Electron Beam Processed Polyelectrolytes

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Abstract. Comparative results obtained by electron beam induced polymerization of water-soluble monomers at low and high absorbed dose level are presented. At high dose rate levels, the polymerization process is incomplete, monomer conversion decreases, polymer parameters become very sensitive to the chemical composition and variations in absorbed dose level. The effect of high-absorbed dose rate is reduced by the additional introduction of NaCl into acrylamide-acrylic acid aqueous solutions that under irradiation markedly increases conversion coefficient to nearly 100% and decreases residual monomer concentration under 0.01. The process has been demonstrated in a pilot-scale operation.

1. Introduction

Radiation induced polymerization is an envolving method which is environmentally friendly and which can produce a wide variety of water-soluble polyelectrolytes. Such polyelectrolytes can be used to increase the efficiency of water clarification, particulate filtration, and improve the performance of centrifugation in the water treatment industry [1-6]. Research activities combined with engineering activities, have culminated in the development of a new electron beam (EB) processing approach that has been scaled-up to produce polyelectrolytes (acrylamide - acrylic acid copolymers) [7-10]. The major advantages of EB induced polymerization are: a) Ease of manipulating the molecular weight from low to very high values by simple changing of the feed composition; b) Precise control of charge density and of molecular weight distribution; c) High production rate: from 500 to 2000 $kg \cdot h^{-1}$ for each kW of electron beam power; d) Mitigation of flammable and toxic solvents with no production of waste matter or evolution of obnoxious gases and no production of hazardous effluents; e) The entire process is very clean and permits to obtain products with very low residual monomer contents that can also be used for potable water applications.

2. Methods and Apparatus

The characteristics of the acrylamide-acrylic acid copolymers 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 $J \cdot kg^{-1}$) and absorbed dose rate level (D* = energy quantity per unit mass and unit time in $Gy \cdot s^{-1}$ or $J \cdot kg^{-1} \cdot s^{-1}$). Many years of investigations of polymeric material properties [7-10] demonstrated that EB induced polymerization yields, under proper irradiation conditions and for fixed chemical composition of the monomer mixtures to be irradiated, higher conversion efficiency (near 100%) and lower residual monomer concentration (under 0.01%) than classical polymerization of the acrylamide-acrylic acid aqueous solutions. EB induced polymerization involves the Coulomb interaction of the accelerated electrons with atoms or molecules in the irradiated medium. These interactions generate reactive ions, thermalized electrons, excited states and radicals to drive the chemical reactions. Polymerization is subsequently induced by ionizing radiation in much the same way as free radical addition polymerization. The main function of the ionizing radiation in a radiation - initiated polymerization is limited to the primary events, the initiation step which leads to the production of free radicals and to a few specific secondary effects. The subsequent steps of propagation, termination and chain transfer proceed as in a chemically catalyzed process. In radiation-initiated polymerization, a completely "inert" solvent is not possible. Any substance when added to a monomer absorbs the radiation energy, and this results in various secondary processes, which finally lead to an additional production of free radicals. Indeed, due to water presence in the EB irradiated system, our experiments show that the role of the radicals originating from irradiated water is predominantly that of the radicals which come directly from the monomer irradiation. Thus, irradiated water radicals facilitate the polymerization process and decrease the required absorbed dose level to the lower range of 0.3-1 kGy for acrylamide-acrylic acid copolymers. Also, due to the larger acrylamide radiation reactivity (r_{AMD} =1.6) in comparison with acrylic acid reactivity (r_{AA}=0.6) and also, because the ratio of the residual monomer contents of acrylamide and acrylic acid is in inverse proportion to their reactivity ratio, the residual monomer concentration of acrylamide is about 2.8 times smaller than the residual monomer concentration of acrylic acid, in the composition of acrylamide-acrylic acid copolymers. This effect leads to the possibility for increasing the quantity of the total residual monomer concentration in the final composition of the acrylamide-acrylic acid copolymers. Large dose rates (higher than 0.1 $\text{kGy} \cdot \text{s}^{-1}$), lead to a decrease in efficiency of the polymerization process because of the dependence of free-radical reactions on the electron beam intensity. At high-absorbed dose rates, the level of the necessary absorbed dose much increases, monomers conversion decreases and the polymer degrades into a product of lower molecular weight due to a random main-chain-scission process. Also, at large dose rates, the copolymer parameters become very sensitive to the chemical composition and variations in absorbed dose level. Low-radiation doses are required for high process efficiency but high dose rates must be used to promote high production capacities. In view of these arguments many experimental studies were carried out in order to improve the process efficiency and the polyelectrolyte properties under high-absorbed dose rate conditions. Comparative studies at low, medium and high dose rates required three electron accelerators: the ALIN-10 electron accelerator (Fig. 1) having 164 W maximum output power (for experiments at low dose rates), the ALID-7 electron accelerator (Fig. 2 and Fig. 3) having 780 W maximum output power (for experiments at medium dose rates) and the ILU-6M electron accelerator (Fig. 4) having 10.8 kW maximum output power (for experiments at high dose rates). ALIN-10 and ALID-7 were built in the Electron Accelerators Laboratory, NILPR, Bucharest, Romania [12]. Both accelerators, ALIN-10 and ALID-7, are of travelling-wave type, operating at a wavelength of 10 cm. 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:

ALIN-10: E_{EB} = 6.23 MeV; I_{EB} =75 mA; P_{EB} = 164 W (f_{EB} = 100 Hz, τ_{EB} = 3.5 μs)
ALID-7: E_{EB} = 5.5 MeV; I_{EB} =130 mA; P_{EB} = 670 W (f_{EB} = 250 Hz, τ_{EB} = 3.75 μs)

ILU-6M, was built at the Institute of Nuclear Physics, Novosibirsk, Russia, and is placed at the Electrical Project and Research Institute, Bucharest, Romania. The ILU-6M electron beam source is a resonator-type accelerator, operating at 115±5 MHz. This accelerator generates electron beam pulses of 1.8 MeV, 0.375 ms duration, up to 0.32 A current peak intensity. In the present work, we have used a sampling method involving an electron collection monitor and its associated instrumentation for monitoring absorbed dose rate and accumulated absorbed dose during the irradiation process. This monitor which intercepts only a fraction of the scanned electron beam gives a relative value of the absorbed dose rate: it has been first calibrated by several chemical systems (such as the Ceric dosimeter) placed at the position of

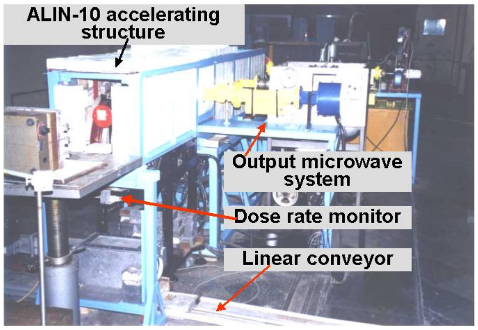

FIG. 1. ALIN-10 accelerating structure (travelling wave) and microwave system

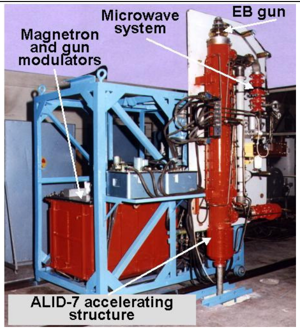

FIG. 2. ALID-7 accelerating structure (travelling wave), microwave system, gun and modulators

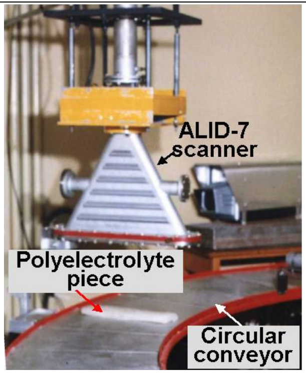

FIG. 3. ALID-7 scanner and circular conveyor (325 cm average diameter, 50 cm width)

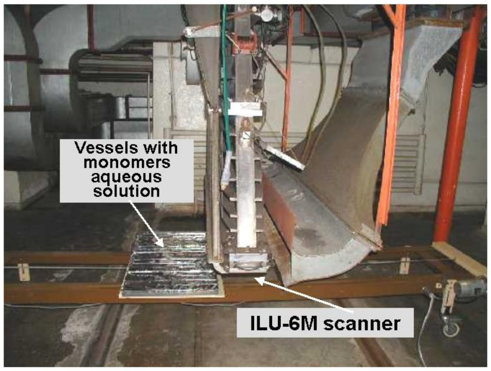

FIG. 4. The irradiation facility for EB processed polyelectrolytes at pilot -scale. Lateral view of the ILU-6M scanner (1.1 m beam width) and conveyor (surface of the platform: 0.5 m^2 to 3 m^2)

the samples to be irradiated. EB irradiation with ALIN-10, ALID-7 and ILU-6M accelerators was performed at 50 Gy · s^{-1}, 100 Gy · s^{-1} and 750 Gy · s^{-1} absorbed dose rate, respectively.

3. Results

Preparation of polyelectrolytes is based on co-polymerization by EB irradiation of the aqueous solutions containing appropriate mixtures of acrylamide (AMD) and acrylic acid (AA) monomers and certain agents, such as complexing agents (CA) for impurity inhibition, chain transfer agents (CTA) to mitigate cross-linking of the polymer structure, and initiators (I) to optimize the monomer conversion process. The thickness of the irradiated samples (monomer aqueous solutions) was 23 mm, 20 mm and 6 mm for the experiments with ALIN-10, ALID-7 and ILU-6M, respectively. The typical chemical composition of aqueous solutions that were irradiated to produce acrylamide-acrylic acid copolymers is presented in Table 1.

TABLE I: TYPICAL CHEMICAL COMPOSITION OF THE AQUEOUS SOLUTIONS

Chemical composition	Characteristics
Total monomer concentration, TMC	30% - 40%
Monomer Ratio, AMD/AA	4/1 - 9/1
Chain transfer agent, CTA (10% solution of sodium formate) concentration	0.05% - 0.25%
Initiator, I (2% solution sodium formate) concentration	0 -1%
Complexing agent, CA (5% solution ethylene diamine tetra acetic acid) conc.	0.02% - 0.2%
NaCl concentration	0 -8%

Our interest was focused on the basic optimization of the characteristics involved in waste water treatment, such as conversion coefficient (CC), residual monomer concentration (M_r), intrinsic viscosity (η_{intr}) or average M_w (molecular weight) and a linearity coefficient given by the Huggins' constant (k_H). The values of η_{intr}, M_w and k_H are established from the following relations:

$\eta_{red} = \eta_{intr} + C \cdot tg\alpha$;

$\eta_{red} = \eta_{sp} \cdot C^{-1} = (\eta_{rel} - 1) \cdot C^{-1}$;

$tg\alpha = \Delta(\eta_{red}) \cdot \Delta^{-1}(C)$;

$k_H = tg\alpha \cdot \eta_{intr}^{-2}$;

$\eta_{intr} = K \cdot (M_w)^a$ (Mark-Houwink-Sakurade relation [11] for a polymer in aqueous solution of 1 N $NaNO_3$ at 30°C, pH=7);

where: C = polymer concentration (%) in very dilute solutions (under 0.1%) of 1 N $NaNO_3$ at 30°C and pH=7; η_{red} = reduced viscosity; η_{sp} = specific viscosity; α is the angle between the plot of η_{red} against C and a parallel axis to the C axis; tg = tangent, η_{rel} = relative viscosity established from appropriate physical measurements with a Hoppler viscometer BH-2. For acrylamide-acrylic acid copolymers: $K = 1.34\ 10^{-3}$; $a = 0.57$ for η_{intr} given by $dl \cdot g^{-1}$ and M_w by atomic mass units (a.m.u.). The acrylamide-acrylic acid copolymers exhibit good water solubility only for $k_H < 0.5$. A typical plot of reduced viscosity η_{red} versus polymer concentration is shown in Fig. 5. The analysis of the experimental results shows that for each chemical composition there is an "optimum" EB absorbed dose (D_0) which strongly depends on the absorbed dose rate (D*) level. At high dose rate levels the results can be bad: the polymerisation process is incomplete under irradiation and continues after irradiation for an uncontrollable time period. Thus, Fig. 6 demonstrates that, at high absorbed dose rate D* of 750 $Gy \cdot s^{-1}$, the conversion coefficient CC obtains high values, over 95%, only for a high absorbed dose level (over 35 kGy), but η_{intr} decrease rapidly as a function of absorbed dose D. Also, as shown in Fig. 6, at a low value of absorbed dose rate D* of 50 $Gy \cdot s^{-1}$, CC and η_{intr} exhibit high values even for a low value, of 600 Gy, of the absorbed dose level. Our experiments demonstrated that only the change of the chemical composition of the monomer aqueous solutions is able to solve this problem. Thus, NaCl addition to the monomer aqueous solutions much improved the polyelectrolyte parameters. The figures 7 - 10 demonstrate that, for the increase of NaCl concentration from 4% to 6%, CC rapidly increases (Fig. 7) and M_r rapidly decreases (Fig. 8). At higher NaCl concentrations they vary slowly with NaCl concentration. For EB irradiation at a low dose rate of 50 $Gy \cdot s^{-1}$, CC and M_r exhibit acceptable values even for zero NaCl concentration, but the additional use of NaCl in the range of 8-10% increases the CC near 99%, decreases M_r under 0.01% and increases the η_{intr} level (Figs. 9 and 10). In the final chemical composition, we kept NaCl concentration at 8%.

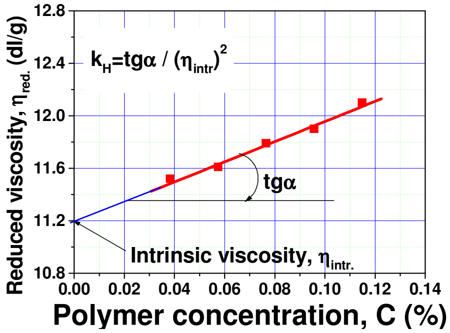

FIG. 5. η_{red} versus C (for an acrylamide-acrylic acid copolymer with M_r=0.00426% and η_{intr} =11.18 $dl \cdot g^{-1}$, k_H=0.06)

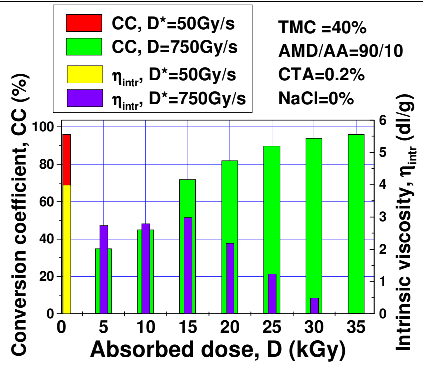

FIG. 6. The effect of EB irradiation at high D (750 $Gy \cdot s^{-1}$) and low D* (50 $Gy \cdot s^{-1}$)*

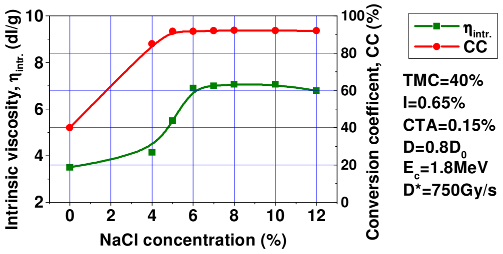

FIG 7. EB irradiation at high D (750 Gy ·s^{-1}). The effect of NaCl on η_{intr} and CC*

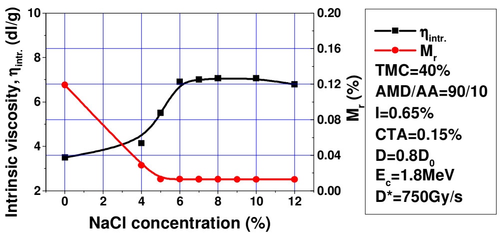

FIG 8. EB irradiation at high D (750 Gy ·s^{-1}). The effect of NaCl on η_{intr} and M$_r$*

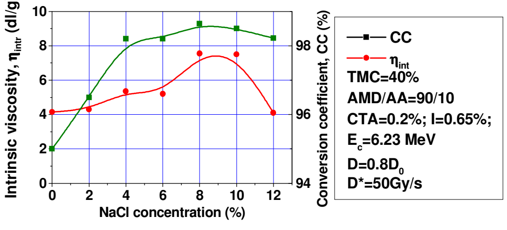

FIG. 9. EB irradiation at low D (50 Gy ·s^{-1}). The effect of NaCl on η_{intr} and CC*

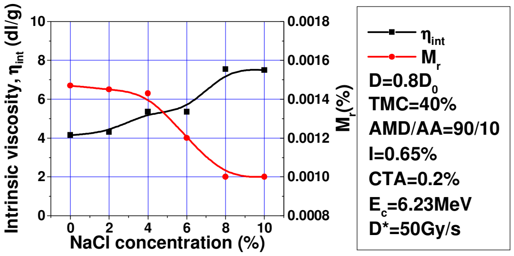

FIG. 10. EB irradiation at low D (50 Gy ·s^{-1}). The effect of NaCl on η_{intr} and M$_r$*

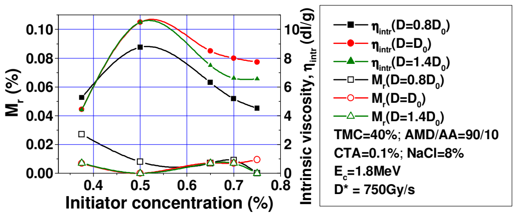

FIG. 11. Initiator effect on M$_r$ and η_{intr} at high D (750 Gy ·s^{-1})*

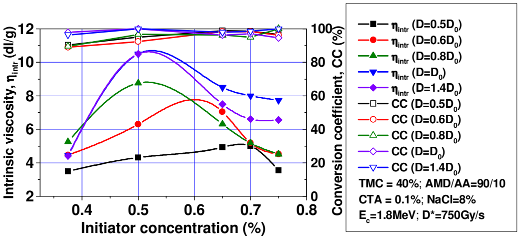

FIG. 12. Initiator effect on η_{intr} and CC at high D (750 Gy ·s^{-1})*

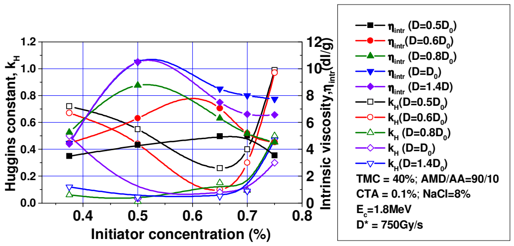

FIG. 13. Initiator effect on k$_H$ and η_{intr} at high D (750 Gy ·s^{-1})*

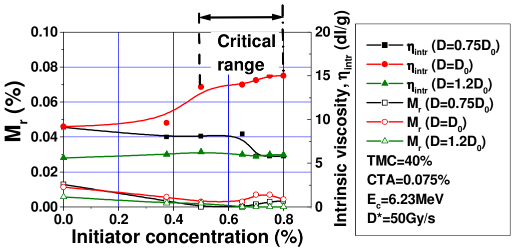

FIG. 14. Initiator effect on M$_r$ and η_{intr} at low D (50 Gy ·s^{-1})*

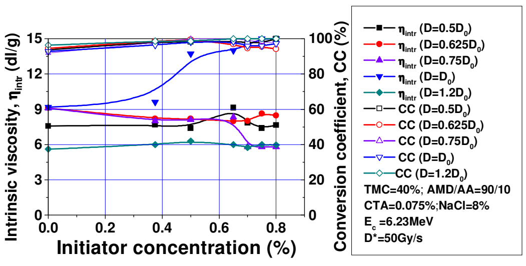

FIG. 15. Initiator effect on η_{intr} and CC at low D (50 Gy ·s^{-1})*

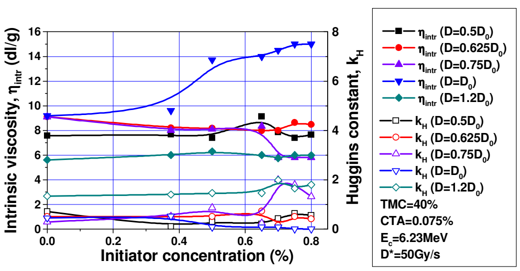

FIG. 16. Initiator effect on η_{intr} and k$_H$ at low D (50 Gy ·s^{-1})*

Besides NaCl, another critical parameters that lead to an increase of CC and a decrease of M_r are: absorbed dose level and initiator concentration. Figures 11-13 (high D* = 750 kGy/s) and figures 14-16 (low D* = 50 Gy/s) show the effect of the initiator (I) concentration upon $\eta_{intr,}$ CC, M_r and k_H. For both, high and low dose rates, initiator concentration decreases M_r (Fig. 11 and Fig. 14) and increases CC (Fig. 12 and Fig. 15) but high I values decrease η_{intr} (Fig. 12 and Fig. 15). Also, the I values above 0.7% (Fig. 13 and Fig. 16) increase k_H (irradiated samples are partially water-soluble or water-insoluble). The value of η_{intr} always exhibits a maximum value associated with a minimum value for k_H, for all irradiation experiments performed as shown in Fig. 13 and Fig. 16. Irradiation over the level of the optimum absorbed dose D_0 leads to a cross-linked structure in the final product, which becomes water-insoluble (k_H >0.5), and to lower values for η_{intr} (Fig. 11 and Fig. 14). Under irradiation conditions below the D_0 level and for solutions containing increased I content, the M_r value decreases (Fig. 11 and Fig. 14) but k_H increases (Fig. 13 and Fig. 16) and leads to the cross-linking effect. Fig. 11 and Fig. 12 demonstrate that, for high D* (750 Gy · s^{-1}), the M_r values are under 0.03% and the CC values are above 95% for I concentrations in the range used. Also, at an optimum absorbed dose D_o, as demonstrated in Fig. 11 and Fig. 12, M_r is under 0.01% and CC is near 100%. η_{intr} gradually increases with I concentration in the range of 0.375-0.5%, reaches a maximum for I concentration in the range of 0.5-0.55% and afterwards, decreases with I concentration increase above 0.55%. At the optimum dose level, the required initiator concentration is greatly diminished and η_{intr} is less sensitive to I, as is shown in Fig. 11. For small D* (50 Gy · s^{-1}), η_{intr}, CC and M_r exhibit acceptable values even for an I concentration of zero, as is shown in Fig. 14 and Fig. 15. Also, η_{intr}, CC and M_r are less sensitive versus I for the small D* case. High intrinsic viscosity values obtained at small D* irradiation and for I in the range of 0.5-0.8%, are sometimes associated with low polyelectrolyte solubility in aqueous solutions (the critical range is shown in Fig. 14). For this reason the absorbed dose level must be controlled and optimised. The main conclusion of the above experimental results is: irradiation over the level of the optimum absorbed dose leads to a cross-linking structure of the final product (polyelectrolytes become water insoluble) and irradiation below the level of optimum absorbed dose leads to an unacceptable residual monomer concentration. Also, the features of an electron accelerator used to produce polyelectrolytes are of special importance to permit efficient power utilisation: enough operating mode flexibility and reproducibility; adequate beam sweeping over the monomer aqueous solution under irradiation (in order to reduce the dose rate effect as small is possible), optimised operating regime; automatic control of the required dose and dose rate; automatic control of the conveyor velocity; adequate auxiliary systems for maximum processing rates. The optimum absorbed dose for the AMD-AA aqueous solution polymerization, established by optimization of chemical composition and EB irradiation conditions, is rather small, of about 1 kGy. This makes the use of electron beam processing very economically attractive in this type of application. Thus, if all auxiliary systems are suitable adapted and automated, the estimation of processing rate for an electron accelerator of 1 kW output power is up to 1800 kg · h^{-1} for an EB utilization factor of 0.5 and absorbed dose D of 1 kGy. For industrial waste water treatment, the acrylamide - acrylic acid copolymers are used in the range of 4 to 8 g per 1 m^3 of waste water and in the range of 0.1 to 0.2 g per 1 m^3 of potable water. A vegetable oil plant, which processes 100,000,000 kg per year of sunflower oil, produces about 1,260,000 m^3 per year waste water. The required quantity of polyelectrolytes for remediation of waste water in this plant is in the range of 5,040-10,080 kg per year. This quantity can by achieved using this technology in a very short time, from 2.8 h to 5.6 h. Also, in Romania the required quantity of potable water is 10,000,000 m^3 per day that need a polyelectrolyte amount of 1000 to 2000 kg per day. In many cases, P_n type polyelectrolytes obtained by EB irradiation are used as coagulation aids together with electrolytes E_m ($Al_2(SO_4)_3$, $FeSO_4$ and $Ca(OH)_2$). In order to provide measurable improvements in water quality we have studied the effects of different classical treatments with electrolytes and the effects of various combined treatments with electrolytes + polyelectrolytes (E_m+P_n treatment type). Also, many polyelectrolytes of P_n type with various characteristics were used. For real waste water treatment the interest was focused upon the following quality indicators established by the Romanian Standard NPTA-002/2002 concerning the conditions for waste water evacuation in the urban sewerage system: Total Suspended Solids (TSS in mg · dm^{-3}), Fatty Matter (FM in mg · dm^{-3}) and Chemical Oxygen Demand (COD in mgO_2 · dm^{-3}). Table II presents the comparative results obtained by classical treatment (E_m) and combined treatment (E_m + P_n) with waste water samples, which ranged from relatively clean to extremely contaminated, taken from a vegetable oil plant (VOP) and from a slaughter house (SH). Only the results that demonstrated a significant reduction of TSS, FM and COD, or which were useful for the comparative analysis, were included in Table II. The most important conclusion is the following: for each waste water type there is a certain combined treatment, based upon a certain polyelectrolyte P_n, which leads to a considerable decreasing of the "fatty matter" indicator as compared with classical treatments. There are no classical treatments that have the ability to reduce the fatty matter under the level of 30 mg · dm^{-3}, established by Romanian Standard NTPA-002/2002. Also, there are many combined treatments, as are shown in Table II, which give smaller values for the TSS and COD indicators than the classical treatments.

TABLE II: COMPARATIVE RESULTS OBTAINED BY CLASSICAL TREATMENT (E_M) AND COMBINED TREATMENT (E_M+P_M)

Treatment type per dm^3 of water	**Polyelectrolyte characteristics**			**Quality indicator**		
	M_r (%)	(η_{intr}) (dl/g)	k_H -	TSS (mg.dm^{-3})	FM (mg.dm^{-3})	COD (mgO$_2$.dm^{-3})
Allowed value	-	-	-	350	30	300
Raw water: VOP-1	-	-	-	2554	***1816***	1519
E$_9$: 0.8g $FeSO_4$+ 1g $Ca(OH)_2$	-	-	-	46	***216***	107
E_9+8mgP_1	0.010	4.36	0.02	32	***26***	102
Raw water: VOP-2	-	-	-	1214	***418***	480
E$_{29}$: 0.5g $Al_2(SO_4)_3$ + 0.5g$Ca(OH)_2$	-	-	-	320	***172***	101
E_{29}+8mgP_1	0.010	4.36	0.02	12	***26***	60
E_{29}+8mgP_2	0.078	9.22	0.28	39	***30***	69
Raw water: SH -1	-	-	-	920	***6117***	256
E$_{10}$: 0.1g $Al_2(SO_4)_3$ + 0.1g$Ca(OH)_2$	-	-	-	836	***5708***	75
E$_{15}$: 0.1g $FeSO_4$ + 0.1g $Ca(OH)_2$	-	-	-	144	***3196***	70
E_{10}+6mgP_3	0.010	8.91	0.27	68	***16***	33
E_{10}+6mgP_4	0.010	9.74	0.08	58	***28***	31
E_{10}+6mgP_5	0.008	11.64	0.2	88	***18***	30
E_{10}+6mgP_6	0.006	10.24	0.11	36	***20***	29
E_{15}+6mgP_3	0.010	8.91	0.27	68	***16***	28
E_{15}+6mgP_4	0.010	9.74	0.08	64	***12***	30
E_{15}+6mgP_5	0.008	11.64	0.2	48	***32***	26
E_{15}+6mgP_6	0.006	10.24	0.11	60	***28***	39

4. Conclusions

The EB absorbed dose rate level is very important. At high dose rate levels, the polymerization process is incomplete, monomer conversion decreases, polymer parameters become very sensitive to the chemical composition and variations in absorbed dose level. The effect of high-absorbed dose rate is reduced by the additional introduction of NaCl into acrylamide-acrylic acid aqueous solutions that under irradiation markedly increases conversion coefficient to nearly 100% and decreases residual monomer concentration under 0.01%. Because the optimum absorbed dose for the acrylamide-acrylic acid aqueous solution polymerization is rather small, about 1 kGy, the use of electron accelerators is economically attractive for commercial production of the polyelectrolytes, if all auxiliary systems are made and suitably adapted. The estimation of processing rate is up to 1800 kg $\cdot$ h^{-1} for an electron beam power of 1 kW and for an EB power utilization factor of 0.5.

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