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Polymeric systems based on poly(acrylic acid) and trivalent metal cations

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SUMMARY: Hydrodynamic properties of the system: poly(acrylic acid) (M_w=18 250)/ iron (III) or aluminum sulfates/ water were investigated via capillary viscometry and size exclusion chromatography. Rheological characteristics of poly(acrylic acid)/ Fe^{3+}or Al^{3+} sulfate systems prepared of more concentrated polymer solutions with M_w =18 250 and 450 000 were measured by rotational Brookfield viscometry. Distinct differences of behaviour of diluted as well as concentrated solutions, hydrogels or heterogeneous compositions were found for both applied metal cations. Fe^{3+} thicken aqueous solutions of poly(acrylic acid) (PAA) to high extent bulk viscosities (up to 70 000 mPa·s) at room temperatures. Mechanism of the thickening effect in the case of PAA/Fe^{3+}/water system has been discussed. Macromolecular systems of PAA/Fe^{3+} and PAA/Al^{3+} (PAA with M_w=18 250, 450 000 and 1 250 000) were tested as hybrid inorganic/organic agents for waste water treatment.

Introduction

Poly(acrylic acid) (PAA) is a water soluble polymer capable of thickening aqueous solutions and forming hydrogels in the presence of polyvalent metal cations. More or less viscous solutions and/or hydrogels differing in their compactness are formed as a result of PAA carboxylic groups interaction with such metal cations like: Mg^{2+}, Zn^{+2}, Fe^{3+} , Al^{3+}, Zr^{4+}, Ti^{4+} and Hf^{4+}. The form of the products depends on the characteristics of the components i.e. PAA and the metal cation compound such as: the molecular weight and concentration of the former one, the nature of the cation (determining ionic/coordinated interactions with COOH groups), the type of the compound and its concentration, as well as a molar ratio of both. Useful materials are based on poly(acrylic acid) and polyvalent metal compounds. The most important are dental hydrogels (cements) based on Zn^{2+} or on special inorganic glasses containing of Al^{3+} 1), or compounds: Fe^{3+}, Zr^{4+}, Ti^{4+} and Hf^{4+} 2,3). The

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similar type materials based on Al^{3+} and Zr^{4+} have found an application as composite membranes in the separation processes such as dialysis and reverse osmosis[4)]. Other Mg^{2+} and Zn^{2+} based materials are used as bound coatings [5,6)].

Polymeric hydrogels based on PAA and trivalent cations of iron and aluminum have an important advantage in comparison with other PAA/Me^{n+} systems - they are nontoxic and biocompatible [2,7)]. These features of the materials decide about specific areas of application like hemostatic pharmaceuticals, microbial agents (PAA/Fe^{3+})[2)] or bone implants (PAA/Al^{3+})[7)]. Although there are literature data about some physicochemical properties of the systems PAA/Fe^{3+} [2,3,8,9)] and PAA/Al^{3+} [10-12)], their viscous flow characteristics for diluted or concentrated aqueous solutions or hydrogels have not been described. In this work hydrodynamic properties of diluted aqueous solutions of PAA and Fe^{3+} or Al^{3+} sulfates were investigated as well as rheological characteristics of more concentrated systems of PAA and the mentioned salts. Interactions between Fe^{3+} and COOH groups of PAA in aqueous solutions responsible for the observed pronounced thickening effect are discussed. Some tests of coagulation (flocculation) efficiency for aqueous PAA/Me^{3+} systems applied for waste water treatment were performed.

Experimental

Materials

Poly(acrylic acid) with three average molecular weights was used: M_w = 1 250 000 - PAA (HM), M_w = 450 000 - PAA (MM) both from Aldrich Chem. Co, and 40 wt % aqueous solution M_w = 18 250, M_n = 2160 - PAA (LM) synthesized at Institute of Heavy Organic Synthesis, Kêdzierzyn-Kozle, Poland.

Hydrous sulfates of iron (III): $Fe_2(SO_4)_3\cdot 9H_2O$ and aluminum: $Al_2(SO_4)_3\cdot 18H_2O$ were purchased from Fluka Chemie AG.

Industrial waste waters from Sugar Rafinery and Dairy Plant from Szczecin, Poland, were used for coagulation/ flocculation tests.

Preparation of PAA/Me^{3+} solutions and gels

The PAA/Me^{3+} compositions were prepared as follows: aqueous iron (III) sulfate or aluminum sulfate solutions were added dropwise to aqueous solution of the respective PAA sample at room temperature (22±1°C) while the mixture was stirred vigorously.

Different concentrations of the component solutions and their molar ratios (expressed in terms of wt % or the ratio R = [Me^{3+}]/[COOH group of PAA recurrent unit] were applied for particular investigations i.e. capillary viscometry, size exclusion chromatography, rheoviscometry and coagulation/ flocculation tests.Table 1 presents data on concentrations of the PAA solutions and both applied salts.

Tab. 1. Description of poly(acrylic acid) and Me^{3+} salts solutions applied for PAA/Me^{3+} compositions

Component	Capillary viscometry*	Size exclusion chromatography	Rheoviscometry** (Brookfield plate/cone)	Coagulation/ flocculation tests
	concentration of the components (PAA or salt)			
Poly(acrylic acid)				
PAA (LM)	1 and 5 wt %	2 wt %	10 ÷40 wt %	40 wt %
PAA (MM)		–	3 and 5 wt %	8 wt %
PAA (HM)	–	–	–	1 wt %
sulfates				
$Fe_2(SO_4)_3{\cdot}9H_2O$	5 wt %	5 wt %	0.15÷0.4 M	0.4 M
$Al_2(SO_4)_3{\cdot}18H_2O$	10 wt %	–	0.15÷0.4 M and the solid salt	0.4 M and the solid salt

*20±0.2°C **20±0.1°C

Capillary viscometry

Viscometric measurements of 1 and 5 wt % aqueous solutions of PAA (LM) as well as solutions prepared by mixing these with 10 wt % $Al_2(SO_4)_3{\cdot}18H_2O$ or 5 wt % $Fe_2(SO_4)_3{\cdot}9H_2O$ were performed using Ubbelohde glass viscometer.

Size exclusion chromatography

SEC analysis of PAA (LM) and the solutions prepared by mixing 2 wt % aqueous polymer solution with 5 wt % $Fe_2(SO_4)_3{\cdot}9H_2O$, at various R ratios was performed on Separon HEMA 40+100+300+1000 (Tessek, Czechoslovakia) columns. Acetate buffer: water/

CH_3COOH)/ sodium acetate (pH = 5.3) was used as SEC eluent; flow rate 0.5 cm^3/min., sample volume 100 µl Knauer HPLC instrument was equipped with a differential refractometer detector. Seven poly(sodium acrylate) standards (M_w = 2100 -165 300 and $M_w/M_n < 2.0$) obtained from Modchrom, Akron, USA, were used for calibration of SEC column set.

Rheoviscometry

Aqueous PAA (LM)/ Me^{3+} systems prepared using higher concentrated polymer solutions (12 - 40 wt %) and Fe^{3+} or Al^{3+} sulfate solutions (0.15-0.4 M) were investigated with the help of Brookfield rheoviscometer type D-III (plate/ cone). Similar measurements were done for PAA (MM)/Fe^{3+} sulfate using 3 and 5 wt % polymer solutions and 0.25 M solution Fe^{3+} sulfate. The measurements were performed with two rotational speeds: 10 and 50 rpm.

Coagulation/ flocculation tests

Two series of tests were performed: (i) using solutions of PAA (LM) and iron (III) sulfate solutions separately, or as PAA/$Fe_2(SO_4)_3 \cdot 9H_2O$ compositions, and (ii) using solutions of PAA with three M_w values: PAA (LM), PAA (MM) and PAA (HM), aluminum sulfate itself or compositions PAA/$Al_2(SO_4)_3 \cdot 18H_2O$. Industrial waste waters (two batches) were used for testing. The evaluation of the coagulant/ flocculant effectiveness was done by the measurement waste water extinction coefficient before and after the treatment, using Spekol 11 spectrophotometer, Carl Zeiss, Jena.

Results and discussion

Hydrodynamic properties of diluted solutions

Measurements performed by capillary viscometry showed that PAA/Al^{3+} solutions manifest lower specific viscosity η_{sp} than those of PAA/Fe^{3+} (Fig. 1 and Fig. 2). Specific viscosity of PAA/Al^{3+} solutions prepared of 1 wt % PAA (LM) and 10 wt % $Al_2(SO_4)_3 \cdot 18H_2O$ slightly grows with R increase and reaches the value η_{sp}= 0.14 for R=1 (Fig.1). Solutions of the aluminum salt (10 wt %) and higher concentrated PAA (5 wt %) gave more viscous systems. Their η_{sp} values lie in a range of 1.04 - 1.50 for the whole investigated molar ratios of Al^{3+}/ COOH (Fig.1).

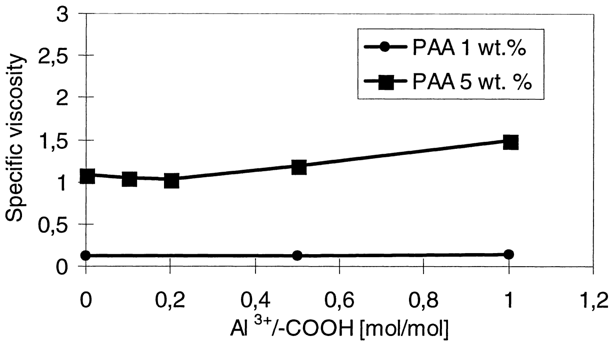


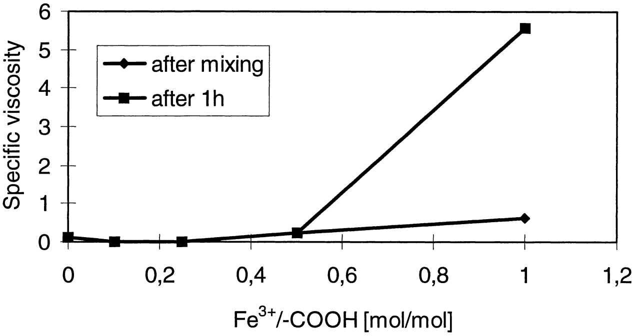
Fig.1: Dependence of the specific viscosity on Al^{3+} /COOH molar ratio for solutions prepared of 1 and 5 wt % PAA (LM) and 10 wt % $Al_2(SO_4)_3 \cdot 18H_2O$

It is evident that specific viscosities of PAA/Fe^{3+} systems prepared with the same PAA solutions and less concentrated $Fe_2(SO_4)_3 \cdot 9H_2O$ (5 wt %) are higher than those of PAA/Al^{3+} (Fig.2).

In addition it was found that η_{sp} values of the solutions measured after 1 hour of their preparation are remarkably higher than those examined directly after mixing. For example specific viscosity of PAA/Fe^{3+} solution obtained of 1 wt % PAA is $\eta_{sp} = 0.64$ for R = 1 and reaches as high value as 5.60 when measured 1 hour later (Fig.2a). For solutions made of 5 wt % PAA and iron (III) sulfate, very high η_{sp} values were measured for low ratio of R = 0.25 (respectively $\eta_{sp} = 4.08$ and $\eta_{sp1h} = 6.42$). Viscometric data show that there is a great increase of PAA/Fe^{3+} polymer chain sizes as compared with those of PAA (LM) itself. It is a result of ionic/complex binding of PAA chains via iron (III) cations [2, 3, 8, 9, 13)].

It was interesting to evaluate differences in polymer chain sizes before and after Fe^{3+}/COOH ionization/complexation. Size exclusion chromatography allows to compare hydrodynamic volumes of polymer molecules in solution. Separon HEMA columns filled with crosslinked hydroxyethyl methacrylate gels were selected for analysis. The SEC system was calibrated with polyanionic polymer standard – poly(sodium acrylate). This polymer is to some extent similar to PAA/Fe^{3+} ionic/complex macromolecules to be analyzed.

a)



b)

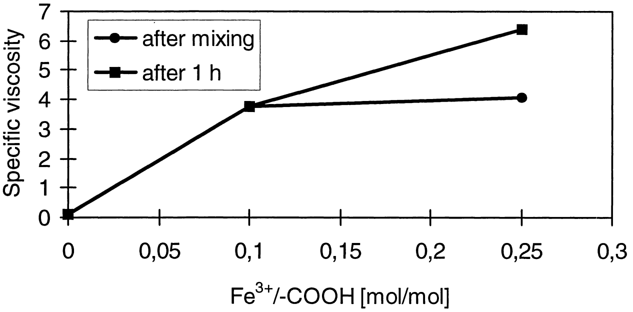


Fig.2: Dependence of the specific viscosity on Fe^{3+} /COOH molar ratio for solutions prepared of 1 wt.% (a) and 5 wt.% (b) PAA (LM) and 5 wt % $Fe_2(SO_4)_3{\cdot}9H_2O$

The results of SEC measurements are collected in Table 2. A certain shift of the polymer peaks in the direction of higher molecular weights in comparison with PAA was found on the PAA/Fe^{3+} chromatograms13). Distinctly outlined peaks of macromolecules excluded from gel pores were observed on the chromatograms. Average molecular weights of PAA/Fe^{3+} ionic/complex macromolecules based on poly(sodium acrylate) calibration should be considered with care because of: (i) possible differences in polymer chain sizes of the respective molecular weights of the anionic polymer standard and anionic/complex polymer PAA/$Fe^{3+}$and (ii) partial exclusion of the highest fractions of PAA/Fe^{3+}

Tab. 2. Average molecular weights of PAA /Fe^{3+} complexes determined by SEC*

Type of average molecular weight	Average molecular weight										
		R= Fe^{3+}/COOH molar ratio									
	PAA	0.1:1		0.125:1		0.25:1		0. 35:1		0.5:1	
		direct	after 24 h	direct	after 24 h	direct	after 24 h	direct	after 24 h	direct	after 24 h
M_n	2200	9300	8100	8400	7300	10 600	9300	9800	7900	8300	–
M_w	18 300	32 700	36 200	45 700	43 600	73 600	75 400	78 000	77 900	68 000	–
M_z	–	110 500	130 200	185 500	208 600	145 000	189 300	205 000	284 500	207 000	–
M_w/M_n	–	3.5	4.49	5.43	4.78	6.93	8.11	7.96	9.86	8.12	–

* solutions prepared of 2 wt % PAA (LM) and 5 wt % $Fe_2(SO_4)_3 \cdot 9H_2O$; poly(sodium acrylate) calibration

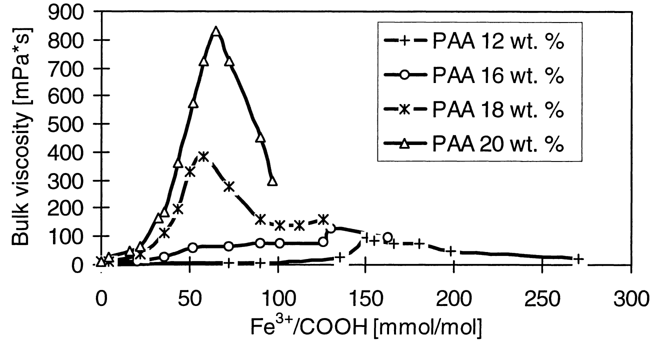
macromolecules from gel pores. Taking above into account we consider SEC results as a semiquantitative measure of molecular weight averages. It was found that for rather short chains of PAA (LM) M_w of the PAA/Fe^{3+} (LM) interaction products increased up to four times (Table 2). Stabilization of M_w on the highest level of value ($M_w > 70\ 000$) is observed for PAA/Fe^{3+} solutions with $R \geq 0.25$. Similarly polydispersity indices (M_w/M_n and M_z/M_w) of PAA and iron (III) sulfate ionic/complexes increase with time and Fe^{3+}/COOH molar ratio.

Rheoviscometry of the concentrated systems

Rheoviscometry was used to characterize rheological properties of PAA/Me^{3+} aqueous systems prepared with more concentrated polymer solutions. Fig. 3, 4 and 5 present the dependence between bulk viscosities η_b and R ratios for PAA/Fe^{3+} compositions measured at 10 rpm. It may be seen from these figures that iron (III) cation causes substantial thickening effect of aqueous PAA solutions. The effect is dependent on the polymer molecular weight and concentration as well as on iron (III) salt concentration. For instance in the case of PAA (LM) the viscosity of PAA/Fe^{3+} compositions exceeds the value of 18 000 mPa·s if the polymer concentration is at least 20 wt % and Fe^{3+} salt concentration 0.25 M (Fig. 3 and 4 or Table 3). On the other hand rather low PAA (MM) concentration (5 wt %) is enough to thicken the system with 0.25 M solution Fe^{3+} salt to $\eta_b > 20\ 000$ mPa·s (Fig.5). Moreover, it can also be found in Fig. 3 and 4 that the maximum values of bulk viscosities for the investigated PAA/ Fe^{3+} system lie in a range of Fe^{3+}/ COOH ratios R = 25 - 70 mmol/mol. Comparison of the maximum values of the respective bulk viscosities of the PAA/iron (III) system measured at 10 and 50 rpm shows that the compositions behave like pseudoplastic fluids (Table 3).

The influence of aluminum sulfate on viscosity of PAA/Al^{3+} system is rather minor (Fig.6). A maximum value of $\eta_b = 4050$ mPa·s was measured for the composition prepared using 0.15 M Al^{3+} salt solution and 40 wt % PAA (LM) (Fig. 6 and Table 3). The highest η_b value (26 000 mPa·s) was observed for heterogeneous composition made by mixing solid $Al_2(SO_4)_3 \cdot 18H_2O$ and 40 wt % PAA (LM) (Table 3).

a)



b)

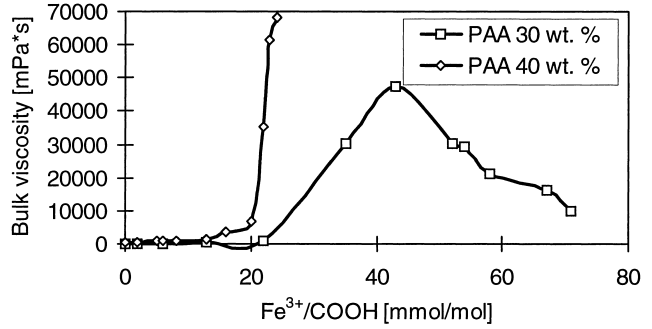


Fig. 3: Dependence of the bulk viscosity on Fe^{3+}/COOH molar ratio for the system PAA/ $Fe_2(SO_4)_3 \cdot 9H_2O$ prepared of 0.15 M $Fe_2(SO_4)_3 \cdot 9H_2O$ solution and various concentration of PAA (LM) solutions measured at 10 rpm:12-20 wt % (a) or 30 and 40 wt % (b)

From data in Table 3 it may be concluded that aqueous solutions of aluminum sulfate and PAA show rather Newtonian flow characteristics. However, the heterogenic composition of solid aluminum sulfate and 40 wt % PAA behaves like a pseudoplastic fluid (Table 3). These observations on distinct differences of viscosities for both investigated systems PAA/Fe^{3+} and PAA/Al^{3+} demonstrate the various nature of these metal cations interactions with carboxylic groups of the polymer.

Table 3. Maximum bulk viscosities of the aqueous systems PAA(LM)/Me^{3+} sulfate

Metal cation sulfate	Concentration of the component solutions		Maximum values of viscosity, mPa·s	
	sulfate, mol·dm^{-3}	PAA(LM), wt %	10 rpm	50 rpm
Fe^{3+}	0.15	20	830	300
		30	47 200	15 500
		40	>65 000	>60 000
	0.25	20	18 000	4400
		30	72 400	5800
		40	78 200	4700
	0.40	20	27 200	4850
		30	58 600	5500
		40	68 500	2500
Al^{3+}	0.15	20	20	20
		30	200	110
		40	4050	5980
	0.25	20	80	80
		30	–	–
		40	510	510
	0.40	20	20	20
		30	120	120
		40	2280	2370
	solid $Al_2(SO_4)_3 \cdot 18H_2O$	40	26 000	5500

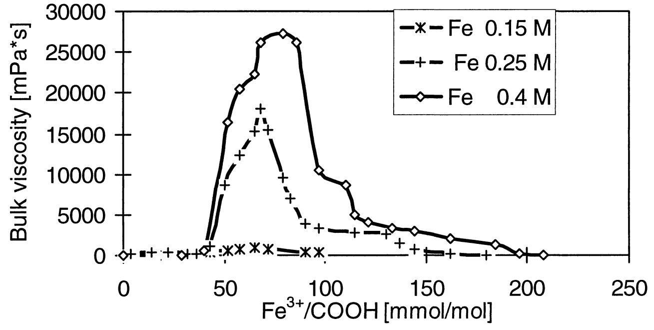


Fig. 4: Dependence of the bulk viscosity on Fe^{3+}/COOH molar ratio for the system PAA(LM)/ $Fe_2(SO_4)_3 \cdot 9H_2O$ prepared of 20 wt% PAA and various concentrations of Fe^{3+} sulfate solution (10 rpm)

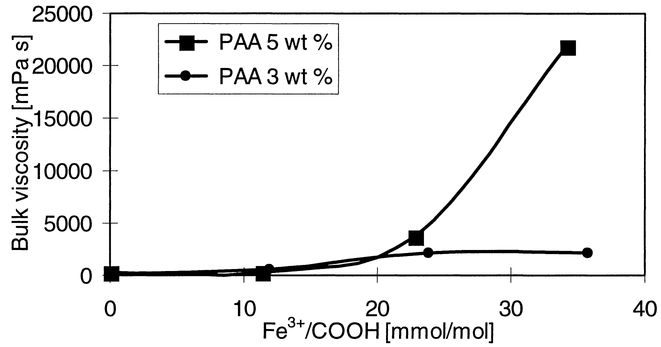


Fig. 5: Dependence of the bulk viscosity on Fe^{3+}/COOH molar ratio for the system PAA (MM)/ $Fe_2(SO_4)_3 \cdot 9H_2O$ prepared of 3 and 5 wt % PAA and 0.25 M Fe^{3+} sulfate solution (10 rpm)

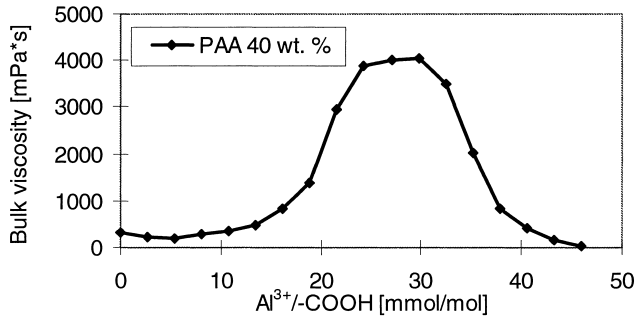


Fig. 6: Dependence of the bulk viscosity on Al^{3+}/COOH molar ratio for the system PAA/ $Al_2(SO_4)_3 \cdot 18H_2O$ prepared of 0.15 M Al^{3+} sulfate solution and PAA (LM) solution 40 wt % (10 rpm)

Interactions between Fe^{3+} and COOH groups of PAA

Hydrodynamic and rheological properties of PAA/Fe^{3+} solutions and hydrogels can be caused by: ion/complex formation between COOH groups and Fe^{3+} cations[3,9] or Fe^{3+} cations behaviour at slightly acidic (pH ≥ 2) aqueous solutions[14]. On basis of IR and UV measurements for PAA/$FeCl_3$ solutions Rabek and Linden[3] concluded that two carboxylic groups of PAA form ionic complex with $FeCl^{2+}$ cations. Yokoi et al.[9] found by EPR that carboxylic groups of one or two PAA chains are bound by Fe^{3+} cations and form some clusters and these function as points of linking COOH groups. Fe^{3+} hydroxocomplexes of the type:

$[Fe(H_2O)_5OH]^{2+}$, $[Fe(H_2O)_4(OH)_2Fe(H_2O)_4]^{4+}$ and $[Fe(H_2O)_4(OH)_2Fe(H_2O)_2(OH)_2Fe(H_2O)_4]^{5+}$ are created at pH ca. 2 or higher14). Equilibrium of the bidentate or polydentate complex formation is slowly established and colloidal gels are formed14). Independent EPR measurements for PAA/Fe^{3+} complexes at low pH values (pH=1.4-2.0) show that polydentate PAA/Fe^{3+} of the type $[Fe_3O(COO^-)_6]^+$ are rather bridged by oxygen atom[15] than by OH groups14). However, complexes with OH bridges between Fe^{3+} cations may be created at pH values above 2.

Poly(acrylic acid)/water/trivalent metal cation sulfate compositions as coagulation - aided agents

Coagulation is a physicochemical process used for waste water treatment in order to remove dispersed matter. Typical inorganic coagulants able to hydrolyze in aqueous environment are sulfate salts of iron and aluminum: $Fe_2(SO_4)_3 \cdot 9H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$. Products of the salt hydrolysis: $Fe(OH)_3$ and $AL(OH)_3$ act as effective coagulants.

Flocculants are applied mainly as coagulation - aided substances. Hydrophilic (co)polymers most often play the role of flocculants (e.g. polyacrylamide and products its hydrolysis) [16]. The flocculant action is based on adsorption binding of particles dispersed in water system trough a long polymeric chain. Bridging of these particles and the formation of floccules which can next bind each other forming agglomerates, increases the sedimentation process. It is generally known that application of polymeric flocculants allows[17]: (i) the increase floccule formation rate and sedimentation, (ii) the increase of floccule surface area and its sorption capacity, (iii) the decrease of negative influence of lower water temperatures, (iv), the broadening of optimum pH range for coagulation and (v) the decrease of inorganic coagulant dose. Polymeric flocculants are usually applied after inorganic coagulants and their concentrations in aqueous solutions are ca. 0.1 wt % and $M \cong 10^6$ 16).

For coagulation tests some PAA/Fe^{3+} and PAA/Al^{3+} compositions were selected; the inorganic sulfates and poly(acrylic acid) with different M_w values were separately used. The waste waters of sugar and dairy industries were subjected to investigation. The most important controlled parameter was relative extinction coefficient measured before and after waste water treatment.

The first series of tests was performed using PAA/Fe^{3+} composition based on 20 wt % PAA (LM) and 0.4 M $Fe_2(SO_4)3·9H_2O$ (composition 1, Table 4). Examined waste waters were treated as well with iron (III) sulfate and then with PAA (LM) or the inorganic coagulant solution with the following introduction of the PAA/Fe^{3+} composition 1 (Table 4). The best results as determined by the lower extinction coefficients were found for the experiments No. 4 when 0.4 M iron (III) sulfate solution and then PAA/Fe^{3+} composition 1 were used (Table 4, extinction 0.46 → 0.23 for sugar refinery waste water, and 0.17 → 0.11 for dairy waste water). Similar results were found for sugar refinery waste water treatment in experiment No. 5 (0.46 → 0.21) and dairy waste water in experiment No.2 (0.17 → 0.12). The last experiment was carried out using separately inorganic coagulant and PAA (LM) solution (Table 4). The results of the coagulation tests in Table 4 show that the effectiveness of waste water clarification determined by the ratio of their extinction coefficients after and before treatment is in most favourable cases within the range 46-50 % (sugar refinery waste water) and 65-71 % (dairy waste water). Total concentration of iron (III) sulfate used in particular tests described in Table 4 was 0.02-0.03 wt % and the polymer 0.01-0.02 wt %.

However, flocculant effectiveness is substantially influenced by molecular weight of the polymeric flocculant[13,16)].

Thus second series of coagulation/flocculation tests was performed using PAA samples with different M_w values (18 250 - 1 250 000), aluminum sulfate and their respective compositions. The results of treatment of the two other batches of waste waters of sugar refinery and dairy industries are presented in Table 5. The best results were obtained in experiments No. 6 with the composition of diluted 1 wt % solution of the highest molecular weight PAA (HM) and 0.4 M solution aluminum sulfate. The respective extinctions were changed from 0.42 → 0.13 for sugar refinery waste and from 0.79→ 0.30 for dairy waste water (Table 5). Extinction coefficients in these cases are reduced to 31 % and 38 %, respectively. A similar effectiveness of dairy waste water treatment was observed for aluminum sulfate solution alone (test No. 5). Total concentrations of aluminum sulfate and PAA (HM) for the most effective composition No. 6 are much lower than those for the system PAA/Fe^{3+} (LM): aluminum sulfate 2.7×10^{-4} wt % and PAA (HM) 0.2×10^{-4} wt %

Tab. 4. Results of waste water treatment using PAA and $Fe_2(SO_4)_3 \cdot 9H_2O$

	Coagulant/ flocculant description	Final concentration in waste water, wt %	Sugar refinery waste water			Dairy waste water		
			Deposit volume after 10 min, cm^3	pH	Extinction in relation to water	Deposit volume after 10 min, cm^3	pH	Extinction in relation to water
1	none	–	–	7.3	0. 46	–	7.7	0.17
2	$Fe_2(SO_4)_3 \cdot 9H_2O$ 0.4 M solution + PAA , 20 wt % solution *	0.022 0.020	14	5.8	0.34	25	5.4	0.12
3	composition 1*	0.027 0.029 (PAA)	7	5.3	0.49	1	6.5	0.26
4	$Fe_2(SO_4)_3 \cdot 9H_2O$ 0.4 M solution + composition 1*	Σ= 0.025 0.020 (PAA)	36	5.9	0.23	26	5.1	0.11
5	$Fe_2(SO_4)_3 \cdot 9H_2O$ 0.4 M solution + composition 1**	Σ=0.024 0.010 (PAA)	38	5.7	0.21	26	5.7	0.21

composition 1 = PAA (LM) 20 % wt solution + $Fe_2(SO_4)_3 \cdot 9H_2O$ 0.4 M solution
* (dose: 0.5 cm^3/500 cm^3)
** (dose: 0.25 cm^3/500 cm^3)

Tab. 5. Results of waste water treatment using PAA and $Al_2(SO_4)_3 \cdot 18\ H_2O$

	Coagulant/flocculant description	Final concentration in waste water, wt %	Sugar refinery waste water		Dairy waste water	
			Deposit volume after 10 min, cm^3	Extinction in relation to water	Deposit volume after 10 min, cm^3	Extinction in relation to water
1	none	–	0.8	0.42	0.8	0.79
2	PAA (MM), 1 wt % solution*	0.002	1.3	0.40	3.5	0.39
3	PAA (MM), 8 wt % solution*	0.016	1.2	0.38	12.3	0.36
4	PAA (LM), 40 wt % solution*	0.080	0.9	0.53	1.7	0.43
5	$Al_2(SO_4)_3 \cdot 18\ H_2O$ (solid)**	0.200	1.7	0.73	15.0	0.28
6	composition 2*	$2.7 \cdot 10^{-4}$ $0.2 \cdot 10^{-4}$ (PAA)	1.7	0.13	15.0	0.30
7	composition 3*	$2.1 \cdot 10^{-3}$ $1.3 \cdot 10^{-3}$ (PAA)	2.0	0.35	30.0	0.58
8	composition 4*	0.011 0.032 (PAA)	1.2	0.25	20.0	0.57

composition 2 = PAA (HM) 1 wt % solution + $Al_2(SO_4)_3 \cdot 18\ H_2O$ 0.4 M solution
composition 3 = PAA (MM) 8 wt % solution + $Al_2(SO_4)_3 \cdot 18\ H_2O$ 0.4 M solution
composition 4 = PAA (LM) 40 wt % solution + $Al_2(SO_4)_3 \cdot 18\ H_2O$ 0.4 M solution
* dose 1.0 cm^3/1000 cm^3
** dose 1 g/1000 cm^3

(Table 5). To get similar result of coagulation of dairy waste water it is necessary to apply 0.2 wt % of Al^{3+} salt (experiment No. 5, Table 5). In accordance with expectations the coagulation capacity for the highest molecular weight PAA/Al^{3+} composition No. 2 was the greatest one.

The results of coagulation tests made for the two industrial waste waters using both PAA/iron (III) sulfate and PAA/aluminum sulfate compositions show their high coagulation capacities, often higher than of those observed for cumulative action separately applied inorganic coagulant and polymeric flocculant.

Conclusions

The results of viscometric and size exclusion chromatography measurements revealed large differences in hydrodynamic properties of diluted aqueous solutions of PAA/Fe^{3+} and PAA/Al^{3+} systems. Time dependent and high specific viscosity values show PAA/Fe^{3+} solutions. Solutions PAA/Al^{3+} exhibit substantially lower viscosities in comparable conditions.

Iron (III) sulfate thicken concentrated aqueous poly(acrylic acid) solutions to high extent dependent on the polymer molecular weight and the polymer concentration as well as Fe^{3+} sulfate concentrations, as measured by rheoviscometric method. These compositions behave like pseudoplastic fluids. On the other hand aluminum sulfate increases bulk viscosities of aqueous PAA solutions in lower extent. Maximum bulk viscosity of PAA/Fe^{3+} sulfate compositions (hydrogels) were found for Fe^{3+}/COOH range R=25-70 mmol/mol. COOH groups of the PAA chain are linked by Fe^{3+} cations occurring as $[Fe_3O(COO^-)_6]^+$ clusters bridged by oxygen atom (at low pH values ≤ 2) or polydentate hydroxocomplexes bridged by OH groups (at pH > 2). It was found that aqueous aluminum and iron (III) sulfate/ PAA systems can act as efficient hybrid coagulation/ flocculation agents for waste water treatment.The lower doses of inorganic and organic components necessary for effective waste water clarification have positive environmental impact.

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References

(1) A. D. Wilson, J.W. Nicholson, *"Acid-based Cements"*, Ser. Chemistry of Solid State Materials, University Press, Cambridge 1993

(2) L. A. Linden, J.F. Rabek, *"Dental Polymers (Hydrogels)"* in *"Polymeric Materials Encycl"*. ed. J.C. Salamone, CRC, Boca Raton 1996, p. 1861

(3) L. A.Linden , J. Rabek, *J. Appl. Polym.Sci.* **50** , 1331 (1993)

(4) P. J. Brookman, J.W. Nicholson, in *"Developments in Ionic Polymers*" - 2, A.D Wilson, H. J. Prosser, eds., Elsevier Appl. Sci. Publ., London 1986, pp. 297 -302

(5) J. Beres, S. Kudla, *Chemik* (1), 3 (1994)

(6) T. Spychaj, *Progr. Org. Coat.* **17**, 71 (1989)

(7) L. M. Jonck, C. J. Grobbelaar, *Clinical Mater.* **6,** 323 (1990)

(8) M. Yokoi, M. Nishi, *Chem. Lett.* 1765 (1989)

(9) M. Yokoi, E. Nomoto, I. Ikoma, *J. Mater. Chem.* **3** , 389 (1993)

(10) J. M. Rabie, A. Sawaby, M. A. Moharram, A. M. Nassar, K. M. Tahon, *J. Appl. Polym. Sci.* **41**, 445 (1990)

(11) J. W. Nicholson, S. J. Hawkins, E. A. Wilson, *J. Mater. Sci. Mat. Med.* **4**, 32 (1993)

(12) M. Shing Wu, H. C. Jone, J. W. Hwang, *J. Appl. Polym. Sci.* **63**, 89 (1997)

(13) B. Schmidt, *Ph.D Thesis*, Technical University of Szczecin, 1999

(14) F. A. Cotton, G. Wilkinson, P. L. Gaus, *"Inorganic Chemistry"*, PWN, Warsaw 1995, p. 575

(15) J. Jezierska, B. Schmidt, T. Spychaj, unpublished results

(16) Sun-Yi Huang, D. W. Lipp, *"Flocculants (Organic, Overview)",* in "*Polymeric Materials Encycl.",* ed. J. C. Salamone, CRC, Boca Raton 1996, p. 2427

(17) A. L. Kowal, M. Świderska-Broz, *"Water Cleaning"*, PWN, Warsaw 1997