsorption at $pH < 5.9$ (the surface is positively charged, and electrostatic repulsion between the adsorbing macromolecules and that surface takes place) testifies to the binding of the polymer with the surface active sites through hydrogen bridges.

The total dissociation of the PAM cationic groups at pH 3 causes considerable development of polymeric chains. This is evidenced by the previously determined values of the hydrodynamic radius (R_h) of macromolecules in the bulk solution (Wiśniewska et al. 2015a). The analysis of the obtained values of this parameter (Table 2) indicates that at pH 3, it is the highest (of all examined polymer samples). Thus, the electrostatic repulsion between the polymer segments (containing positively charged functional groups) belonging to the same or different macromolecules leads to the adoption of more developed conformation in the solution.

Adsorption of these developed chains on the positively charged solid surface takes place under unfavourable electrostatic conditions. Mutual adsorbate–adsorbent repulsion results in the lowest adsorption of polyacrylamide at pH 3. The structure of the polymer adsorption layer is characterized mainly by the loop and tail structures extended into the bulk solution. Only a few polymer segments are directly bound to the adsorbent surface groups forming train structures. Probably hydrogen bonds

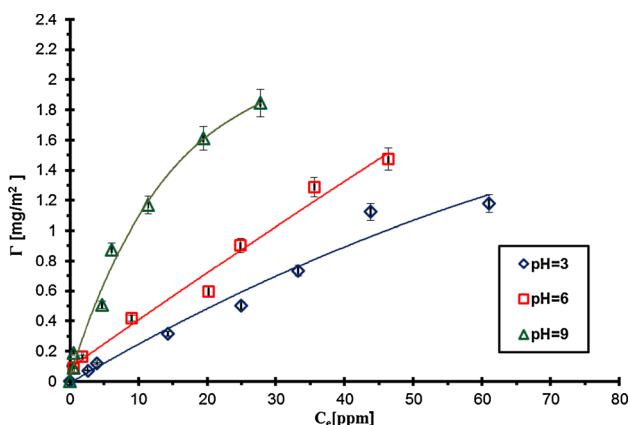


Fig. 1 Adsorption isotherms of PAM 7.0_80 % on the Cr_2O_3 surface for different solution pH

Table 2 Hydrodynamic radius (R_h) of polymer macromolecules in the solution

Polymer	pH	R_h (nm)
PAM 8.5_20 %	3	71.9
	6	56.1
	9	40.1
PAM 7.0_35 %	3	74.8
	6	58.1
	9	45.3
PAM 7.0_50 %	3	86.7
	6	79.5
	9	74.3
PAM 7.0_80 %	3	87.5
	6	81.4
	9	76.5



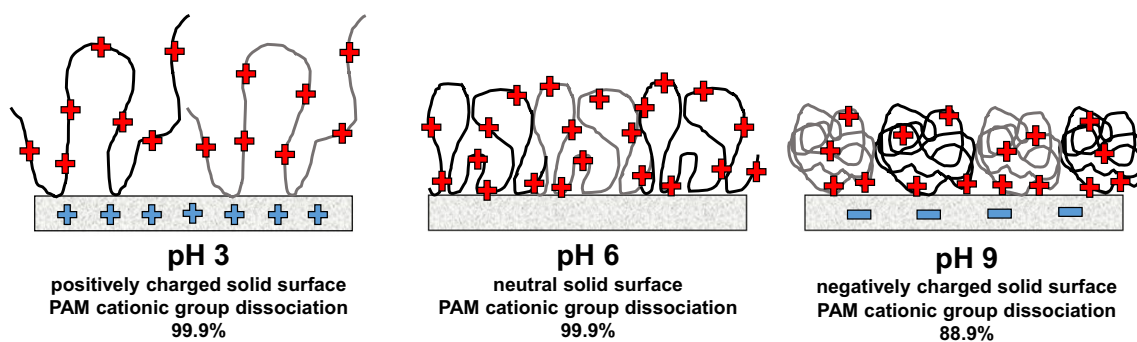


Fig. 2 Schematic presentation of cationic PAM adsorption mechanism on the Cr_2O_3 surface for different solution pH

between the hydroxyl groups of chromium(III) oxide and the functional groups of the polymer are responsible for PAM adsorption. Both amide and cationic groups of PAM as well as all types of Cr_2O_3 surface groups (i.e. neutral and charged $=\text{CrOH}$, $=\text{CrO}^-$, $=\text{CrOH}_2^+$) can be involved in formation of hydrogen bonds (Kasprzyk-Hordern 2004).

At pH 6, PAM adsorption on the solid surface increases significantly. Under these conditions, the resultant surface charge is practically zero ($\text{pH}_{\text{pzc}} = 5.9$). On the other hand, adsorbing macromolecules exhibit significant expansion due to the almost complete ionization. In the absence of electrostatic adsorbate–adsorbent interaction, more polymer segments are directly bonded with the surface (through train structures), which manifests in less developed conformation towards bulk solution. Such a conformation of the adsorbed macromolecule provides higher packing density of the adsorption layer (comparing to that at pH 3), which leads to polymer adsorption increase.

The most favourable electrostatic conditions for the adsorption of cationic polyacrylamide on the surface of chromium(III) oxide are found at pH 9. The surface charge of Cr_2O_3 assumes a negative value, and positively charged macromolecules have a more coiled conformation (dissociation degree of cationic groups in their chain reaches 88.8–92.6 %). As a result, more of the polymer molecules can locate on the unit of the solid surface, which results in the highest packing of adsorption layer (the largest adsorbed amount of PAM).

The mechanism of cationic PAM adsorption on the Cr_2O_3 surface for different solution pH is schematically illustrated in Fig. 2.

The polyacrylamide adsorption at the chromium(III) oxide–solution interface also affects significantly the content of the cationic groups in the polymer chains. For a given pH of the solution, it is observed that the more numerous the cationic groups in the polymer chain are, the larger the amount of adsorbed PAM is. The comparison of the adsorption amount of polyacrylamide samples

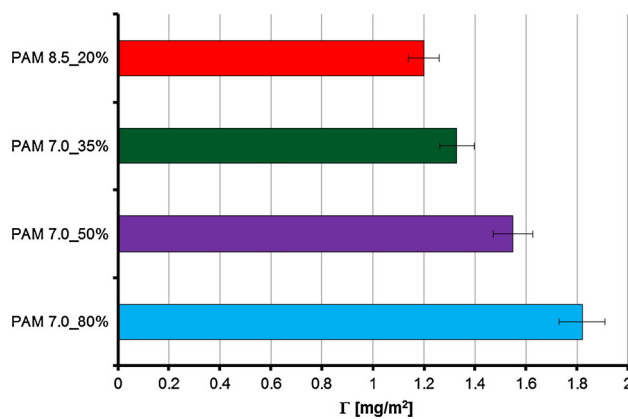


Fig. 3 Adsorbed amounts of PAM on the Cr_2O_3 surface for different cationic group contents in the polymer chains, $C_{\text{PAM}} = 100$ ppm

characterized by different contents of cationic groups in their chains at pH 9 is presented in Fig. 3. A larger number of these groups are equivalent to the more positively charged macromolecules, which leads to a higher adsorption on the negative metal oxide surface at pH 9.

In addition, the presence of a similar trend for two other tested pH values (i.e. 3 and 6), at which there is no adsorbent–adsorbate attraction, shows preferential binding of cationic PAM groups with the solid surface, in relation to the nonionic amide groups of the polymer.

Influence of cationic polyacrylamide adsorption on the electrokinetic properties of chromium(III) oxide–aqueous polymer solution system

Figure 4 presents the curves showing the dependence of the surface charge density of Cr_2O_3 (σ_0) as a function of solution pH obtained for the systems with and without polymer. On the other hand, Fig. 5 represents the changes in the zeta potential (ζ) of Cr_2O_3 particles in the absence and presence of PAM. Their analysis shows that the

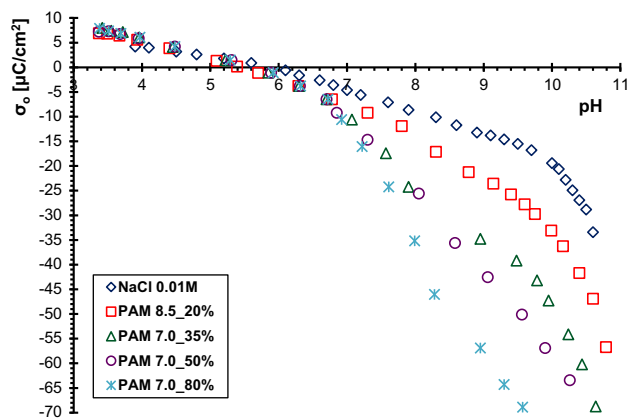


Fig. 4 Surface charge density of Cr_2O_3 in the absence and presence of cationic PAM, $C_{\text{PAM}} = 10$ ppm

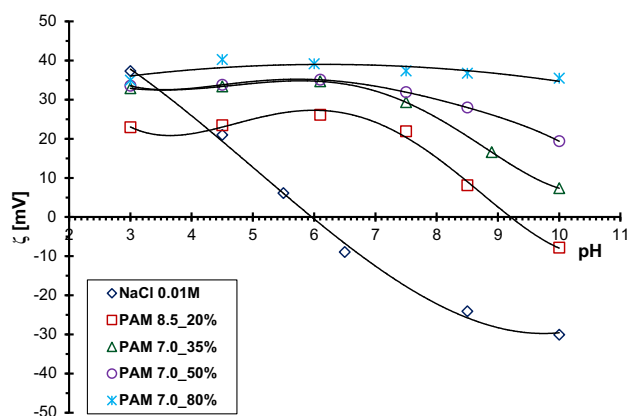


Fig. 5 Zeta potential of Cr_2O_3 particles without and with cationic PAM, $C_{\text{PAM}} = 10$ ppm

adsorption of cationic polyacrylamide results in a noticeable reduction in the surface charge density of the solid compared to the system without PAM in the pH range lower than pH_{pzc} . The effect of this reduction is greater for a higher polymer concentration (Table 3). A different situation is observed in the case of zeta potential changes, where the presence of the PAM adsorption layer around the solid particles causes a significant increase in the value of the electrokinetic potential.

The changes in the structure of the electrical double layer at the solid–solution interface due to the polymer adsorption are reflected in the location of pH_{pzc} and pH_{iep} points, compared to those obtained for the systems without polyacrylamide (Table 3). pH_{iep} point (iep—isoelectric point) determines the pH at which the zeta potential characterizing the charge of slipping plane is zero. Adsorption of cationic polymer causes a shift of pH_{pzc} of Cr_2O_3 towards lower values of pH. In turn, the pH_{iep} point

Table 3 pH_{pzc} and pH_{iep} values for Cr_2O_3 systems without and with PAM

System	pH_{pzc}		pH_{iep}	
	1 ppm	10 ppm	1 ppm	10 ppm
Cr_2O_3	5.9	6.0		
Cr_2O_3 –PAM 8.5_20 %	5.01	5.44	9.1	9.2
Cr_2O_3 –PAM 7.0_35 %	5.38	5.69	9.5	>10
Cr_2O_3 –PAM 7.0_50 %	5.58	5.68	9.9	>10
Cr_2O_3 –PAM 7.0_80 %	5.6	5.65	13.4	>10

of the systems containing polymer moves considerably in the direction of alkaline pH.

The presence of cationic polyacrylamide results in minimal changes in the surface charge density in the range of $\text{pH} < \text{pH}_{\text{pzc}}$. This is probably due to the lowest adsorption of the polymer under these conditions and expanded conformation of macromolecules at the solid–solution interface. Mutual electrostatic repulsion of positively charged fragments of the polymer chains in the adsorption layer and their repulsion from the positively charged surface of chromium(III) oxide enable binding only a few PAM segments to the adsorbent surface. This results in barely noticeable changes in the σ_0 value of the polymer presence.

In turn, in the range of $\text{pH} > \text{pH}_{\text{pzc}}$, PAM adsorption causes marked reduction in the Cr_2O_3 surface charge density in relation to the polymer absence system. This is due to the interactions of the polycation macromolecules with the surface active sites, whose presence in the surface layer imposes formation of the additional negatively charged groups of the adsorbent. As a result, the total value of σ_0 is reduced. This effect is particularly pronounced in the case of higher polyacrylamide concentrations. In this case, the higher is the observed reduction in the surface charge density of metal oxide, the larger is the content of cationic groups in the polymer chain. Thus, a larger number of positive charges located along the adsorbing macromolecules induce an increasing number of negative surface groups.

The presence of PAM adsorption layers around chromium(III) oxide particles results in significant changes in the value of the diffusion layer potential, particularly evident in a large increase in the zeta potential (Fig. 5). In addition, the more significant the shift of pH_{iep} to higher pH values caused by the polymer presence is, the higher the percentage of cationic functional groups in the polymer chain is (Table 3).



The observed increase in the electrokinetic potential of the solid in the cationic polymer presence is due to the placement of positive charges originating from the functional groups of adsorbed PAM macromolecules in the slipping plane. These groups are present in the loop and tail structures of polyacrylamide chains bounded with the surface. Therefore, it is obvious that the higher the content of these groups in the adsorbed macromolecules is, their greater number is located in the electrical double layer (edl) formed around the particles of chromium(III) oxide. Another effect which influences the value of the zeta potential in the polymer presence is the slipping plane shift from the surface of the colloidal particle. This phenomenon causes the decrease in the electrokinetic potential. However, the experimentally observed value of zeta potential is dependent on the contribution of the effects: the presence of polymer cationic groups in the diffusion part of edl and the slipping plane shift.

Stability of chromium(III) oxide suspension in the cationic polyacrylamide presence

The selected results of turbidimetry measurements obtained for the suspension in the absence of the polymer at pH 9 and in the presence of PAM 7.0_80 % at pH 3 are presented in Figs. 6 and 7, respectively. The first one is an example of highly unstable system, whereas the latter one is characterized by higher stability. Changes in the stability

of Cr_2O_3 suspension without and with polyacrylamide can be examined based on the transmission and backscattering curves course.

The levels of the transmission and backscattering (expressed in %) are indicated on the ordinate axis, whereas the height (expressed in mm) corresponding to different levels of the test suspension in the measurement vial is marked on the abscissa axis. The length of this vial is 70 mm, but the suspensions were poured into the level of approximately 45 mm. Thus, the value of 0 mm means the bottom of the vial, whereas 45 mm is the upper level of the suspension. The total measurement time for the single system was 15 h, during which every 15 min the individual curves (i.e. scans) were recorded. Different colours of transmission and backscattering curves correspond to these intervals of time, e.g. $t = 0$ h (pink), $t = 7$ h (green), $t = 15$ h (red).

The analysis of these curves indicates that the NaCl– Cr_2O_3 system at pH 9 (Fig. 6) is much less stable than the NaCl– Cr_2O_3 –PAM 7.0_80 % suspension at pH 3 (Fig. 7). In the case of the former unstable system, the transmission level reaches 60–75 % practically at the entire length of the measurement vial, with the exception for the range 0–11 mm, when the transmission falls to zero. In the same range (0–11 mm), the backscattering light reaches its maximum level of 50–55 % as a result of an appearing peak. Its width determines thickness of the formed sediment, which in this case is large being about 11 mm. The

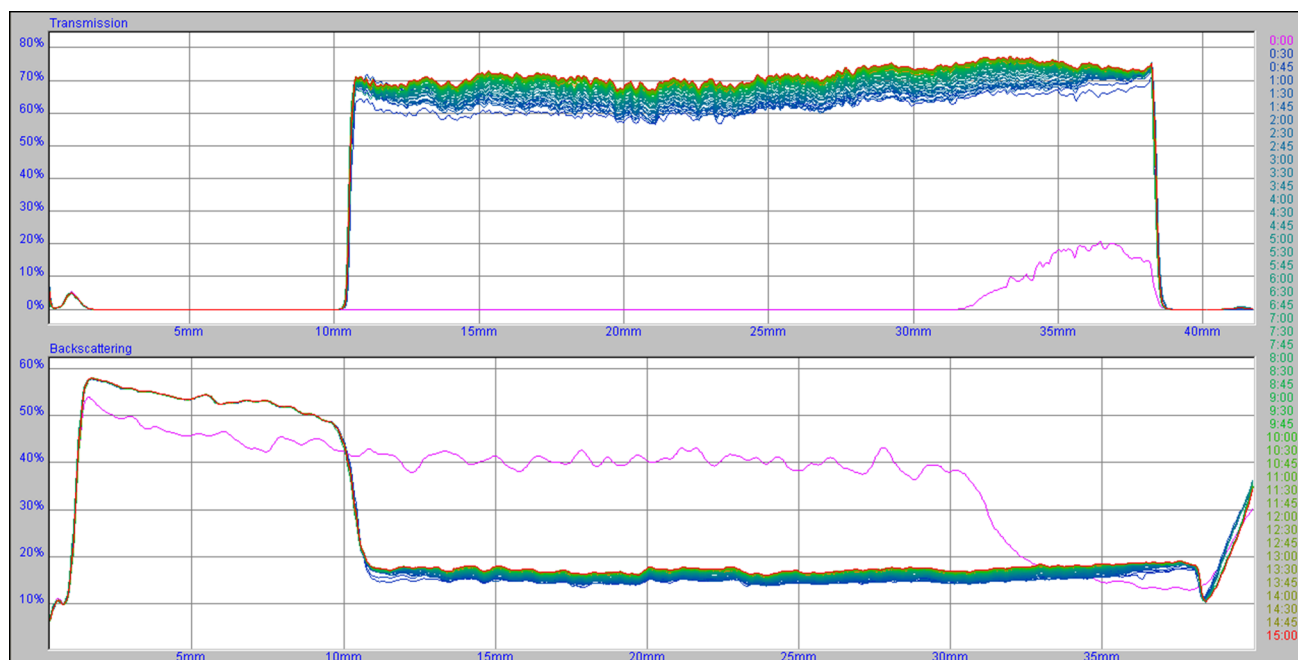


Fig. 6 Transmission and backscattering for Cr_2O_3 –NaCl at pH 9

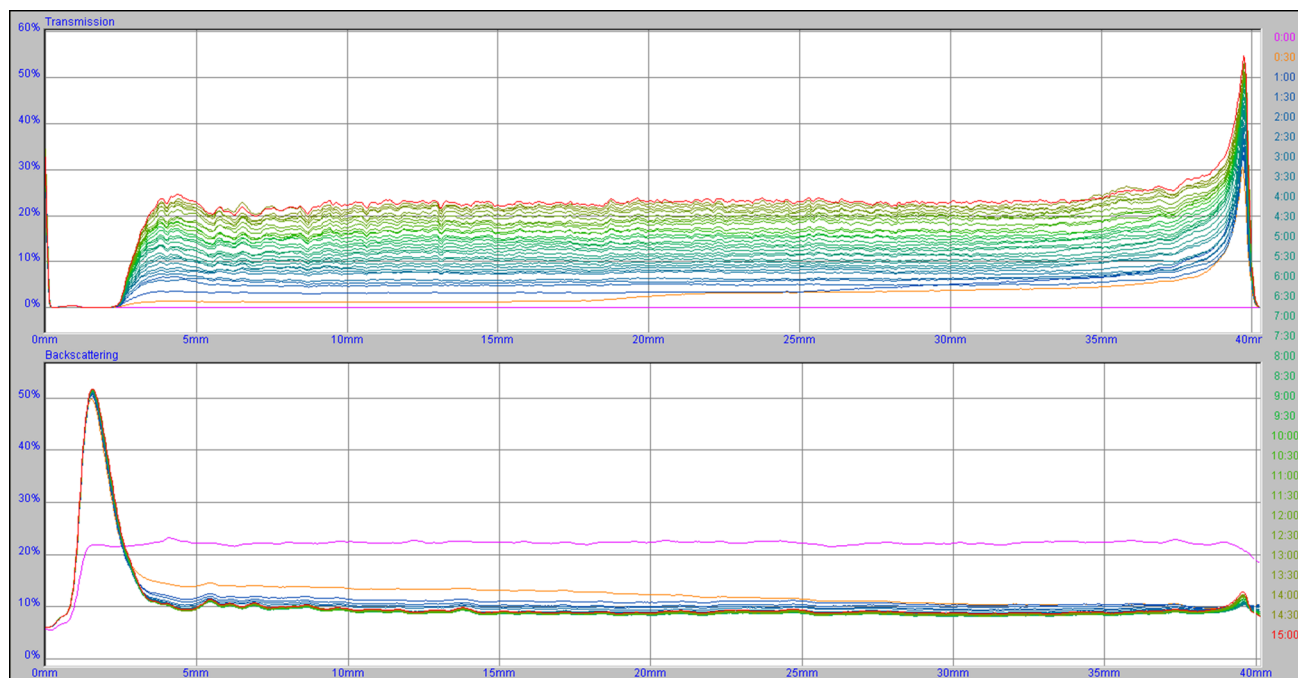


Fig. 7 Transmission and backscattering for NaCl-Cr₂O₃-PAM 7.0_80 % at pH 3

individual curves in Fig. 6 are located very close to each other or even overlap (with the exception for the first scan corresponding to $t = 0$). This means that in the initial stage of the measurement, the suspension quickly reached a state of near the end, i.e. high instability.

For a more stable system (Fig. 7), the sediment thickness is about 2.5 mm. In addition, the transmission is maintained at a much lower level about 20–25 %. The clarification process occurs only in a thin surface layer of the sample—the curves show a transmission peak of about 1 mm thickness. Moreover, migration of aggregates in the sample is more gradual (individual transmission curves do not overlap, but are clearly far apart).

A convenient parameter that allows estimation of the suspension stability is the stability coefficient TSI (TSI—Turbiscan Stability Index). Possible values of TSI are in the range 0–100. For highly stable systems, TSI assumes a value close to zero, whereas increase in this parameter indicates decrease in the system stability. Moreover, for all examined systems, the following parameters characterizing their stability were determined: thickness of sediment layer, size of aggregates and velocity of their migration in the suspension. Their values are given in Tables 4 and 5.

The chromium(III) oxide suspension without the polymer is relatively stable at pH 3 (TSI = 12.8). On the other

Table 4 TSI stability coefficients and sediment thicknesses for Cr₂O₃ suspension in the absence and presence of PAM, C_{PAM} = 100 ppm

System	TSI			Sediment thickness (mm)		
	pH 3	pH 6	pH 9	pH 3	pH 6	pH 9
Cr ₂ O ₃	12.8	61.0	29.3	9.5	15.8	11.0
PAM 8.5_20 %	31.8	27.0	34.1	2.5	2.1	2.8
PAM 7.0_50 %	28.1	21.2	33.9	2.3	2.0	2.6
PAM 7.0_80 %	34.5	38.1	44.4	2.5	2.4	3.1

hand, at pH 6 it undergoes considerable destabilization (TSI = 61), and at pH 9 it reaches an intermediate state (TSI = 29.3). These data are in accordance with other parameters characterizing the system stability, namely at pH 6 the greatest thickness of sediment and the fastest aggregates migration are observed.

The addition of polyacrylamide causes noticeable deterioration of Cr₂O₃ suspension stability at the pH values 3 and 9. This effect is the greatest for the polymer samples characterized by the largest content of cationic groups. This is manifested in the increase in aggregates size formed with solid particles and polymer chains (i.e. flocks). However, at pH 6 improvement of examined suspensions

stability in the polymer presence is observed. Under these conditions, the polymer containing the smallest number of cationic groups improves Cr_2O_3 suspension stability most effectively. This is demonstrated in decrease in aggregate sizes, their slower migration and smaller thickness of formed sediment.

Impact of cationic polyacrylamide on the mechanism of chromium(III) oxide suspension stability

Cr_2O_3 suspensions not containing the polymer are characterized by the highest stability at pH 3. This is a result of electrostatic stabilization mechanism. The zeta potential of solid particles achieved a high value of about +40 mV (Fig. 4). It turns out that it is sufficient to obtain an effective repulsion between particles surrounded by electrical double layers (composed of supporting electrolyte ions). Thus, the process of solid particle aggregation in the system is significantly inhibited.

The main reason for the drastic destabilization of the suspension at pH 6 is the fact that at this pH value is the pH_{iep} point of Cr_2O_3 (zeta potential is equal to zero). Zero charge of diffusion layer means that there are no electrostatic repulsion forces between particles. This greatly facilitates their mutual collisions leading to system coagulation.

The system without polyacrylamide at pH 9 is characterized by the intermediate stability obtained at the pH values 3 and 6. Under these conditions, the absolute value of the ζ potential of chromium(III) oxide particles is about 25 mV (Fig. 4), which is not sufficient to ensure such effective stabilization of the suspension as it is at pH 3.

Reduction in the Cr_2O_3 suspension stability due to the polymer addition at pH 3 is caused by bridging interactions appearance. This is facilitated by the lowest adsorption of cationic PAM and the most extended conformation of its macromolecules on the solid surface. The polymer chain stretched in the direction of bulk solution can be adsorbed on the surface of at least two colloidal particles, linking

them together and forming flocks. Lower degree of polymer packing in the adsorption layer at pH 3 makes that there are free places on the solid surface, which could adsorb a fragment of the macromolecule already connected with another solid particle. This results in the formation of single polymer bridges and the appearance of bridging flocculation.

At the highest percentage of cationic groups in the PAM macromolecules, the greatest effect of stability deterioration is achieved. Development of the polymer chain on the surface in this case is significant, leading to a more efficient process of bridging.

Significant improvement of the Cr_2O_3 suspension stability in the PAM presence at pH 6 is due to higher adsorption of the polymer and creation of more hermetic adsorption layers on the metal oxide surface. The mechanism of this process is electrosteric. In addition to the steric interactions resulting in increase in the effectiveness of repulsion between the colloidal particles coated with a polymer, electrostatic repulsion between the polymer cationic groups located in the adsorption layers is also of significant importance. The least extended conformation of PAM (with the lowest content of carboxyl groups) makes that the adsorption layer is the most packed (as compared to the others formed by the polymers containing an increasing number of cationic groups). In this case, the steric effects are the most effective, providing the greatest stability of Cr_2O_3 -PAM 7.0_20 % at pH 6.

In turn, at pH 9, the presence of polyacrylamide results in slight deterioration of the solid suspension stability. The main reason for the observed destabilization may be neutralization of the negative charge of the metal oxide particles by adsorbed cationic polymer chains. They adopt less extended conformation on the solid surface because the degree of functional groups ionization decreases. Solid particles covered with more coiled macromolecules do not repel efficiently enough to prevent them from joining in larger units and flocks formation. PAM 7.0_80 % at pH 9 shows the greatest destabilization properties for the chromium(III) oxide water suspension.

Table 5 Aggregate sizes and its migration velocity for Cr_2O_3 suspension in the absence and presence of PAM, $C_{\text{PAM}} = 100$ ppm

System	Aggregate size (μm)			Aggregate sedimentation velocity ($\mu\text{m}/\text{min}$)		
	pH 3	pH 6	pH 9	pH 3	pH 6	pH 9
Cr_2O_3	0.08	0.54	0.13	0.83	4.1	2.23
PAM 8.5_20 %	0.04	0.095	0.1	0.19	1.14	1.15
PAM 7.0_50 %	0.12	0.06	0.14	0.16	0.25	1.24
PAM 7.0_80 %	0.16	0.074	0.34	0.34	0.28	1.26

Our previous studies indicated that cationic polyacrylamide causes the most effective destabilization of chromium(III) oxide suspension at pH 9. Other examined polymers—both synthetic [poly(acrylic acid) PAA, anionic polyacrylamide PAM, poly(aspartic acid) ASP, block copolymer of poly(aspartic acid) with poly(ethylene glycol) ASP-b-PEG] and natural (bovine serum albumin BSA, ovalbumin OVA, human serum albumin HSA, bacterial polysaccharide EPS)—are not as effective destabilizers under this pH condition (Wiśniewska and Szewczuk-Karpisz 2013; Ostolska and Wiśniewska 2014a, b, 2015; Szewczuk-Karpisz and Wiśniewska 2014; Szewczuk-Karpisz et al. 2014).

Conclusion

The stability mechanism of the chromium(III) oxide suspension containing cationic polyacrylamide (PAM) was determined. The influence of the content of polymer functional groups (positively charged) was examined.

At pH 3, the reduction in the Cr_2O_3 suspension stability in the PAM presence was obtained. It is caused by polymer bridges formation between the solid particles and adsorbed macromolecules assuming extended conformation. The lowest adsorption of cationic PAM facilitates bridging flocculation occurrence due to incomplete coverage of the solid surface by the adsorbate.

Higher adsorption of the polymer and the creation of more packed adsorption layers on the solid surface at pH 6 are the main reason for significant improvement of the Cr_2O_3 suspension stability. The mechanism of this process is electrosteric—repulsion of solid particles was provided by the presence of both polymeric layer (steric forces) and charges of PAM chains (electrostatic forces).

Slight deterioration of the solid suspension stability at pH 9 due to polyacrylamide addition is observed. This destabilization is a result of neutralization of the negative charge of the metal oxide particles by positively charged polymer chains (more coiled conformation).

The greater the content of cationic groups in the polymeric chains is, the greater the deterioration of suspension stability occurs (pH values 3 and 9). Development of the polymer chain containing more numerous cationic groups is greater, leading to more efficient destabilization processes in the suspension.

The greatest destabilization properties in relation to chromium(III) oxide particles in the aqueous suspension

show PAM 7.0_80 % at pH 9. The mechanism of this process is solid surface charge neutralization by the adsorbed macromolecules.

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