HEAVY METALS REMOVAL FROM CONTAMINATED WATER USING POLY(ACRYLAMIDE-CO-ACRYLIC ACID)-SODIUM ALGINATE FLOCCULANT OBTAINED BY ELECTRON BEAM IRRADIATION

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The goal of the paper is to present the obtaining, characterization and testing of a new type of polyelectrolyte based on acrylamide, acrylic acid and sodium alginate for flocculation purposes. Polyelectrolytes, also called flocculants, were obtained by electron beam irradiation in atmospheric conditions and at room temperature. They have been characterized using various physical and chemical methods in order to determine conversion coefficient, residual monomer content, intrinsic viscosity and molecular weight. The heavy metals removal (Cu^{2+} and Cr^{6+}) was evaluated at room temperature on synthetic water having the contents of 0.05 wt/vol % $CuSO_4$ and 0.05 wt/vol % $K_2Cr_2O_7$, respectively.

Keywords: flocculants, heavy metals, electron beam

INTRODUCTION

Over the past decades, increasing effort has been concentrated on developing various methods that can effectively remove heavy metal ions from aqueous environments. There are many methods for removing heavy metals that include chemical precipitation adsorbents (Meunier *et al*., 2006), membrane filtration adsorbents (Bessbousse *et al*., 2008), ion exchange adsorbents (Alyuz and Veli, 2009), liquid extraction adsorbents (Sprynskyy, 2009), reverse osmosis adsorbents (Liu *et al*., 2008), activated carbon adsorption adsorbents (Ucer *et al*., 2006) and the use of biopolymer adsorbents (Guclu *et al*., 2003). 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 is the phenomenon in which the system consisting of colloidal particles from water is destabilized. 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. Flocculants are of two types, i.e., inorganic and organic. The organic flocculants are essentially polymeric in nature. Both, synthetic and natural water soluble polymers are used as flocculants. The synthetic polymers are mostly linear and water soluble, such as polyacrylamide, polyacrylic acid, poly(diallyl dimethyl ammonium chloride) or poly(styrene sulphonic acid). They are available in all the three forms, i.e., cationic, anionic and non-anionic. High molecular weight synthetic polymers like polyacrylamides are very effective flocculating agents. However these polymers are quite unstable in shear fields and hence lose their flocculation effectiveness. The natural polymers like polysaccharides exhibit good resistance to shear degradation, but they are less effective flocculating agents compared with synthetic polymers and their aqueous solutions are also susceptible towards biodegradation (Tripathy and De, 2007).

The goal of the paper is to present the obtaining, characterization and testing of a new type of flocculant based on acrylamide, acrylic acid and sodium alginate for flocculation purposes. In the present study, the alginate - one of the most nontoxic sulphated polysaccharides - has been chosen as a backbone. The flocculants were obtained by electron beam irradiation (EB) using doses in the range of 2 kGy to 10 kGy in atmospheric conditions and at room temperature. They were characterized by various physical and chemical methods in order to determine conversion coefficient, residual monomer content, intrinsic viscosity, molecular weight and radius of gyration. The heavy metals (Cu^{2+} and Cr^{6+}) removal efficacy was evaluated at room temperature.

EXPERIMENTAL

Materials

In order to obtain the flocculants, the following materials have been used: acrylamide - AMD (molar mass of 71.08 g mol^{-1}; density of 1.13 g/cm^3); acrylic acid - AA (molar mass of 72.06 g mol^{-1}; density of 1.051 g/mL), sodium alginate - SA (molar mass of 216.12 g mol^{-1}) and potassium persulfate (molar mass of 270.322 g mol^{-1}; density of 2.477 g/cm^3) - used as initiator in the copolymerization process. All materials were from E-Merck, Germany.

Preparation and Irradiation of the Samples

Two different types of aqueous solutions based on acrylamide, acrylic acid and sodium alginate for the irradiation experiments were prepared: (a) the first type based on acrylamide (20 wt/vol %, acrylic acid 20 vol/vol % and sodium alginate 2 wt/vol %) noted POL-I and (b) the second type on acrylamide (20 wt/vol %, acrylic acid 20 vol/vol %, sodium alginate 2 wt/vol % and sodium persulphate 0.2 wt/vol %) noted POL-II. Each mixture was stirred at 250 rpm at room temperature for 30 min. 5 ml from each type of solution was then transferred into 50 cm^3 glass tubes and irradiated using electron beam with various doses in atmospheric conditions and at room temperature of 25°C. Electron beam dose rate was fixed at 2 kGy/min in order to accumulate irradiation doses between 2-10 kGy.

Experimental Installation and Sample Irradiation

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 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}.

Sample Characterization (Physical and Chemical Characteristics)

In order to determine the conversion coefficient (CC) and the residual monomer concentration (M_r), 2 grams of polymer (flocculant) were placed in 200 ml distilled water for 24 hours and then every sample was stirred for 1 hour at 400 rpm to ensure a very well mixing. CC and M_r were determined by titrimetric method. The intrinsic viscosity ($\eta_{intr.}$)

and the Huggin's constant (k_H) were determined by the viscosity measurements, using the Hoppler type BH-2. Hoppler viscometer is a falling ball one. The measured parameter is the time of fall of the ball in a cylindrical tube inclined by 10 deg with respect to the vertical plane and filled with the liquid subjected to investigation. The principle of falling-ball viscosimeters is based on the fact that the viscosity of liquid modifies the speed of the ball falling through this liquid. The time of fall of the ball through the polymeric solution was measured for five different concentrations. As a solvent, the sodium nitrate 1N ($NaNO_3$) was used and the working temperature was of 30°C. Using the time of fall of the ball through the polymeric solution (t) and the time of fall of the ball through the solvent (t_0) the relative viscosity was obtained:

$$\eta_{rel.} = t / t_0 \quad (1)$$

Specific viscosity was calculated from the relation:

$$\eta_{sp.} = (\eta_{rel.} - 1) \quad (2)$$

Reduced viscosity was determined using the relation:

$$\eta_{red.} = \eta_{sp.} / c \quad (3)$$

where *c* is the polymer concentration (g/dL).

From the graphical representation of the η_{red} as a function of the copolymer concentration, by extrapolation, was obtained the intrinsic viscosity η_{intr} and tgα. Linearity constant was determined from the following relation:

$$k_H = tg\alpha / [\eta_{\text{int}r.}]^2 \quad (4)$$

Intrinsic viscosity is a measure of the hydrodynamic volume occupied by the individual polymer molecules in isolation (Richardson and Kasapis, 1998). In dilute solutions, the polymer chains are separate and the [η_{intr}] of a polymer in solution depends only on the dimensions of the polymer chain. From the Mark-Houwink equation, the relationship among the molecular weight and viscosity is given below:

$$[\eta] = K \times M_w^a \quad (5)$$

where [η] is the intrinsic viscosity (dl/g), M_w is viscosity average molecular weight, K and *a* are constants for a particular polymer – solvent system (K and *a* are $3.73*10^{-4}$ and 0.66 in 1N aqueous sodium nitrate at 30°C) (Richardson and Kasapis, 1998; Zeynali and Rabbii, 2002).

Flocculation Studies

Water samples containing Cu^{2+} and Cr^{6+} were synthesized using $CuSO_4*5H_2O$ (0.1 mol/l), $K_2Cr_2O_7$ (0.05 wt/vol %), kaoline (0.2 wt/vol %) and distilled water. The jar test apparatus (Velp FC 6S, Italy) consists of 6 stirrer blades connected to a variable speed (0-100 rpm) motor through a gear system. In each beaker, 500-mL of synthetic water (with Cu^{2+} or Cr^{6+}) was taken and placed on the flocculator. Under a slow stirring condition, the polymer solution was added by means of a pipette in order to determine the polymer concentration influence (5-20 ppm). Immediately after the addition of polymer solution, the suspensions were stirred at a constant speed of 60 rpm for 15 min, and than allowed to sediment for 15 min. Clear supernatant was drawn from the top layer (up to depth 1-2 cm) and its absorbance at 275 nm for Cu^{2+} (Wen *et al*., 2013) and 540 nm for Cr^{6+} (Iva and Zeiner, 2008) was measured using the Cary Bio-100 UV-VIS spectrophotometer. The heavy metals (Cu^{2+} and Cr^{6+}) removal was evaluated from the calibration curves. For dilute solutions, there is a linear relationship between absorbance and concentration.

RESULTS AND DISCUSSION

Physical and Chemical Characteristics

In Figures 1-5 are represented the conversion coefficient (CC), the residual monomer concentration (M_r), the intrinsic viscosity ($\eta_{intr.}$), the linearity constant (k_H) and the molecular weight (M_w) depending on the absorbed dose, for all the 10 samples subjected to electron beam irradiation.

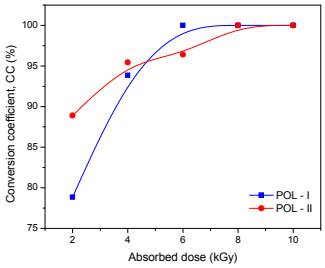


Figure 1. Conversion coefficient of the flocculants versus EB absorbed dose

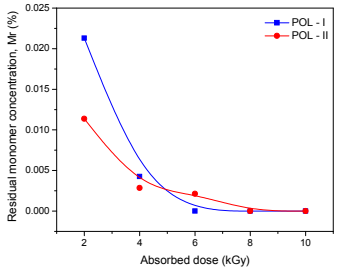


Figure 2. Residual monomer concentration of the flocculants versus EB absorbed dose

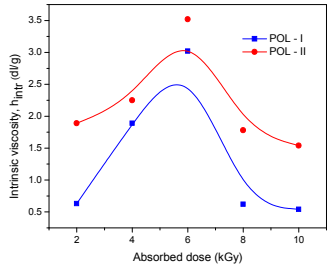


Figure 3. Intrinsic viscosity of the flocculants versus EB absorbed dose

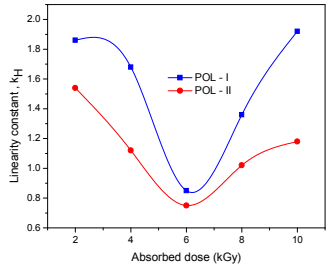


Figure 4. Linearity constant of the flocculants versus EB absorbed dose

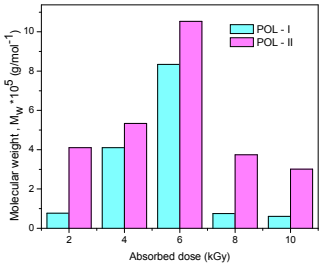


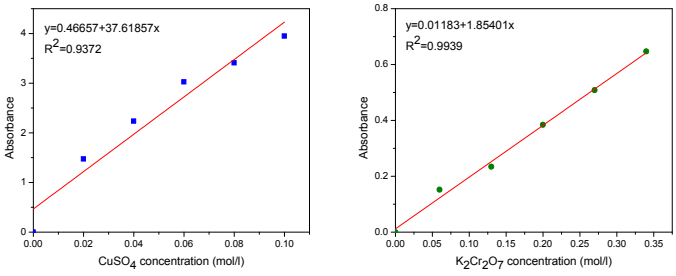
Figure 5. Molecular weight of the flocculants versus EB absorbed dose

The solutions subjected to EB irradiation have lead to the obtaining of polymers having relatively high conversion coefficients and molecular weights, especially at the upper limit of the used dose range (2 kGy - 10 kGy). Also, all the samples have presented low residual monomer in the polymer (<0.05%, which is the limit imposed by

the standards of use of AMD as a flocculant) and a good linearity. It was found that the CC has increased with increasing of absorbed dose. The probability of molecular contact became higher with increasing of the absorbed dose, more polymer molecules react, resulting in the propagation of the active chain and the continuously CC increasing. Intrinsic viscosity of a polymer is indicative of its hydrodynamic volume in solution, which depends on its molecular weight, structure and nature of the solvent as well as the temperature of the medium. For two polymers with approximately similar molecular weights, the branched polymer has lower hydrodynamic volume compared to its linear counterpart and thus has lower intrinsic viscosity value. Furthermore, long branches determine higher intrinsic viscosity and vice versa (Xie *et al.*, 2009).

Flocculation Results

By UV–VIS spectrophotometry it is possible to easily determine the concentration of different heavy metals from water samples. The disadvantage is the relatively low linear working range, as can be observed in Figure 6. Two types of samples have been tested for Cu^{2+} and Cr^{6+} removal: POL – I and POL – II, both obtained at 6 kGy. We chose to use these samples, because all physical properties have maximum values. The results are presented in Figure 7. The Cu^{2+} and Cr^{6+} removal from synthetic water was done by determining the concentration of both metals from water using the spectrophotometric method and calibration curves.



(a) (b)

Figure 6. Calibration curve for (a) Cu^{2+} and (b) Cr^{6+}

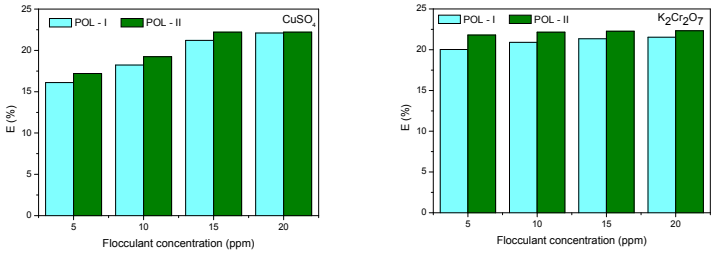


Figure 7. Heavy metals removal efficiency as a function of flocculant concentration

The heavy metals removal performance is presented in terms of "efficiency" calculated as follows:

$$E(\%) = \frac{C_0 - C_1}{C_0} \times 100 \quad (6)$$

where C_0 is the initial heavy metals concentration (Cu^{2+} and Cr^{6+}) and C_1 is the heavy metals concentration after flocculation.

Four concentrations from each flocculant were used, obtained from stock solutions of 0.1%, 5, 10, 15, and 20 ppm, respectively. In Figure 7 the heavy metals removal efficiency is represented as a function of the flocculant concentration and it is observed that the flocculation efficiency has increased with the concentration of flocculant.

CONCLUSIONS

This study was carried out to illustrate the synthesis of poly[acrylamide-co-acrylic acid]-sodium alginate flocculants in presence and absence of initiator under the effect of electron beam irradiation. For the samples obtained this way it was found that the conversion coefficient (CC) and residual monomer concentration M_r shows a linear dependence on radiation dose, while the intrinsic viscosity ($\eta_{intr.}$), the linearity constant (k_H) and the molecular weight (M_w) shows good values only in the middle of dose range. From the flocculation studies, in order to determine the heavy metals removal efficiency, it is observed that the flocculation efficiency has increased with the concentration of flocculant and also that the best results correspond with the use of flocculants obtained in the presence of initiators.

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