Photo-oxidative Degradation of Polyacrylamide in Wastewater

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Introduction

Water soluble polymers are popular in industry; they are produced in large scale with a wide spectrum of applications. Acrylamide polymers represent almost 25% of the total world consumption of synthetic water soluble polymers. They are widely used as a flocculants, coagulants, thickeners, lubricants, and paint dispensers.

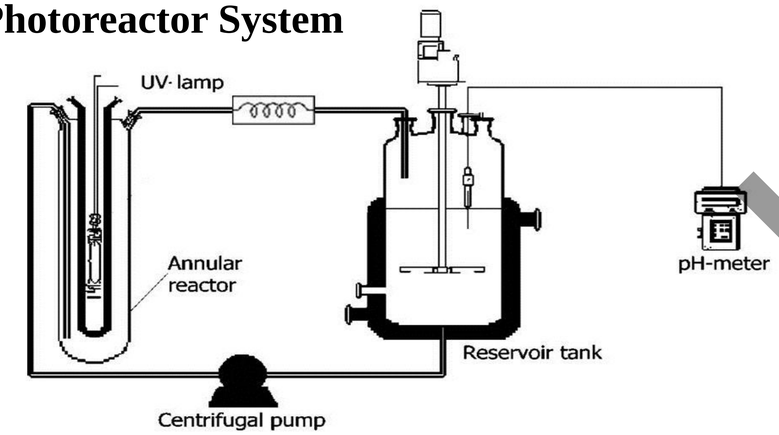
Industrial effluents of polyacrylamide (PAM) end up into wastewater while they are non-biodegradable. Therefore; they evidently contaminate water resources, thus creating obvious pollution concerns. Health and environmental regulations require a complete treatment of PAM.

Advanced oxidation by UV/H_2O_2 process is applied to degrade PAM in aqueous solution. Generated radicals can react with persistent polymers transferring them into intermediate products which can be degraded much more easily towards water and carbon dioxide.

Research Objectives

- Conduct a series of photo-oxidative degradation (Depolymerization) reactions for polyacrylamide in aqueous solution by UV/ H_2O_2 process.
- Investigate the effects of initial polymer concentration, initial H_2O_2 dosage, pH, and recirculation rate on the rate of degradation.
- Develop a mathematical model that uses discrete distributions to represent degrading polymer populations by chain end scission.
- Validate the model.

Photoreactor System



Parameter		Value
Reactor	Type	Batch,with recirculation
	Inner diameter	2.44cm
	Outer diameter	5.11cm
	Length	30.5 cm
Reservoir tank volume		3 liter
Circulation flow rate		5 lit/min
Lamp	Type	Germicidal UV
	Radiation wavelength	254 nm
	Length	20.5 cm
	Power	15 W
Temperature		25 ◦C
Pressure		1 atm
Polyacrylamide initial concentration		50 mg/lit
Hydrogen peroxide dosage		700 mg/lit

Mechanism of Formation of Hydroxyl Radicals from H_2O_2

$$H_2O_2 + h\nu \xrightarrow{\phi 1} 2\,[\cdot OH]$$

$$[\cdot OH] + H_2O_2 \xrightarrow{\kappa_1} [HO_2^{\cdot}] + H_2O$$

$$H_2O_2 + HO_2^{\cdot} \xrightarrow{\kappa_2} [\cdot OH] + H_2O + O_2$$

$$[\cdot OH] + [\cdot OH] \xrightarrow{\kappa_3} H_2O_2$$

$$[HO_2^{\cdot}] + [\cdot OH] \xrightarrow{\kappa_4} H_2O + O_2$$

$$[HO_2^{\cdot}] + [HO_2^{\cdot}] \xrightarrow{\kappa_5} H_2O_2 + O_2$$

Mechanism of polymer degradation by chain-end scission

$$P(x) + [\cdot OH] \xrightarrow{ke_1} R_e^{\cdot}(x) + H_2O$$

$$P(x) + [HO_2^{\cdot}] \xrightarrow{ke_2} R_e^{\cdot}(x) + H_2O_2$$

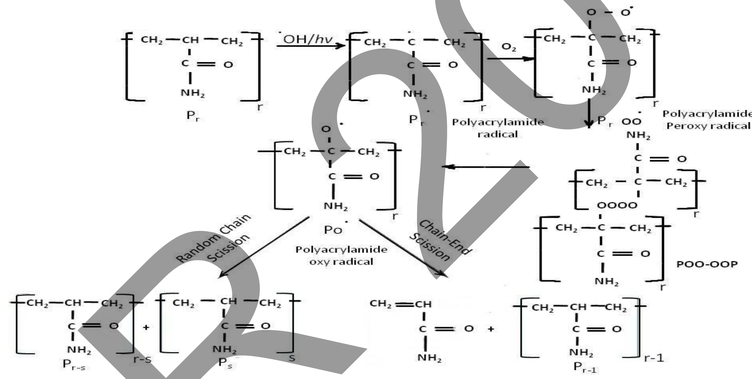
$$R_e^{\cdot}(x) \xrightarrow{ke_3} R_e^{\cdot}(x\text{-}x_m) + M(x_m)$$

$$R_e^{\cdot}(x\text{-}x_m) + R_e^{\cdot}(x_m) \xrightarrow{kte_1} P(x)$$

$$R_e^{\cdot}(x_m) + [\cdot OH] \xrightarrow{kte_2} M(x_m) + H_2O_2$$

$$R_e^{\cdot}(x_m) + [HO_2^{\cdot}] \xrightarrow{kte_3} M(x_m) + H_2O$$

Degradation mechanism for PAM by UV /H_2O_2



Mathematical Model

$$\frac{dp_r}{dt} = -k\,(p_r - p_{r+1})$$

$$P_r(x,t) = \sum_{r=2}^{N} P_r(t)\,\delta(x - rx_m)$$

$$\boxed{P_r(\theta) = \frac{PN_\circ\,\theta(N-r)\,exp(-\theta)}{(N-r)!}} \qquad 2 \le r \le N \qquad \text{,where } \theta = kt$$

$$P^{(0)} = P_N(0)$$

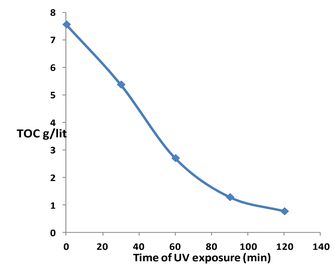
$$P^{(1)} = x_m\,P_N(0)\,(N - \theta)$$

$$P^{(2)} = x_m^{\,2}\,P_N(0)\,[\,\theta + (N - \theta)^2]$$

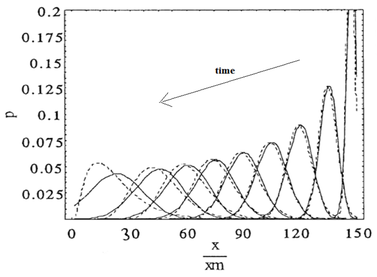
$$M_n = x_m\,(N - \theta)$$

$$M_w = x_m\,[\,1 + (N - \theta)^2]/\,N - \theta$$

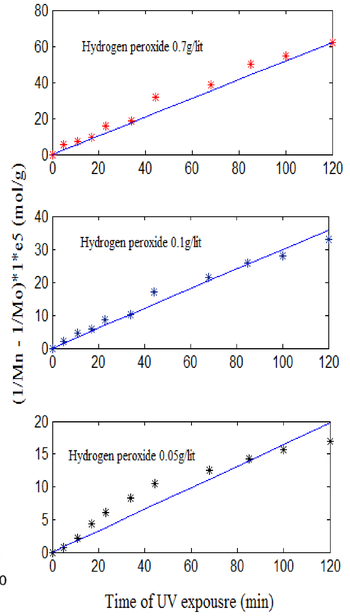
Results



Variation of TOC for PAM solution as a function of treatment time



Time evolution (θ) of MWD, P_N for chain-end depolymerization



Variation of Mn with time for PAM degradation by UV in the presence of different concentration of hydrogen peroxide

Concluding Remarks

- Experimental results indicate that it is technically feasible to degrade polyacrylamide in aqueous solution by photo-oxidative degradation utilizing UV/H_2O_2 process.
- The breakage population balance equation provides a simple mean to analyze the change of molecular weight distribution during polymer degradation processes.
- For the discrete distribution of the chain-end scission, the fragmentation process will eventually stops as the system becomes composed entirely of monomers .
- At 20mg/l polyacrylamide with molecular weight of $1.1*10^4$ g/mol, 700mg/l H_2O_2, pH4,and 1lit/min recirculation rate, 89% TOC removal was achieved after 2 hours of reaction.
- Accordingly, the number and weight average molecular weight were 1400, 2500 g/mol respectively.

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