NOVEL FLOCCULANTS BASED ON ACRYLAMIDE AND ACRYLIC ACID OBTAINED BY ELECTRON BEAM IRRADIATION

ELENA MANAILA[1], GABRIELA CRACIUN[1], DANIEL IGHIGEANU[1], DANIELA MARIA STELESCU[2]

[1] *National Institute for Laser, Plasma and Radiation Physics, Electron Accelerators Laboratory, #409 Atomistilor St., 077125 Magurele, Romania, email: elena.manaila@inflpr.ro; gabriela.craciun@inflpr.ro*

[2] *INCDTP – Leather and Footwear Research Institute, 93 Ion Minulescu St., Bucharest, Romania*

Water pollution results from all human activities: domestic, industrial and agricultural. The literature reports a multitude of processes for the decontamination of contaminated water and wastewater such as coagulation, precipitation, extraction, evaporation, adsorption on activated carbon, ion-exchange etc. Coagulation/flocculation is a frequently applied process in the primary purification of industrial wastewater. There are two major classes of materials used in coagulation/flocculation processes: (1) inorganic and organic coagulants including mineral additives, hydrolyzing metal salts, pre-hydrolysed metals and polyelectrolytes (coagulant aids); (2) organic flocculants including cationic and anionic polyelectrolytes, non-ionic polymers, amphoteric and hydrophobically modified polymers, and naturally occurring flocculants (starch derivatives, guar gums, tannins, alginates, etc.). In Romania, the obtaining and using of polyelectrolytes for residual and surface water treatment is not so developed because the advantages of their use are not well known, these being the following: (a) reduce the quantity of classic electrolytes needed by 25% up to 50%; (b) concentrations of 10 to 100 times smaller of classic materials are used, the final volumes of reagents which are used in water treatment are considerably decreased, saving space, labour, energetic consume, means of transport; (c) they do not produce metallic residuals in the mud left after water purge; (d) reduce by almost 60% the volume of the resulted mud by using them in comparison with the volume resulted from classic material treatment, which it reflects in the space economy for depositing the mud resulted from the purifying stations; (e) reduce by approximately 5-10 times the contact, stationary and decantation time which determines a shorter process of water purifying; etc.

Keywords: flocculants, copolymerization, acrylamide, acrylic acid, electron beam

INTRODUCTION

Wastewater and industrial effluent treatment require removal of suspended solids for purification and possible re-usage. The removal can be accomplished by gravitation (very slow), by coagulation (dependent on electric charge situation) and by flocculation (not dependent on electric charges and the fastest) (Brostow *et al.*, 2009). Coagulation and flocculation are phenomena which give names for two distinct stages of physical and chemical treatment processes applied in water and waste water treatment. Coagulation is the phenomenon in which the system consisting of colloidal particles from water is destabilized. It is the result of the adhesion of chemical reagents (ferric chloride, ferrous sulfate, aluminum sulfate) to the suspended particles from the water and results in the formation of larger aggregates. Flocculation is the phenomenon in which destabilized colloidal particles join together in larger agglomerations. It is caused by the addition of small quantities of chemicals known as flocculants and the effectiveness is manifested especially in the situations where colloidal particles are already destabilized (Singh *et al.*, 2000). During the last three decades, polyacrylamide and acrylic acid converted by different methods in polyelectrolytes are used increasingly as flocculants worldwide. These polymers are relatively nontoxic, but for health concerns, even for wastewater treatment has been subjected to closer evaluation during the last decade (Fetting *et al.*, 1991). For this reason, a strict condition of use is that the residual acrylamide monomer content in the final product to be less than 0.05% (Martin *et al.*, 2006). From their apparition until today, flocculants were obtained by different chemical methods, but the method of producing by irradiation and particularly by electron beam irradiation has now become more attractive. The major advantages of radiation induced polymerization processes are: (1) very easy to manipulate the molecular weight, from low to very high, by simply changing the feed composition as well as the composition of the product by incorporating different monomers; (2) precise control of charge density as the monomer feed composition is controlled at the initial stages only; (3) precise control of molecular weight distribution; (4) no flammable and toxic solvents used; (5) no production of waste matter or evolution of noxious gases; (6) no production of hazardous effluents; (7) very low monomer contents; (8) very clean process (Martin *et al.*, 2006). Physical and chemical properties of flocculants based on polyacrylamide and acrylic acid obtained by electron beam irradiation are strictly related to the efficiency of waste water treatment expressed by the level of treated water quality indicators. There are many situations in which organic flocculants should be used together with classic coagulation aids (inorganic flocculants) such as $Al_2(SO_4)_3$, $FeSO_4$ or $Ca(OH)_2$ because in the case of very charged waste waters, treatments based only on organic flocculants or inorganic flocculants (classical treatment) are less efficient than in the case of their combined use. Moreover, the so-called flocs are larger and more strongly bound than the aggregates obtained by coagulation (Brostow *et al.*, 2007). It is well known that each waste water type, depending on its origin, has its particularities and more than that the same type of waste water shows significant variation during the same day. For this reason treatments based on polyelectrolyte should be seen as treatment schemes for each type of waste water. These treatment schemes should also be easily adaptable to the significant variations of the same type of waste water characteristics. There is no polyelectrolyte with universal destination regardless of the method of production. This is one of the reasons why the field of flocculants obtaining by radiation technologies is still open (Craciun *et al.*, 2013). Grafting of synthetic polymers on natural polymers has become increasingly attractive for scientists and technologists on the one hand because it provides a potential biodegradability and on the other hand because it reduces the amount of synthetic monomers used in the reaction. Among grafted guar gum, xanthan gum, carboxymethyl cellulose, and starch, grafted starch performs the best (Singh *et al.*, 2000).

The goal of the paper is to present some flocculation results obtained on kaolin suspension (0.2 wt %), at room temperature (20-25°C) using a novel flocculant based on grafted starch with acrylamide and acrylic acid, obtained by electron beam irradiation.

EXPERIMENTAL

Materials

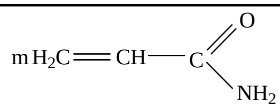
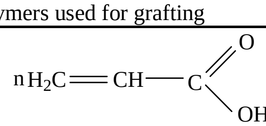
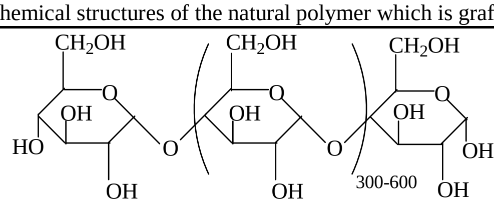
For flocculants obtaining the following materials were used: acrylamide (molar mass 71.08 g mol^{-1}; density 1.13 g/cm^3; solubility in water 2.04 kg/L at 25°C); acrylic acid (molar mass 72.06 g mol^{-1}; density 1.051 g/mL; solubility in water: miscible); sodium formate (molar mass 68.01 g mol^{-1}; density 1.92 g/cm^3; solubility in water 97 g/100 mL at 20°C) - serves as chain transfer agent in the copolymerization process; potassium persulfate (molar mass 270.322 g mol^{-1}; density 2.477 g/cm^3; solubility in water 1.75

g/100 mL at 0°C), - serves as initiator in the copolymerization process; starch (molecular weight 342.3 g/mol, density 1.5 g/cm^3).

Preparation and Irradiation of the Samples

Two classes of flocculants having the same quantities of acrylamide (AMD), acrylic acid (AA), chain transfer agent (CTA) and initiator (I) but with and without starch (S) were synthesized. The chemical structures of the synthetic and natural polymers used in grafting reaction by electron beam are presented in Table 1, as follows:

Table 1. The chemical structures of the synthetic and natural polymers used in grafting reaction

Chemical structures of the synthetic polymers used for grafting	
 Acrylamide (AMD) structure	 Acrylic acid (AA) structure
Chemical structures of the natural polymer which is grafted	
 Starch (S) structure	

Flocculant synthesis details are presented in Table 2.

Table 2. Flocculants synthesis details

Sample code	AMD (mol/L)	AA (mol/L)	I (mol/L)	CTA (mol/L)	S (mol/L)	Irradiation dose, (kGy)
F1						0.5
F2	5	0.05	2.75×10^{-6}	1.1×10^{-4}	-	1
F3						1.5
F4						0.5
F5	5	0.05	2.75×10^{-6}	1.1×10^{-4}	0.07	1
F6						1.5

Experiments were carried out with an experimental installation consisting mainly of the following units: an electron linear accelerator (ALIN-10) of 6.23 MeV energy and 75 mA peak current of the electron beam and an irradiation chamber containing the samples of monomer solution. The ALIN 10 is a travelling-wave type, operating at a wavelength of 10 cm and having 164 W maximum output power. The accelerating structure is a disk-loaded tube operating in the $\pi/2$ mode. The optimum values of the EB peak current I_{EB} and EB energy E_{EB} to produce maximum output power P_{EB} for a fixed pulse duration τ_{EB} and repetition frequency f_{EB} are as follows: E_{EB} = 6.23 MeV, I_{EB} =75 mA, P_{EB} = 164 W (f_{EB} = 100 Hz, τ_{EB} = 3.5 μs). The EB effects are related to the absorbed dose (D) expressed in Gray or J kg^{-1} and absorbed dose rate (D*) expressed in

Gy s^{-1} or J kg^{-1} s^{-1}. Electron beam dose rate was fixed at 2kGy/min in order to accumulate doses between 0.5-1.5 kGy and samples were irradiated in atmospheric conditions and at room temperature of 25°C (Craciun *et al.*, 2011).

Methods for the Physical and Chemical Characteristics Determination

Flocculants thus obtained should present a good solubility in water and high flocculation capacity, and for this they must have specific physical and chemical characteristics such as: conversion coefficient (C_c), residual monomer concentration (M_r), intrinsic viscosity (η_{intr}) and linearity coefficient expressed by Huggin's constant (k_H). The conversion coefficient (C_C) and the residual monomer concentration (M_r) are determined on the basis of the bromation reaction of the double-bond (Dimonie *et al.*, 1986). The intrinsic viscosity (η_{intr}) and the Huggins' constant (k_H) are determined by the viscosimetry method, using a Hoppler BH-2 (Dimonie *et al.*, 1986). Sodium nitrate was used as a solvent 1N ($NaNO_3$) and the working temperature was 30°C.

RESULTS AND DISCUSSION

Conversion coefficient (C_c), and residual monomer concentration, M_r are the first important parameters in polyelectrolyte characterization. The first one is required to be higher than 90% and the second less than 0.05 % in accordance with rules established by the IPCS - International Programme in Chemical Safety in the document named "Environmental Health Criteria-49-Acrylamide". A high value of conversion coefficient demonstrates a good monomer transformation efficiency in polymerization process and ensures a substantial reduction in residual monomer concentration. This is a very important aspect in polimerization process because of the well known toxicity of acrylamide in the monomer state. Regarding intrinsic viscosity, η_{intr}, and linearity constant, k_H, they must be such as to ensure linearity and water solubility of polymeric flocculant. All those characteristics are influenced by the following factors: chemical composition of the solutions to be irradiated, absorbed dose level (D = energy quantity per unit mass in Gy or J kg^{-1}) and absorbed dose rate level (D* = energy quantity per unit mass and unit time in Gy/s or J kg^{-1} s^{-1}). In our experiments we obtained two classes of flocculants: the first one based only on AMD and AA and the second one based on grafted starch with AMD and AA. For getting both of them, CTA and I were used. Differences between physical and chemical characteristics of them come not only from the chemical composition but from irradiation treatment also. In Table 3 are presented the above mentioned physical and chemical characteristics of flocculants from both classes.

Table 3. Physical and chemical characteristics of flocculants

Sample code	Conversion coefficient C_c (%)	Residual monomer M_r (%)	Intrinsic viscosity η_{intr} (dL/g)	linearity constant k_H	Irradiation dose (kGy)
F1 (class 1)	97.51	0.025	2.8	0.6	0.5
F2 (class 1)	97.83	0.021	2.6	0.8	1
F3 (class 1)	99.28	0.028	3.6	0.5	1.5
F4 (class 2)	99.36	0.016	3.8	0.5	0.5
F5 (class 2)	99.68	0.011	4.5	0.2	1
F6 (class 2)	99.67	0.012	4.6	0.2	1.5

As can be seen, the conversion coefficient C_c and intrinsic viscosity η_{intr} increases slightly with the electron beam absorbed dose. The highest C_c values obtained in the same time with the best values of η_{intr} were obtained for the samples from class 2. For all samples the M_r is much under the limit value of 0.05 %. All samples obtained by grafting AMD and AA on starch (F4-F6/class 2) present superior physical and chemical characteristics than the samples from class 1. This last result is in accordance with our expectations.

Flocculation tests were carried out on kaolin suspension (0.25 wt%), at room temperature (25°C) using the standard Jar test apparatus (Velp FC 6S, Italia). For these experiments, solutions of four different concentrations of flocculants from each flocculant listed in Table 2 were prepared: 5, 10, 15 and 20 mg/L. Due to their good linearity (k_H <1) all flocculants were well dissolved in water. Under a slow stirring condition, the flocculant solution was added by means of a pipette in each beaker of 500 mL, in order to determine the polymer concentration influence (5-20 mg/L). Immediately after the addition of polymer solution, the suspensions were stirred at a constant speed of 60 rpm for 15 min, and then allowed to sediment for 15 min. Clear supernatant was drawn from the top layer and its transmittance was measured at 203-206 nm using a Cary Bio-100 UV-VIS spectrophotometer. The results are presented in Table 4.

Table 4. The results of flocculation tests

Flocculation characteristics	Flocculant concentration (mg/L) 5	10	15	20
F1				
Sediment (mm)	40	50	60	60
Transmittance (%)	95.13	92.46	92.3	90.41
F2				
Sediment (mm)	40	40	50	50
Transmittance (%)	95.24	93.12	92.17	91.85
F3				
Sediment (mm)	40	50	40	60
Transmittance (%)	95.13	95.74	95.46	92.64
F4				
Sediment (mm)	40	40	60	90
Transmittance (%)	97.33	97.12	96.43	95.12
F5				
Sediment (mm)	40	40	50	40
Transmittance (%)	98.25	97.46	97.38	96.41
F6				
Sediment (mm)	40	40	40	40
Transmittance (%)	98.63	98.84	97.43	97.22

The pH of the kaolin suspension was measured and it was found as been 6.99. The pH of the clear supernatant was also measured and it was found between 7.02 and 7.30. We can say, however, that the treatment with flocculant improved the pH of kaolin suspension. During the flocculation experiments, pH corrections were not necessary.

As can be seen there are not significant differences between the values of sediment, except for the flocculant concentration of 20 mg/L. All samples obtained by irradiation grafting of AMD and AA on starch exhibit very good values of light transmittance. But it is easy to observe that for all samples, the flocculant concentration increasing decrease the light transmittance.

CONCLUSIONS

The grafting of synthetic polymers (acrylamide and acrylic acid) on a natural polymer (starch) by electron beam irradiation of 6.23 MeV was carried out. The obtained flocculants exhibit very good conversion coefficients (>99%) and as a consequence small residual monomer concentrations (<0.05%). Also, this class of flocculants has a better intrinsic viscosity than the class of flocculants obtained by simple polymerization of acrylamide and acrylic acid. Both class of flocculants were found to have good linearity (k_H <1). Flocculation tests were carried out on kaolin suspension (0.25 wt %), at room temperature (25°C). For these experiments solutions of four different concentrations of flocculants from each obtained flocculant were prepared: 5, 10, 15 and 20 mg/L. Even there were not significant differences between the values of sediment (except for the flocculant concentration of 20 mg/L) notable differences were obtained in light transmittance. Also, is seams that the flocculant concentration increasing decrease the light transmittance of clear superantant. Further studies regarding the biodegradability potential of this class of flocculants will be performed.

REFERENCES

Brostow, W., Lobland, H.E.H., Pal, S., Singh, R.P. (2009), "Polymeric flocculants for wastewater and industrial effluent treatment", *Journal of Materials Education*, 31(3-4), 157-166.

Brostow, W., Pal, S., Singh, R.P. (2007), "A model of flocculation", *Materials Letters*, 61, 4381-4384.

Craciun, G., Manaila E., Ighigeanu, D. (2011), "Polymeric flocculants based on acrylamide and acrylic acid obtained by electron beam irradiation", *Revista de Pielarie Incaltaminte* (*Leather and Footwear Journal*), 11(2), 121-132.

Craciun, G., Manaila, E., Stelescu, D.M. (2013), "Flocculation Efficiency of Poly(Acrylamide-Co-Acrylic Acid) Obtained by Electron Beam Irradiation", *Journal of Materials*, Hindawi Publishing Corporation, Article ID 297123, http://dx.doi.org/10.1155/2013/297123, 7 pages.

Dimonie, M., Boghina, C., Cincu, C., Marinescu, M., Marinescu, N. (1986), *Polyacrylamide* (in Romanian), Tehnical Press, Bucharest, 36-36 and 194-197.

Fetting, J., Ratnaweera, H., Odegaard, H. (1991), "Synthetic Organic Polymers as Primary Coagulants in Wastewater Treatment", *Water Supply*, 9, 19-26.

Martin, D., Craciun, G., Manaila, E., Ighigeanu, D., Togoe, I., Oproiu, C., Margaritescu, I., Iacob, N. (2006), "Waste treatment by microwave and electron", Proceedings of the 2nd Environmental Physics Conference, 91-100.

Singh, R.P., Karmakar, G.P., Rath, S.K., Karmakar, N.C., Pandey, S.R., Tripathy, T., Panda, J., Wan, K., Jain, S.K., Lan, N.T. (2000), "Biodegradable Drag Reducing Agents and Flocculants Based on Polysaccharides: Materials and Applications", *Polymer Engineering and Science*, 40(1), 19-26, 46-60.