Chapter from the book *Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update*

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1. Introduction

1.1 Production and possible hazards of hydrating polyacrylamide (HPAM) pollutants

In recent years, many Chinese oilfields have been in their mid- or final-stage of development. The oil recovery cannot be improved further with water flooding. Enhanced oil recovery (EOR) by means of polymer flooding is an important technology for the strategic development of oilfields in China. In order to improve the oil recovery, polymer flooding (injected water containing polymer), alkaline-surfactant-polymer flooding (injected water containing alkaline, surfactant and polymer, ASP) and surfactant-polymer flooding (injected water containing surfactant and polymer) have subsequently been used in oil production, which is often called tertiary oil extraction (Han et al., 1999). The liquid which is produced from stratum should be dehydrated using three-phase separators, and then, the crude oil of upper layers will be carried to the oil refinery, and the produced water (oily water) of under layer is generated. A large part of produced water should be injected back into the stratum for reuse (Taylor et al., 1998; Zhang et al., 2010), and the rest will be discharged into water bodies or surrounding soils.

In crude oil exploitation, water-soluble, polyacrylamide (PAM) is one of the most widely used polymers to enhance oil recovery in the east oilfields of China. The produced water from polymer flooding (PWPF) which contains a lot of residual hydrolyzed polyacrylamide (HPAM) is the wastewater of polymer flooding. And PWPF which is also characterized by its high temperature, heavy metals, high mineralization, low biodegradability and high content of oil and other oilfield chemicals (OCs), is different from that produced from water flooding. Moreover, partially hydrolyzed polyacrylamide (HPAM) present in production water causes some problems. For example, after polymer flooding, HPAM will remain in the produced water generated by oilfields, increasing the difficulty in oil-water separation. Consequently, the oil content in sewage is greatly increased, and there is a high probability that the wastewater will exceed the local discharge limit. When HPAM enters an oil reservoir with injected water, it can also hardly avoid infiltrating groundwater horizontally in connection with strata configuration. In addition, the costs and difficulties of produced water treatments will be increased because of the high concentration of the HPAM remaining in the wastewater. Furthermore, the residual HPAM in the wastewater can
slowly degrade into the toxic acrylamide monomer naturally. The toxicity of acrylamide monomer has been studied by numerous researchers all over the world (Bao et al., 2010). Since HPAM can remain in surface water and groundwater for a long period of time, it may endanger human health. Therefore, it is necessary to conduct studies on transforming HPAM into innocuous substance effectively and rapidly.

1.2 Study progress on treatment of HPAM pollutants in wastewater
With the amount of HPAM residue increasing in the produced fluid, the separation of oil from water is more and more difficult and the treating difficulty becomes stern. Therefore, the effective treatment on the wastewater became urgent and important. Some methods have been used to treat it in some oil fields, such as gravity settling, floatation (Thoma et al., 1999), de-emulsification (Bilstad & Espedal, 1996) and membrane separation (Cheryan & Rajagopalan, 1998; Kong & Li, 1999; Scholz & Fuchs, 2000) and biotechnology (Li et al., 2005; Zhao et al., 2006; Su, 2007). The research progress of HPAM wastewater treatment methods is reviewed in this paper, which include the coagulation treatment method, membrane treatment method, photocatalysis degradation method and photo-Fenton treatment method.

1.2.1 Coagulation treatment process of HPAM in wastewater
At present, the most applicable and effective method is flocculation. The general operation is adding flocculant to the settling tanks in the existing treatment systems to accelerate oil-water separation. There are two kinds of flocculants, inorganic and organic. The typical inorganic flocculant is polyaluminum chloride (PAC) and the organic is cationic polyacrylamide (CPAM), which play an important role on wastewater treatment (Zhao et al., 2008).

The influences of HPAM residue on the flocculation behavior of wastewater from polymer flooding had been investigated by Zhao (Zhao et al, 2008). The main conclusions from their work were listed as the following:
1. Using PAC as inorganic flocculant, the flocculation performance improved with the increase of temperature under the same dosage. At 37°C and 40°C, flocculation results were markedly better than that of 30°C and 33°C. The floc formed quickly and the treating cost was low. However, the floc was much, tiny, loose and unstable.
2. Using CPAM as organic flocculant, the flocculation performance decreased with the increase of temperature under the same dosage. Compared with PAC, the floc was less and more stable. However, the treating results were poor and the cost was expensive.
3. At the constant temperature and dosage, the flocculation performance of PAC and CPAM decreased dramatically with the content of residual HPAM. At 37°C, when HPAM residue in wastewater increased from 100mg/L to 600mg/L, the light transmission decreased from 96.4% to 70% after treating with PAC at the dosage of 600mg/L and from 87.3% to 50.0% with CPAM at the dosage of 150mg/L.

1.2.2 Ultra-filtration membrane treatment technologies for the HPAM-containing wastewater
Unfortunately, none of these traditional separation techniques can meet complex demands for purifying the polymer-flooding wastewater of tertiary oil extraction. How to treat the oilfield polymer-flooding wastewater efficiently still remains unsettled.
Currently, ultrafiltration technology plays a more prominent role in the treatment of oily wastewater (Wu et al., 2008; Lu et al., 2009). However, the major problem arising from the membrane process is the decline in flux due to the concentration polarization and membrane fouling. The scientific practice suggests that the membrane fouling can be avoided (Field et al., 1995) when the operating flux is lower than a certain flux (critical flux). In contrast, when the operating flux exceeds this flux, the colloids initially present in the polarized layer will transform from the liquid phase into an irreversible cake layer (Chen et al., 1995; Bacchin et al., 2002a, 2002b). Since then, many studies have focused on the critical flux, including the effect of hydrodynamic factors such as cross-flow velocity (CFV) (Defrance & Jaffrin, 1995), sufficient shear stress (Li et al., 2000), sludge concentration (Le-clech, 2003) and particle size (Kwon et al., 1998; Kwon, 2000) on the critical flux for colloidal suspension, mineral suspension (Benkahla et al., 1995), protein or yeast suspension (Causserand et al., 1996) and activated sludge water (Bouhabila et al., 1998). As the study of the critical flux, the membrane resistance at sub-critical flux was investigated all along (Cho et al., 2002; Ognier et al., 2004). In addition, Chiu et al. (Chiu et al., 2005) reported that the gas could be used as a means of enhancing the critical flux in a non-circular multi-channeled (star-shaped) ceramic membrane module. Chong et al. (Chong et al., 2008) developed a sodium chloride tracer response technique to determine the critical flux of colloidal silica in reverse osmosis process.

In view of the characteristics of oilfield produced water quality, Wang (Wang et al., 2011) used the ultrafiltration membrane technique to treat synthetic oilfield polymer-flooding wastewater. In the experiment of fouling mechanism research, the first part and second part of filtration met the standard blocking and cake filtration model respectively. But the standard blocking period was very short at the beginning and the cake filtration period predominates in all filtration run. The critical flux was determined by transmembrane pressure (TMP)-step method in dead-end ultrafiltration test cell. The total fouling resistance increased with the increase of TMP. When the operating flux was below the critical flux, there was only concentration polarization phenomenon. The increasing trend of membrane resistance with the increase of TMP was unconspicuous. The intrinsic membrane resistance was the dominant resistance and the membrane fouling force was negative in this situation. And the filtration proceeds reached the biggest value. But once the operating flux exceeded the critical flux, the membrane pollution happened and the increasing rate of resistance accelerated.

The fouling resistance was the dominant resistance and the membrane fouling driving force became positive and higher. Moreover, the filtration proceeds were smaller and smaller. In the experiments of quantitative analysis of the critical flux, according to comparative results of the average rates of change of the critical flux for the concentration of HPAM, oil and suspended solid in the single solute solution, double solute solution and oilfield polymer-flooding wastewater, HPAM can decrease the average rate of change of the critical flux for oil and suspended solid. It has the crucial effect on the critical flux. The sequence of influence degree on the critical flux is the HPAM concentration > oil concentration > SS concentration and the percentage contribution is 84.58%, 14.36% and 1.06% respectively in the oilfield polymer-flooding wastewater. SEM images indicated that there was no membrane fouling formation at constant sub-critical flux. In contrast, the membrane was covered with a cake layer on the top surface of the membrane and the interaction between the particles and the membrane pore caused the pore narrowing, constriction and plugging at a constant supra-critical flux.
1.2.3 Photocatalysis degradation of HPAM in wastewater

Advanced oxidation processes (AOPs) are defined as oxidation processes in which hydroxyl radicals are the main oxidants involved. This radical is a very powerful oxidant ($E^0$: 2.80V versus SHE) which leads to a very effective oxidation process, such as Fenton and photo-Fenton catalytic reactions, $H_2O_2$/UV processes and TiO$_2$ photocatalysis (Faouzi et al., 2006). Among the AOPs, heterogeneous photocatalysis oxidation using TiO$_2$ as photocatalyst has been extensively studied because of its low cost, high photoactivity, nontoxicity, photocorrosion resistance and other physical and chemical properties, and proved to be efficient and potentially advantageous. This semiconductor absorbs photons whose energy is higher than or equal to the band-gap energy. Thus, valence band electrons are promoted into the conduction band generating an electron-hole pair ($e^-/h^+$). These pairs are able to initiate oxidation and reduction reactions in the surface of TiO$_2$. The positive holes can oxidize the organic molecules adsorbed, through the formation of •OH radicals. Simultaneously, the photogenerated electron can produce radical species such as superoxide •O$_2^-$ and hydroperoxide •HO$_2$. All these radicals initially oxidize the substrate in intermediate compounds which subsequently undergo a total mineralization in most of the cases (Serpone & Pellizzetti, 1989; David & Ollis, 2000).

The interest in photocatalysis is extensive, as shown by the number of publications on this subject which regularly appear in some journals, and thousands of papers have been published since the 1970s. Photocatalysis has come to describe the field of study and the technology in which irradiated semi-conductors generate photocharges that are ultimately poised at the surface. These photocharges undergo various processes, the most important of which are effectively separated and transferred to the contacting liquid, gas or solid for photooxidation of a large variety of organic substances to their complete mineralization. Wang et al. early works (Wang et al, 2006) discovered that TiO$_2$ particles can be self-potentially absorbed and orientedly arranged onto oil-water interface of emulsions. While the TiO$_2$ particles on the oil-water interface and in bulk water can be photocharged by UV radiation, reactive photoholes generated by photocatalytic process primarily oxidize the touched organic substances and damage the film between oil and water.

In their paper, Wang et al. (Wang et al, 2006) reported on a novel approach efficiently to achieve viscosity breaking of wastewater containing PAM. Initially by analyzing emulsification action and role of PAM in the wastewater, a process using photocatalytical technique was investigated by taking aim at viscosity breaking and degradation of PAM. Wang et al. refer to this process as “photocatalytical visbreaking”. The experimental results show that viscosity of wastewater produced from polymer flooding was greatly decreased and the rate of PAM photodegradation is above 90% under short time of illumination by using photocatalysis over TiO$_2$ powders. The efficient breaking of viscosity favors treatments to feed the conventional system used in the water flooding with low viscosity of wastewater. The photocatalytic visbreaking can promisingly be used by efficient performance in oilfields. Chen et al. also think that it is a good method to treat PAM in water by photocatalytic oxidation (Chen et al., 2001).

Recently, the photocatalysts prepared by doping of rare earth oxides into anatase TiO$_2$ matrix have attracted much attention. TiO$_2$ is considered as a good host candidate for doping rare earth oxides due to its attractive properties such as mechanical, thermal, and anticorrosive properties. It is well known that the surface composition and structure of photocatalyst can greatly influence its activity. Some important results have been achieved by studies on the rare earth oxide-doped TiO$_2$ composites. For example, Saif et al. (Saif &
Abdel-Mottaleb, 2007) reported that TiO$_2$ nanocomposites doped with trivalent lanthanide ions (e.g. Tb$^{3+}$, Eu$^{3+}$, and Sm$^{3+}$) exhibited remarkable enhanced photocatalytic activity to textile dye degradation compared to pure TiO$_2$. Yan et al. reported that rare earth oxide-doped TiO$_2$ composites increased conversion of phenol and selectivity to CO$_2$ compared with pure TiO$_2$. Although some successful methods have been reported concerning about the preparation of the rare earth oxide-doped TiO$_2$ composites, new routes still need to be developed in order to lead to the composites with nanoscale, unique physicochemical properties, and interesting surface compositions. In current Li’s work (Li et al., 2009), a single step sol-gel-solvothermal method is applied to prepare rare earth oxide-doped titania nanocomposites, RE$^{3+}$/TiO$_2$, where RE$^{3+}$=Eu$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Gd$^{3+}$, and Y$^{3+}$. The morphology, phase structure, surface composition and structure, optical property, and textural property of the composites are well characterized. As-prepared Eu$^{3+}$-, Pr$^{3+}$-, Gd$^{3+}$-, Nd$^{3+}$-, and Y$^{3+}$-doped TiO$_2$ composites with anatase phase, nanosize, and mesoporosity exhibited remarkably high UV-light photocatalytic activity to HPAM degradation. Moreover, Eu$^{3+}$ (Pr$^{3+}$, Gd$^{3+}$)/TiO$_2$-2.4 were the most photoactive among all tested materials including Degussa P25. This enhanced photocatalytic activity is attributed to the following properties of as-prepared RE$^{3+}$/TiO$_2$ composites: (a) quantum size effect; (b) unique textural properties (mesoporosity with larger BET surface areas and pore sizes); and (c) interesting surface compositions (more hydroxyl oxygen and adsorbed oxygen and some Ti$^{3+}$ species existed at the surface of the products with respect to pure TiO$_2$). As-prepared photocatalysts are also essential for any practical application of photocatalytic oxidation process.

1.2.4 Photo-Fenton treatment of simulated HPAM in wastewater

Recently, some investigators have reported the successful application of advanced oxidation processes (AOPs) for PAM degradation (Vijayalakshmi & Giridhar, 2006; Ren & Chunk, 2006). One of advanced oxidation processes, Fenton’s reagent, a mixture of H$_2$O$_2$ and Fe$^{2+}$ (a powerful source of oxidative •OH generated from H$_2$O$_2$ in the presence of Fe$^{2+}$ ions) or photo-Fenton reaction has been used in the degradation of many organic compounds because of its ease of operation (Murray & Parsons, 2004; Yardin & Chiron, 2006). The iron is the first most abundant metal and contained in many inexpensive natural minerals including tourmaline used in this study. Furthermore, hydrogen peroxide used as oxidant in these processes is cheaper than other oxidants.

In our study, we investigated the photo-assisted Fenton (photo-Fenton) reaction for its ability to oxidize HPAM. The photo-assisted Fenton can promisingly be used by efficient performance in oilfields. Effects of operating parameters such as initial hydrogen peroxide concentration, ratio of Fe$^{2+}$/H$_2$O$_2$ (mole ratio), HPAM concentration, and pH on the degradation rate of HPAM have been quantitatively discussed. The experimental data demonstrated that photo-Fenton processes are promising techniques for the degradation of HPAM from aqueous solution. Based on the results, the following conclusions can be drawn.

1. Fenton and photo-Fenton processes lead to complete degradation of HPAM in relatively short time (~30 min).
2. The optimal parameters for photo-Fenton process are: pH=3.0, the ratio of Fe$^{2+}$/H$_2$O$_2$=1:10 (mole ratio) and amount of H$_2$O$_2$=6 mmol/L.
The employment of the UV lamp benefits the HPAM degradation. So, it is possible to conclude that the UV lamp, though has little power, is very useful in Fenton process to increase the HPAM degradation. More results can be obtained in Li’s study (Li, et al., 2006; Li, et al., 2007).

Even though these systems are considered as a very effective approach to remove organic compounds, it should be pointed out that there is a major drawback because the post-treatment of Fe sludge is an expensive process. This shortcoming can be overcome by using heterogeneous photo-Fenton reaction. Therefore, a lot of effort has been made in developing heterogeneous photo-Fenton catalysts. For example, Parra et al. prepared Nafion/Fe structured membrane catalyst and used it in the photo-assisted immobilized Fenton degradation of 4-chlorophenol (Parra et al., 2004). However, Nafion/Fe structured membrane catalyst is much expensive for practical use. Thus, the low cost supports such as the C structured fabric (Parra et al., 2003; Yuranova, 2004), activated carbon (Ramirez, 2007), mesoporous silica SBA-15 (Calleja et al., 2005; Martinez et al., 2007; Martine et al., 2005), zeolite (Noorjaha et al., 2005; Kusic et al., 2006) and clay (Feng et al., 2006; Chen & Zhu, 2007), have been used for the immobilization of active iron species. Ramirez et al. prepared the catalysts using four iron salts as precursors for the heterogeneous Fenton-like oxidation of Orange II solutions (Ramirez et al., 2007). The results showed that the nature of the iron salt had a significant effect on the process performance. So, it is necessary to discuss the photocatalytic activities of the catalysts by using different iron salts as precursors.

Liu (Liu et al., 2009) prepared a series of Fe(III)-SiO$_2$ catalysts at different OH$^-$/Fe mole ratio and by using two iron salts as precursors, namely Fe(NO$_3$)$_3$ and FeSO$_4$ and as-prepared catalysts were characterized by the BET, XRD and XPS method. The percentage of chemisorbed oxygen on the surface of catalysts prepared by FeSO$_4$ is higher than that prepared by Fe (NO$_3$)$_3$. The results confirm the formation of Fe (II)-SiO$_2$ when Fe (III)-SiO$_2$ was irradiated by photon. The photocatalytic activities of Fe (III)-SiO$_2$ catalysts were evaluated by the degradation of PAM from aqueous solution in the photo-Fenton reaction and all the catalysts exhibited a better photocatalytic activities. However, the precursor species and the OH$^-$/Fe mole ratio have influence on the photocatalytic activities of the catalysts. At the same OH$^-$/Fe mole ratio, the catalysts could present the better photocatalytic activities when using FeSO$_4$ as precursor. The best efficiency for the degradation of PAM in heterogeneous photo-Fenton reaction was 94.0% degradation in 90 min and 70.0% TOC removal in 180 min at an initial pH of 6.8. Moreover, it was observed that Fe leaching from Fe(III)-SiO$_2$ catalysts was negligible, indicating that the catalysts have a long-term stability and the degradation of PAM from aqueous solution are almost caused by the heterogeneous photo-Fenton reaction.

2. Sono-photocatalytic degradation of hydrating polyacrylamide in wastewater

Recently, some investigators have reported the successful application of advanced oxidation processes (AOPs) for HPAM degradation (Vijayalakshmi & Giridhar, 2006; Ren et al., 2006). One of advanced oxidation processes, photocatalytic degradation has been used in the degradation of many organic compounds and showed greatly obvious effects (Augugliaro et al., 1991). However, very few commercial applications of this technology are available at present due to low quantum efficiency and reuse of catalyst. Most of the photoinduced positive holes (h$^+$) and electrons (e$^-$) had recombined before they were trapped by hydroxyl
or oxygen and quantum efficiency was usually less than 5%. In order to enhance the quantum efficiency, many measures were taken. Recently, the sonochemical method has been proven to be a useful technique (Hu et al., 2004). Sonolysis is a relatively innovative advanced oxidation processes based on the use of low to medium frequency (typically in the range 20-1000 kHz) and high energy ultrasound to catalyze the destruction of organic pollutants in waters. The chemical effects of ultrasound irradiation are the result of acoustic cavitation which is the formation and subsequent collapse of micro-bubbles in a liquid. At the extreme conditions generated inside the cavitation bubbles during collapse, vapor is homolytically cleaved leading to the formation of hydroxyl radicals that can oxidize the organic pollutants found in wastewaters (Vajnhandl & Marechal, 2005). Sonochemical treatment typically operates at ambient conditions and does not require the addition of extra chemicals or catalysts. The efficacy of AOPs to treat pollutants is eventually dictated by the rate of generation of free radicals and other reactive moieties and the degree of contact between the radicals and the contaminants both of which should be maximized. In this view, process integration is conceptually advantageous in water treatment since it can eliminate the disadvantages associated with each individual process. The simultaneous application of ultraviolet and ultrasound irradiation in the presence of TiO$_2$, i.e. sono-photocatalysis, represents an example of recent advances targeted at improving photocatalytic processes (Adewuyi, 2005; Gogate & Pandit, 2004). It is obvious that if the two irradiation modes are operated simultaneously, an additional source of free radicals will be available for the oxidative destruction of various pollutants.

The sono-photocatalytical degradation of a variety of organic substrates has attracted much attention. It might be also an efficient way to eliminate HPAM. However, there are only few studies investigating the sono-photocatalytic degradation of HPAM in aqueous system (Li et al., 2010a; 2011b). In this paper, HPAM was chosen as a model compound to obtain detailed information of the innovative photocatalysis. The photodegradation of the HPAM catalyzed by coupling system of ultraviolet irradiation (20 W UVA) over TiO$_2$ suspensions and ultrasound irradiation (42 kHz, 100 W) (US/UV/TiO$_2$) was investigated. Many factors are involved during the degradation of HPAM in US/UV/TiO$_2$ systems. The important operating parameters that affect the overall photocatalytic oxidation efficiency were investigated in detail, including amount of catalyst, initial concentration of reactant, and the dosage of hydrogen peroxide.

2.1 Materials and methods
2.1.1 Chemical
HPAM (Mw 500×10$^4$, hydrolysis degree 25%) was obtained from Shengli oil refining and chemical plant, Shengli, China and was used without further purification. Hydrogen peroxide (H$_2$O$_2$), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were all of analytical grade and obtained from Tianjin Kermal Chemical Reagents Co. (Tianjin, China). TiO$_2$ photocatalyst (64.5% anatase, 35.5% rutile, specific surface area 40-45 m$^2$/g) was prepared by ultrasonic assisted method. The particle diameter of TiO$_2$ is 47.1-67.5 nm. The density is 690 kg/m$^3$. All experiments were carried out with use of deionized water.

2.1.2 Apparatus
Lambda-17 spectrophotometer (US Perkin-Elmer Company) was used to inspect the degradation processes of HPAM. Branson 2510E-DTH apparatus (Branson company, US)
was adopted to irradiate the solution of HPAM, operating at an ultrasonic frequency of 42 kHz and output power of 100 W.

2.1.3 Analysis
HPAM concentration was measured by the starch-cadmium iodine method (Li et al., 2009). The temporal concentration changes of HPAM during experimental processes were monitored by measuring characteristic absorption intensity of HPAM at 590 nm. The maximal absorbency of 0-100 mg/L HPAM solution abides by Lambert-Beer's law and the calibration curve of standard HPAM solutions are used to estimate the degradation rate of HPAM. The degradation rate of HPAM was defined as follows Eq. (1):

\[
\text{Degradation rate (\%) = (1-\frac{C_t}{C_0}) \times 100\%}
\]

Where \(C_0\) is the concentration of HPAM after adsorption equilibrium in the dark \((t=0)\), and \(C_t\) is the concentration of HPAM at reaction time \(t\) (min).

All these experiments were conducted in triplicates and the results were showed at the mean values.

2.1.4 Procedures
Experimental procedure was performed as follows: 100 mL of HPAM solution were introduced in the reaction vessel (bottom area=50 cm\(^2\)) and the appropriate amount of TiO\(_2\) was added to achieve the desirable concentration. The resulting TiO\(_2\) suspension was magnetically stirred for 30 min in the dark to ensure complete equilibration of adsorption/desorption of HPAM on the catalyst surface. After that period of time, UVA irradiation was provided by a 20 W ultraviolet lamp, which emit predominantly UV radiation at a wavelength of 254 nm, the lamp was turned on (this was taken as “time zero” for the reaction). In the experiment, the distance between the lamp and the interface irradiated by UV light is required to be 10 cm. Ultrasound irradiation was provided by an apparatus operating at 42 kHz frequency and 100 W of electric power output. Samples periodically drawn from the reaction vessel were centrifuged at 4000 rpm for 15 min to remove TiO\(_2\) particles and then subjected to analysis.

2.2 Results and discussion
2.2.1 Photocatalytic and sono-photocatalytic degradation
In order to check the feasibility of sono-photocatalysis process for the degradation of HPAM, the following control experiments were performed and the results are presented in Fig.1, ultrasound alone (US), ultrasonic degradation of HPAM in the presence of TiO\(_2\) (US/TiO\(_2\)), photocatalysis (UV/TiO\(_2\)) and sono-photocatalysis (US/UV/TiO\(_2\)) in the presence of TiO\(_2\). It is evident from Fig.1 that are relatively higher degradation of HPAM was achieved by combining sonolysis and photocatalysis than that observed during the individual processes. The preliminary experiments revealed no significant degradation of HPAM in the presence of US alone. However, an enhancement in the sonolytic reaction rate in the presence of semiconductor or particles was recently reported by Pandit et al. (Pandit et al., 2001; Shirgaonkar & Pandit, 1998) which is referred to as sonocatalysis. The suspended solids may also increase the extent of cavitation generated in solution and hence the sonochemical degradation rate by providing additional nuclei for bubble generation. Therefore, in order to study the effect of TiO\(_2\) on the sonolytic degradation of HPAM in the
absence of photo irradiation, the following experiment was conducted under the experimental conditions of [HPAM]=200 mg/L and TiO\textsubscript{2} amount of 600 mg/L, and the results obtained are shown in Fig. 1.

![Degradation rate comparison](image)

**Fig. 1.** Comparison of degradation rates of HPAM (200 mg/L) in the presence of TiO\textsubscript{2} (600 mg/L) using different processes

It was noted that about 26.7% degradation in 90 min under the sonocatalytic conditions was observed. An approximately 6.5% increase in the degradation amount observed in the presence of TiO\textsubscript{2} particles during sonolysis. This increase might be due to additional cavitation activity.

In the case of photocatalytic degradation, about 50.5% degradation (Fig. 1) was achieved in 90 min and can be explained using the general degradation mechanism available in the literature (Bhatkhande et al., 2002). The photoirradiation of the TiO\textsubscript{2} forms an electron in the conduction band and a hole in the valence band. As a consequence of such photoinduced charge separation on the semiconductor surface, electron exchange reactions occur at the water-semiconductor interface. The superoxide radical anion O\textsubscript{2}\textsuperscript{-}• is formed by interaction of photo-generated conduction band electrons with adsorbed oxygen molecules, while •OH are formed via valence band hole oxidation of adsorbed water or hydroxyl anions (Carp et al., 2004) to generate •OH that subsequently oxidize the adsorbed pollutant molecules. Holes may also directly oxidize the adsorbed organic pollutant.

However, when both the US and UV are combined (sono-photocatalysis), a significant enhancement in the degradation (77.6% in 90 min) of HPAM was observed. About 27.2% increment in the degradation under the same processing time suggests that the hydroxyl radicals formed by both the advanced oxidation processes, viz., photocatalysis and sonolysis are involved in the sono-photocatalytic degradation of HPAM.

### 2.2.2 Effects of TiO\textsubscript{2} dosages on the degradation rate

The effect of TiO\textsubscript{2} powder concentration on the photocatalytic degradation of organics in the absence of ultrasound irradiation in aqueous solution has already been studied in the literatures (Ai et al., 2005). The necessity to optimize this factor was pointed out. Catalyst concentration has an optimum value, as using excess catalyst reduces the amount of photo-energy being transferred in the medium due to opacity offered by the catalyst particles. Fig. 2 shows the change of HPAM as a function of reaction time in US/UV/TiO\textsubscript{2} detected at different catalyst dosages 600, 800 and 1000 mg/L. On the whole, it was observed that along
with the increase of catalyst dosage from 600 to 800mg/L, the degradation rate of HPAM in solution increased. However, the catalyst concentration amounting 800mg/L did not further enhance the degradation rate. The increased degradation is likely due to the increase of the total surface area (or number of active sites) of the photocatalysts available for photocatalytic reaction when increasing the dosage of TiO$_2$. When TiO$_2$ was overdosed, the intensity of light penetration attenuated and light scattering increased, which counteracted the positive effect coming from the dosage increment and therefore the overall performance reduced. As the concentration of TiO$_2$ reaches a certain level, the suspension with a high concentration results in a lower light transmission of the system and then effective photons are decreased. As a result, it slows down the degradation of HPAM (Zhang et al., 2005). So, 800mg/L was the optimum amount of TiO$_2$ in terms of photodegradation under our experimental condition.

![Graph](image)

**Fig. 2.** Effect of added amount of TiO$_2$ on degradation rate of HPAM

### 2.2.3 Effect of initial concentration of HPAM on the degradation rate

The effect of initial concentration of HPAM on the sono-photocatalytic degradation rate was investigated over the concentration range of 80-200 mg/L, since the pollutant concentration is an important parameter in water treatment. Experimental results are presented in Fig. 3. It can be seen in Fig. 3 that degradation rate decreases with increasing initial concentration of the HPAM. The possible explanation for this behaviour is that as the initial concentration of the HPAM increases, the path length of photons entering the solution decreases and in low concentration the reverse effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration. This suggests that as the initial concentration of the HPAM increases, the requirement of catalyst surface needed for the degradation also increases. Since illumination time and amount of catalyst are constant, the OH radical (primary oxidant) formed on the surface of TiO$_2$ is also constant. So the relative number of free radicals attacking the HPAM molecules decreases with increasing amount of the catalyst. The major portion of degradation occurs in the region (termed as reaction zone) near to the irradiated side, since the irradiation intensity in this region is much higher than that at the other side. Hence, at higher concentration, degradation decreases at sufficiently longer distances from the light source or reaction zone due to the retardation of penetration of light. Thus, the rate of degradation decreases with increase in concentration of HPAM (Neppolian et al., 2002).
Fig. 3. Effect of initial concentration of HPAM on sono-photocatalytic degradation rate.

2.2.4 Effects of H$_2$O$_2$ dosages on the degradation rate

The use of inorganic peroxides has been demonstrated to enhance the rate of degradation because they trap the photo-generated electrons more efficiently than O$_2$. The effects of addition of the H$_2$O$_2$ into TiO$_2$ dispersion were examined (Fig. 4). The degradation rate of HPAM was increased in the presence of H$_2$O$_2$ and influenced by the dosages of H$_2$O$_2$. With the addition of H$_2$O$_2$, the degradation rate of HPAM were increased abruptly at the low dosages of H$_2$O$_2$, but increasing H$_2$O$_2$ concentrations beyond 18 mmol/L had a negative effect on the process. This is because the addition of H$_2$O$_2$ can enhance the formation of ·OH. H$_2$O$_2$ would act as an electron donor to produce hydroxyl radicals by its reduction at the conduction band. The self-decomposition of H$_2$O$_2$ by UV light illumination or ultrasound irradiation would also produce hydroxyl radicals. Although more ·OH radical could be produced in the solution at higher oxidant concentrations, higher dosages of H$_2$O$_2$ may also act as an effective hydroxyl scavenger at higher H$_2$O$_2$ concentration (>18 mmol/L) as shown in the following reaction (Thandar et al., 2003): H$_2$O$_2$ + ·OH →H$_2$O+HO$_2^·$.

Fig. 4. Effect of dosage of H$_2$O$_2$ on degradation of HPAM in the solution containing 150 mg/L HPAM.
2.3 Degradation pathway of HPAM

During the process of TiO$_2$ sono-photocatalysis, numerous intermediates and products could be formed since OH radicals did not exhibit a high degree of functional group selectively. UV-light irradiation of HPAM solution in the presence of TiO$_2$ was carried out under atmosphere, and three intermediates were identified with LC/MS (Fig. 5). The obtained peaks with $m/z$ of 59.1, 59.7 (82.6), and 96.1, respectively, in the mass spectra corresponded to M-1 fragment of acetic acid (intermediate 1, M=60), M+1 (M+23) fragment of acetamide (intermediate 2, M=59), and M+23 fragment of propionamide (intermediate 3, M=73). An inorganic product, NO$_3^-$ (M=62), was also detected with $M+1/z=63$. Moreover, acetic acid and NO$_3^-$ were found to be dominant over the other two (Li & Mei, 2008). Therefore, a possible pathway for the degradation of HPAM had been proposed in Fig. 5.

To evaluate the conversion of the intermediates including acetic acid and acetamide and the formation of the product NO$_3^-$ during the process of photocatalytic degradation of HPAM, a test was carried out in the suspension including TiO$_2$ and HPAM (200 mg/L, initial TOC 75 mg/L). The results demonstrated that TOC of the system decreased to 70% after 240 min UV-light irradiation, and further increasing the time of UV-light irradiation may result in total mineralization of HPAM (Fig. 5). As for the acetic acid, its concentration gradually increased as increasing UV-light irradiation time from 0 to 120 min, and then its concentration decreased slowly, indicating that it will continuously degrade into more small molecules. The changes of the concentrations of acetamide were slow during the process of UV-light irradiation. As for the final product, NO$_3^-$, its concentration increased from 0 to 7.4 mg/L after 240 min UV-light.

![Fig. 5. Tentative pathway of sono-photocatalysis degradation of HPAM under UV-light irradiation of TiO$_2$](image)

3. Conclusion

Among the treating technologies, AOPs constitute a promising technology for the treatment of wastewaters containing HPAM. UV/Fenton and Fenton-based reactions are capable of extensively degrading HPAM in a variety of aqueous solutions. Rigorous economic comparisons using an accepted standard measure of treatment efficiency are scarce. However, Fenton reactions can be performed at ambient temperature and do not require
illumination, although they are usually enhanced by it. The reagents are readily available, easy to store, relatively safe to handle, and non-threatening to the environment. Drawbacks associated with the use of Fenton oxidation are the need to firstly reduce the pH, followed by a subsequent neutralization. This is not surprising since Fenton processes application requires strict pH control and sludges can be formed with related disposal problems. These drawbacks are intrinsic. Photocatalytic or photochemical degradation processes are gaining importance in the area of wastewater treatment, since these processes result in complete organics mineralization with operation at mild conditions of temperature and pressure. However, there is still a problem that the photocatalytic efficiency of TiO$_2$ need to be improved since TiO$_2$ is photoactive only under near UV-light irradiation. On the other hand, recombination of photogenerated electron-hole pairs (e$^-$/h$^+$) also results in low photo quantum efficiency of TiO$_2$. The effective separation of e$^-$/h$^+$ pairs, therefore, is one of the most important subjects for broadening applications of TiO$_2$ photocatalyst.

In this study, the sono-photocatalytic oxidation of HPAM was examined in aqueous suspension. The evaluations of treatment performance were conducted for different amounts of TiO$_2$, initial concentration of HPAM, H$_2$O$_2$ dosage and reaction time. Based on the experimental findings, the following conclusions were drawn:

1. Coupling photocatalysis with ultrasound irradiation results in increased efficiency compared to the individual processes operating at common conditions. Interestingly, the overall sono-photocatalytic effect is greater than the additive effects of the two processes, thus indicating possible synergy.

2. TiO$_2$ had a good performance in US/UV/TiO$_2$ degradation HPAM. The concentration of 800 mg/L was the optimum dosage of TiO$_2$ under the experimental condition in terms of photocatalytic oxidation rate. Photocatalytic degradation increased with increasing TiO$_2$ loading (in the range 600-800 mg/L) and decreasing HPAM concentration (in the range 200-80 mg/L). Addition of H$_2$O$_2$ up to 18 mmol/L hindered degradation of HPAM, scavenging the photogenerated holes and hydroxyl radicals.

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5. References


Pandit, A. B.; Gogate, P. R. & Mujumdar, S. (2001). Ultrasonic degradation of 2, 4, 6-

novel Nafion membrane with superior performance in photoassisted immobilized

structured C-Nafion/Fe-ion surfaces by photo-Fenton reactions leading to
carboxylate intermediates with a remarkable biodegradability increase of the
1520-6106

polymer flooding by UV/H$_2$O$_2$/O$_3$ and fine filtration. *J. Environ. Sci.*, Vol.18, pp.29-
32, ISSN 1001-0742

degradation by heterogeneous Fenton-like reaction using carbon-Fe catalysts. *Appl.
Catal. B: Environ.*, Vol. 75, pp.312-323, ISSN 0926-3373

solutions using heterogeneous catalysts based on saponite clay. *Appl. Catal. B:
Environ.*, Vol.71, pp.44-56, ISSN 0926-3373


1004-9541

York, ISBN 0471626031

trivalent lanthanide ions of Tb, Eu and Sm: Preparation, characterization and
potential applications. *Inorganica Chimica Acta*, Vol.360, No.9, pp.2863-2874, ISSN
0020-1693

of 2, 4, 6-trichlorophenol. *Ultrason. Sonochem.*, Vol. 5, pp. 53-61, ISSN 1350-4177

flow injection analysis method for the determination of acrylamide copolymers in

pp.101-107, ISSN 1383-5866

1914, ISSN 0360-1234

oxide) and polyacrylamide. *Journal of Applied Polymer Science*, Vol.100, pp. 3997-
4003, ISSN 1097-4628

www.intechopen.com


Ten years after coming into force of the Stockholm Convention on Persistent Organic Pollutants (POPs), a wide range of organic chemicals (industrial formulations, plant protection products, pharmaceuticals and personal care products, etc.) still poses the highest priority environmental hazard. The broadening of knowledge of organic pollutants (OPs) environmental fate and effects, as well as the decontamination techniques, is accompanied by an increase in significance of certain pollution sources (e.g. sewage sludge and dredged sediments application, textile industry), associated with a potential generation of new dangers for humans and natural ecosystems. The present book addresses these aspects, especially in the light of Organic Pollutants risk assessment as well as the practical application of novel analytical methods and techniques for removing OPs from the environment. Providing analytical and environmental update, this contribution can be particularly valuable for engineers and environmental scientists.

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