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APPLICATION OF ACRYLAMIDE POLYMERS AS FLOCCULANTS IN SEWAGES COAGULATION PROCESS

ZASTOSOWANIE POLIMERÓW AKRYLOAMIDOWYCH JAKO FLOKULANTÓW W PROCESIE KOAGULACJI ŚCIEKÓW

Summary: In sewages treatment processes on a large scale polymers and acrylamide copolymers are used. In recent years there is increasing competition between the companies producing flocculants on basis of acrylamide, which are applied with good effect in technologies of sewages treatment, both municipal as well as industrial. In connection with forming sewages of varied physical-chemical parameters it is necessary to synthesize newer and more effective polyelectrolytes. As a result of performed polymerisation and copolymerisation processes there were received polyacrylamides, acrylamide copolymers, with acrylic acid and also acrylamide with acrylnitrile, which were tested as flocculants in process of municipal sewages assistance. Flocculants application not only caused decrease of turbidity but also decrease of soluble pollutants concentration and also improvement of wastes quality parameters.

Keywords: polymers and copolymers acrylamide, flocculants, sewages treatment

The constant deteriorating of water purity and growing requirements of drinking water quality and growing demand on water, force changes in water resources management system.

It is known that Polish water resources are one of lowest in Europe. Because of this it is necessary the economical water management and its multiply using. Due to a limiting access to water being ready to use without initial preparation and growing requirements of sewage quality carrying away to water-courses grows the interest of new materials and solutions accelerating processes of sewage treatment, lowering sludge humidity, and facilitating sludge dewatering and filtration.

All this forces the continuous searching of new technologies and optimising of applied technologies of water treatment and conditioning. In these processes coagulation is still basic process. However more often is used for aiding of coagulation process. Polyelectrolytes are materials that are using widely for improving of water properties.

Colloidal organic and inorganic impurities, suspensions, and partly soluble substances are removing in process of sewage coagulation. In water reconditioning coagulation is used for diminishing water turbidity, concentration of phosphoric and organic compounds. Separated sludge can be used and water is submitting for further treatment. Most often coagulation connected with pressure flotation of precipitated sludge is performed.

Aluminium and iron compounds are mostly used as coagulants. Recently because of economical regards there is a tendency of replacing an aluminium coagulant by iron salts. Ion polymers of different molecular weights and different functional groups are also used as coagulants. Nowadays, small amounts of flocculents are aiding a process of chemical precipitation by means of coagulants. Anionic and non-ionic polyelectrolytes are also used as flocculents. Its using diminishes a dose of a basic coagulant and improves sedimentation conditions [1-3].

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The mechanism of coagulation with using of polyelectrolyte relies on mutual repulsive forces' reduction between suspension's particles. Particles are connecting to polymer chains. In this mechanism there is also a mutual repulsive force reduction between suspension's particles adsorbed on a polymer and non-adsorbed, being in water. Conditions of coagulation allow for creation of intermolecular and intramolecular bonds in polymer chains lowering in such a way polymer-suspension particle dimension and creating flocs which easy sediments.

Flocculent increases a size of flocs, alters theirs falling and allowing for increasing a hydraulic load of treatment plant, decreases a volume of produced sludge and influences on treated sewage quality.

Synthetic polyelectrolytes are water-soluble polymers, which differ in ion activity and degree of polymerization. They differ also in outer form. They exist as powders, granulated product, emulsion or water solutions. According to literature and data of polyelectrolytes producers the best flocculation properties exhibit materials obtained from polyacryloamide or modified polyacryloamide. Foreign producers offer the whole flocculents pallet of different properties and field of application, but of unknown structure and composition [4]. On a home market flocculents exist in form of polyacryloamide water solutions named Rokrysol and produced by "Rokita" Factory in Brzeg Dolny. The other one is Gigtar 3 low molecular polyacryloamide and Gigtar S partly hydrolysed polyacryloamide, produced by "Tarnów" Nitrogen Factory.

Moreover, producers do not give most of the necessary characteristics of material structure and properties. It is possible to find their properties but it is not possible to determine a manner of their production, structure, and relations between theirs properties and flocculation ability. So, it was decided to conduct polymerisation of acryloamide and modification of this polymer to find these relationships.

Materials and methods

For polymerization and copolymerization the acryloamide from "Rokita" S.A. Chemical Factory in Brzeg Dolny, water, acetone, dioxane, ethanol, hydrogen peroxide, acrylic acid (POCh, Gliwice), acrylonitrile (Fluka Chemie AG, Ch-9470 Buchs), potassium persulfate (Rechim Exported by V/O Sojuzchimexport), sodium persulfate (The British Drug House LTD) were used.

Molecular weights of synthesized polyacryloamide were found out from viscosity measurements by means of an Ubbelohde capillary viscometer. Viscosity average molecular weights were calculated from Mark-Houwink equation.

The flocculation investigation were done according to Polish standard PN-71/C-04583.

In flocculation studies, an aluminium sulfate (POCh, Gliwice) and Jaroszów clay (for preparation of high turbidity water according to PN-71/C-04583 standard), and mine water from "Wesoła" coal mine were used.

Results and discussion

Well-known radical polymerization initiators were used in the polymerization of acryloamide. Colourless, solid products were obtained in water polymerization of acryloamide after precipitation in acetone. In polymerization of acryloamide in ethanol, acetone and dioxane the white powders were obtained in reaction medium (Table 1).

Magnitudes of determined molecular weights of polyacryloamide obtained in different manners are comparable. Molecular weights range from few to several dozen of molecular units (Table 1). Viscosities of copolymers were measured by means of an Ubbelohde capillary viscometer. Intrinsic viscosity of acryloamide and acrylonitrile copolymers is in range of 0.26÷0.28 dm^3/g (below intrinsic viscosity measured for polyacryloamide). Intrinsic viscosity of acryloamide and acrylic acid copolymers is in range of 11.40÷16.40 dm^3/g (Tables 2, 3) considerably above viscosity of polyacryloamide. In polymerization of acryloamide the white milky powders were obtained. It was found that polyacryloamide obtained in different conditions dissolves in cold and hot (at boiling temperature of solvent) in water and nitrobenzene. Copolymers of acryloamide and acrylonitrile are solid, light yellow products and exhibit lower intrinsic viscosity than polyacryloamides. It was found that these copolymers dissolve in cold and hot (at boiling temperature of solvent) in water.

Table 1

Selected conditions of polyacryloamide preparation, viscosity and molecular weights (examples)

Polymer No.	Initiator	Solvent	Reaction time [h]	Reaction temperature [K]	Precipitatant	Intrinsic viscosity [dm^3/g]	∗Molecular weight
1	$K_2S_2O_8$	water	2	333	Acetone	2.98	$3.30 x 10^5$
2	$K_2S_2O_8$	water	2	333	Acetone	2.90	$3.16 x 10^5$
3	$K_2S_2O_8$	water	5	333	Acetone	3.10	$3.50 x 10^5$
4	$K_2S_2O_8$	water	5	333	Acetone	2.90	$3.16 x 10^5$
5	$Na_2S_2O_8$	ethanol	3	293	Reaction medium	0.90	$3.51 x 10^4$
6	$Na_2S_2O_8$	acetone	3	293	Reaction medium	1.80	$1.43 x 10^5$
7	$Na_2S_2O_8$	dioxane + water	2	293	Reaction medium	1.77	$1.50 x 10^5$
8	$Na_2S_2O_8$	dioxane + water	3	293	Reaction medium	1.82	$1.53 x 10^5$

∗ Molecular weight was calculated from equation [5]: $[\eta] = 6.8 x 10^{-4} (\overline{M}_n)^{0.66}$
where: η - intrinsic viscosity, $\overline{M}_n$ - viscosity average molecular weight

Table 2

Selected preparation conditions and intrinsic viscosity of acryloamide and acrylonitrile copolymers

Polymer No.	Comonomer	Initiator	Solvent	Reaction time [h]	Reaction temperature [K]	Precipitatant	Intrinsic viscosity [dm^3/g]
9	Acrylonitrile	$K_2S_2O_8$	water	3	333	Acetone	0.28
10	Acrylonitrile	$K_2S_2O_8$	water	3	333	acetone	0.26

Table 3

Selected preparation conditions, intrinsic viscosity of acryloamide and acrylic acid copolymers

Polymer No.	Comonomer	Initiator	Solvent	Reaction time [h]	Reaction temperature [K]	Intrinsic viscosity [dm^3/g]
11	Acrylic acid	$K_2S_2O_8$	water	3	333	11.40
12	Acrylic acid	$K_2S_2O_8$	water	3	333	12.02
13	Acrylic acid	H_2O_2	water	3	333	16.33
14	Acrylic acid	H_2O_2	water	3	333	16.40

Copolymers of acryloamide and acrylic acid are solid, light yellow products. They have very high intrinsic viscosity in comparison with polyacryloamides, and copolymers of acryloamide and acrylonitrile. It was found that these copolymers dissolve in cold and hot water.

The application tests of polyacryloamides as flocculent aiding the process of suspension sedimentation in model and in mine water were conducted (Tables 6, 7). To obtain a highest transparency of water after coagulation, the selection of an optimum dose of a coagulant was carried out (Tables 4, 5).

It was found that optimum dose of coagulant per 1000 cm^3 of mine water from "Wesoła" coal mine was 50 mg and maximum turbidity of mine water was 49 mm H_2O in relation to 21 mm H_2O before coagulation. For standard water it was 79 mm H_2O in comparison with 14 mm H_2O before coagulation.

Application of obtained polelectrolytes as flocculents allow for considerable improving of flocculation process and receiving mine water transparency from "Wesoła" coal mine equal to 280 mm H_2O at flocculent dose of 16.7 mg/dm^3 (coagulant dose - 50 mg/dm^3, at constant transparency 21 mm H_2O before flocculation). For polymer sample No. 4 of intrinsic viscosity 1.8 dm^3/g, a very good water transparency equal 160 mm H_2O was obtained at 1.3 mg/dm^3.

Table 4

Selection of a coagulant optimum dose for mine water from Kleofas coal mine of transparency before coagulation equal to 21 mm H_2O

Sample No.	Dose of coagulant [mg]	Transparency of water after coagulation [mm H_2O]
1	0	27
2	10	40
3	20	43
4	25	45
5	**30**	**49**
6	35	47
7	40	47
8	50	45

Table 5

Selection of a coagulant dose for model water prepared from Jaroszów clay of transparency before coagulation equal to 14 mm H_2O

Sample No.	Dose of coagulant [mg]	Transparency of water after coagulation [mm H_2O]
1	0	24
2	10	32
3	20	42
4	**30**	**68**
5	40	62
6	50	60
7	60	40
8	70	40

Table 6

Flocculation process of mine water from "Wesoła" coal mine of initial transparency 21 mm H_2O conducted with using of polyacryloamide of $M_\eta = 3.51x10^4 – 3.50x10^5$

Sample No.	**Dose of flocculent [mg]**	**Transparency of water after flocculation [mm H_2O]**
1	1.3	125
	6.7	**175**
2	1.3	124
	6.7	**174**
3	1.3	53
	10.0	**74**
4	1.3	160
	16.7	**280**
5	1.3	96
	10.0	**178**
6	1.3	115
	13.0	**196**

Table 7

Flocculation process of water prepared from Jaroszów clay of initial transparency 14 mm H_2O conducted with using of polyacryloamide with $M_\eta = 1.53x10^5$

Sample No.	**Dose of flocculent [mg]**	**Transparency of water after flocculation [mm H_2O]**
6	6.7	96
	10.0	**110**
	13.0	100
	16.7	96

Table 8

Flocculation process of water from "Wesoła" mine of initial transparency 21 mm H_2O conducted with using copolymers of acryloamide and acrylonitrile

Sample No.	**Dose of flocculent [mg]**	**Transparency of water after flocculation [mm H_2O]**
7	1.3	88
	6.7	92
	10.0	**115**
	13.0	80
8	1.3	90
	13.0	108
	16.7	**110**
	20.0	108

Table 9

Flocculation process of water from "Wesoła" mine of initial transparency 21 mm H_2O conducted with using copolymers of acryloamide and acrylic acid

Sample No.	**Dose of flocculent [mg]**	**Transparency of water after flocculation [mm H_2O]**
9	1.7	126
	16.7	**250**
10	1.7	125
	16.7	**260**
11	1.3	82
	3.3	**164**
12	1.7	225
	10.0	**279**

Table 10

Flocculation process of water prepared from Jaroszów clay, conducted with using copolymers of acryloamide and acrylic acid. Initial water transparency 14 mm H_2O

Sample No.	Dose of flocculent [mg]	Transparency of water after flocculation [mm H_2O]
12	3.3	160
	6.7	200
	10.0	**232**
	13.0	215
	16.7	210

The lowest aiding effect of mine waters coagulation was obtained using polymer No. 2 of intrinsic viscosity 0.9 dm^3/g, where at coagulant dose 10 mg/dm^3 a water transparency was 74 mm H_2O. Using of other polymers gave good effect at coagulant dose 1.3 mg/dm^3 where a water transparency was 125, 124, 96, 115 mm H_2O, respectively for samples No. 1, 2, 5, 6.

Polymer No. 6 intrinsic viscosity 0.9 dm^3/g was used for flocculation study of standard water prepared from Jaroszów clay. Chemical composition of this water was similar to sewage from of power plant. Acting of these polyelectrolytes on this type of water is less effective. However, at 10 mg/dm^3 a transparency was 110 mm H_2O in comparison with 14 mm H_2O before coagulation and 79 mm H_2O after coagulation.

Results of flocculation process study with using copolymers of acryloamide and acrylonitrile are following. It was found that at coagulant dose 50 mg/dm^3 and a standard water transparency of 14 mm H_2O before and 79 mm H_2O after coagulation the good effects for this polyelectrolyte were obtained for high doses (Table 8). At coagulant dose 10 mg/dm^3 and 16.7 mg/dm^3 a water transparency was 115 and 110 mm H_2O, respectively. These results are worse than for polyacryloamide.

Studies of flocculation process conducted with using copolymers of acryloamide and acrylonitrile at constant dose of coagulant 50 mg/dm^3 and initial water transparency 21 mm H_2O before coagulation showed that the best results were obtained for polymer No. 12 of intrinsic viscosity 16.4 dm^3/g. At dose of polyelectrolyte 10 mg/dm^3 a water transparency 279 mm H_2O was obtained. Copolymers No. 9, 10, 11 gave similar effect and at doses 16.7 mg, 16.7 mg, 3.3 mg/dm^3 the transparency of water was 250, 260, 164 mm, respectively.

Flocculation studies of water prepared from Jaroszów clay conducted with using copolymer No. 12 having η = 16.4 dm^3/g at 50 mg/dm^3 dose of coagulant and initial water transparency 14 mm H_2O was performed. It was found that the best flocculation effect was obtained at 10 mg/dm^3 dose of coagulant for which water transparency was 14 mm H_2O.

It was found that very good flocculation effects were obtained using copolymers of acrylamide and acrylic acid both for mine water from "Wesoła" coal mine and standard water for which flocculation action conducted with polyacryloamide was not so effective.

Investigations showed that radical polymerization initiated by different initiators and at different temperatures gave polymers having similar molecular weights. Polyacryloamide and its copolymers with acrylic acid and acrylonitrile exhibit good flocculation properties. They can be used with good effect as flocculents for mine waters and for other kind of sewage (*eg* sewage from power plant).

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ZASTOSOWANIE POLIMERÓW AKRYLOAMIDOWYCH JAKO FLOKULANTÓW W PROCESIE KOAGULACJI ŚCIEKÓW

Streszczenie: W procesach oczyszczania ścieków na szeroką skalę wykorzystywane są polimery i kopolimery akryloamidu. W ostatnich latach obserwuje się rosnącą konkurencję firm produkujących flokulanty na osnowie akryloamidu, stosowane z dobrym efektem w technologiach oczyszczania ścieków zarówno komunalnych, jak i przemysłowych. W związku z powstawaniem ścieków o różnych parametrach fizykochemicznych konieczne jest syntezowanie coraz to nowych, skutecznych polielektrolitów. W wyniku przeprowadzonych procesów polimeryzacji i kopolimeryzacji otrzymano poliakryloamidy, kopolimery akryloamidu z kwasem akrylowym oraz akryloamidu z akrylonitrylem, które testowano jako flokulanty w procesie wspomagania koagulacji ścieków przemysłowych. Stosowanie flokulantów nie tylko spowodowało spadek mętności, ale również zmniejszyło stężenia zanieczyszczeń rozpuszczalnych oraz poprawę parametrów jakości oczyszczanych ścieków.

Słowa kluczowe: polimery i kopolimery akryloamidowe, flokulanty, oczyszczanie ścieków