

Decomposition of organic resin by radio-sensitive photocatalyst

C.T. Yu^{a,b,*}, C.F. Wang^a, W.Z. Wang^a

^a Department of Atomic Science, National Tsing Hua University, Hsinchu 300, Taiwan

^b Chemical Analysis Division, Institute of Nuclear Energy Research, No. 1000, Wunhua Road, Jiaan Village, Taoyuan Country, P.O. Box 3-19, Longtan 325, Taiwan

Received 15 June 2006; received in revised form 23 August 2006; accepted 8 September 2006

Available online 9 October 2006

Abstract

A TiO₂ based radio-sensitive photocatalyst has been prepared to study the feasibility of organic resin degradation induced by ionization radiation. The synthesis of TiO₂/BaF₂/ceramic composites was performed using TiCl₄ hydrolysis, ethylene diamine tetraacetic acid (EDTA) chelating agent and calcinations at 450 °C. Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), X-ray diffraction (XRD) and inductively coupled plasma–atomic emission spectrometry (ICP–AES) were used to characterize the surface characteristics of the prepared composites. The photocatalytic activities of these prepared composites such as TiO₂/ceramic, BaF₂/ceramic and TiO₂/BaF₂/ceramic were characterized by the decomposition of ethylene blue (MB) under UV and ⁶⁰Co irradiation, respectively. The result showed that TiO₂ and BaF₂ nanoparticles were successfully co-embedded on the ceramic substrate, which significantly improved MB decomposition rate at γ radiation. Purolite resin was also fully decomposed by the prepared composites under 1×10^6 Bq ⁶⁰Co irradiation at different pH conditions. Radio-degradation of resin was discussed with SEM inspection and variations in weight of resin residue and in total organic concentration (TOC) of solution.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Radiocatalytic degradation; Radiation sensitive photocatalyst; Spent resins; TiO₂; BaF₂

1. Introduction

The spent ion-exchange resin is one kind of solid waste produced by nuclear facilities. Direct cement-solidification was considered a possible immobilization process to dispose them. However, it was realized that due to volume bulging and organic swelling problems, direct cement-solidification requires more improvement before utilization [1]. While scientists seek for better options in disposing the spent ion-exchange resins, most of them are currently put in high integrity containers (HIC) for temporary storage. There is no doubt that much effort has been devoted to volume reduction in spent resin to develop an effective waste treatment be economically eco-friendly. Several pretreatment technologies, such as pyrolysis [2], oxidation [3], vitrification [4] and supercritical water oxidation [5], had been suggested as methods in diminishing the resin. Wet oxidation, which uses the Fenton reagent was proposed as an efficient method in destructing spent resin [6]. These techniques mentioned above possess disadvantages such as high cost of

treatment facility, consumption of extra energy, and release of chemical pollutant or radioactive off-gas, etc.

Recently, increasing attention had been drawn toward the oxidation–reduction reaction using titanium oxide (TiO₂) based photo-catalyst, which is one possible method for the destruction of organics in the environment. Photo-generated hydroxyl radical on the surface of TiO₂ has been proven as an efficient oxidant for most of the organics such as chlorophenol [7], azo dyes [8] and crude oil [9]. The majority of organic ion-exchange resins have a cross-linked styrene–divinyl benzene structure with 50–60% moisture content. Photo-generated hydroxyl radicals thus play critical oxidants to mineralize hydrocarbon matrix of resin under room temperature. In fact, it is quite appropriate to treat spent resin with photo-catalyst in consideration of environmental protection. International atomic energy agency (IAEA) had explored the feasibility of photo-catalytic treatment of liquid radioactive waste [10].

However, the decomposition of organic resin by TiO₂ based material in accordance with the conventional photo-catalytic reaction has so low an efficiency that the idea of practical utilization is still far from expectation. This is because, to form electron–hole pairs in the TiO₂ crystal and to cause the oxidation–reduction reaction, photons of energy at least about

* Corresponding author. Tel.: +886 3 4711400 5013.
E-mail address: ctyu@iner.gov.tw (C.T. Yu).

3 eV are necessary but only a limited ultra-violet range of radiation is available in the solar radiation, thus the practical applications are yet limited by the following problems. First, in order to use solar energy or UV lamp, the apparatus must be made of transparent materials. Second, due to the characteristic of weak penetration as well as uni-direction of UV photons only transparent sample and plane-wise photo-catalyst can be used. Lastly, the performance of photo-catalytic process strongly depends on the weather and day/night conditions. As a result, high energy radiation, especially from spent resin itself, is considered to be an appropriate energy source for photo-catalyst. Little literature has been found on the facilitation of photo-catalytic reaction by ionization energy. Examples indicated that at least 10,000 Gy of dosage is required to initiate photo-catalytic reactions of EDTA [11] and phenol [12]. In other words, the efficiency of using high energy radiation for photo-catalyst is yet to be improved.

Inorganic scintillator, barium fluoride (BaF_2), is an excellent material to enhance radio-catalytic ability of TiO_2 based photo-catalyst. It interacts with high energy radiation and serves as an energy source by emitting 210 or 310 nm UV photons for surrounding TiO_2 crystals. It is expected that the oxidation–reduction reaction can be carried out with high efficiency in dark, under the circumstances that both TiO_2 and BaF_2 are embedded on the surface of porous materials. The theme of this paper is to develop a novel composite material to study the feasibility of radio-catalytically destructing Puro-lite resin by high energy radiation. This composite material is made up of nano-sized TiO_2 and BaF_2 particles deposited on the surface of ceramic substrates. Analytical techniques, such as Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), X-ray diffraction (XRD) and inductively coupled plasma–atomic emission spectrometry (ICP–AES), were utilized to investigate the characteristics of prepared composites. An experiment of decomposing methylene blue (MB) using UV light or ^{60}Co source was performed to validate the photo- as well as radio-catalytic capability of the prepared composite material. The radio-destruction behavior of organic resin was thoroughly examined by monitoring the TOC variation in the aqueous solution and weight loss of resin in different pH during the process.

2. Materials and methods

2.1. Materials

Titanium tetrachloride (TiCl_4), citric acid, ethylene diamine tetraacetic acid (EDTA), Barium nitrate ($\text{Ba}(\text{NO}_3)_2$), sodium

fluoride (NaF), methylene blue (MB), borate buffer solution, ceramic powder and Puro-lite resin were purchased from Merck Co. A ^{60}Co source means an ampoule of 1×10^6 Bq ^{60}Co solution, which was obtained from National Institute of Standards and Technology (NIST).

In order to solve the immobilization and dispersion problem of nanoparticle, nanophase BaF_2 and TiO_2 were embedded on the ceramic via chemical synthesis and calcinations in this experimental. The nanoparticles were prepared by TiCl_4 hydrolysis in HCl medium then EDTA chelating of $\text{Ba}(\text{NO}_3)_2$ and NaF under alkaline condition. The $\text{TiO}_2/\text{BaF}_2/\text{ceramic}$ photocatalyst was first prepared then its nano-properties were being characterized by using BET, SEM, XRD and ICP–AES. Photocatalytic performance of prepared radio-catalyst was examined by degradation of MB under UV and ^{60}Co irradiation. The influence of photo-catalytic degradation of resin was compared of in different pH condition. The photo-degradation rate of resin was studied by the measurement of total organic concentration (TOC) in solution and weight loss in residue.

2.2. Synthesis

The preparation method of $\text{TiO}_2/\text{ceramic}$, $\text{BaF}_2/\text{ceramic}$, and $\text{TiO}_2/\text{BaF}_2/\text{ceramic}$ were described there [13]. Table 1 lists the amount of reactants added and the ICP results for each sample. TiO_2 suspension solution was made up of appropriated amount of citric acid and TiCl_4 hydrolysis [14]. The chelating solution was performed by dissolving 1 g citric acid in 20 ml 0.5 M HCl and stirring get clear solution. TiCl_4 was slowly dropped into the solution in ice bath. Ceramic powder was mixed with solution stirred for 2 h and then was dried using hot plate. The collected residue was calcinated in 450°C to obtain the composite sample of $\text{TiO}_2/\text{ceramic}$.

The EDTA chelating solution was first made by dissolving an appropriate amount of EDTA and ammonia in pH 10 borate buffer. The mixture was stirred magnetically for 30 min and then both $\text{Ba}(\text{NO}_3)_2$ and NaF solutions were separately poured in slowly to obtain a suspended nanoparticle BaF_2 solution. The solution was then mixed with previous prepared of $\text{TiO}_2/\text{ceramic}$ powder and stirred for 2 h to deposit BaF_2 onto the substrate and then was dried using hot plate. The collected residue was calcinated in 450°C to obtain the composite sample of $\text{TiO}_2/\text{BaF}_2/\text{ceramic}$.

A sample that contains only BaF_2 on the ceramic was prepared by 5.1 g $\text{Ba}(\text{NO}_3)_2$, 1.8 g NaF and 5 g ceramic. The $\text{BaF}_2/\text{ceramic}$ was used to evaluate the photocatalytic and radio-catalytic activity reaction without TiO_2 .

Table 1
Amount of reactant added and ICP results ($n = 3$)

Product	Amount of reactant added			ICP results (mg/g)	
	TiCl_4 (g)	$\text{Ba}(\text{NO}_3)_2$ (g)	NaF (g)	Ti	Ba
Ceramic	–	–	–	8.50 ± 0.24	0.50 ± 0.01
$\text{TiO}_2/\text{ceramic}$	1.6	–	–	41.2 ± 2.5	0.40 ± 0.01
$\text{BaF}_2/\text{ceramic}$	–	5.1	1.8	8.30 ± 0.21	138 ± 5
$\text{TiO}_2/\text{BaF}_2/\text{ceramic}$	2.0	5.1	1.8	41.1 ± 2.3	140 ± 5

2.3. Characterization

The specific surface area of composite was determined by N_2 adsorption at 77 K using a Quantachrome NOVA 2000 instrument. Hitachi S-800 SEM/EDX instrument was used to examine nanophase morphology of BaF_2 and TiO_2 immobilized on substrates. The overall crystalline of sample were examined by XRD measurements performed on an American Scintag XDS-2000 diffractometer using $Cu\ K\alpha$ radiation ($\lambda = 0.1541\text{ nm}$) at 30 kV and 30 mA.

Eight milliliters acid mixture of $HNO_3 + HClO_4 + HF$ (5:3:2, v/v) and sample in a 25 ml polytetrafluoroethylene (PTFE) vessel was digested in a high-pressure bomb system (Berghof, Germany). A PE-Optima 3000DV ICP-AES instrument was employed for both Ti and Ba determination.

In reaction bottle, a volume of 70 ml slurry solution was made of 10 ppm MB and approximately 0.3 g photocatalyst. For UV irradiation, a 400 W medium pressure Hg lamp (purchased from LUXMEN Co.) was employed to slurry. The irradiations distance between the UV source and the center of the reaction bottle was 15 cm.

Seventy milliliters slurry solution was also irradiated by inserted a ^{60}Co source at different dosage. The average irradiation dose rate of applied in slurry solution was $2 \times 10^{-3}\text{ Gy/h}$, which was roughly estimated by MicroShield commercial code.

After catalytic reaction, the variation of MB absorbance at 663 nm wavelength was recorded using a Shimadzu pharmaSpec UV-1601 spectrometer. Degradation ratio (A_t/A_0) of MB was calculated by A_t of after and A_0 of before irradiation, respectively. The kinetic rate constant (k_{app}) is estimated by plotting $\log(A_t/A_0)$ versus irradiation time.

2.4. Photocatalytic decomposition of resin

A ^{60}Co source was placed into 100 ml reaction bottle containing photocatalyst, resin and $Di-H_2O$. The boric buffer was used to adjust the solution pH to 9 and 11. Small organics were formed and gradually dissolved in water during decomposition of resin. In naked eye' observation, resin beads were obvious decomposed and final disappeared with enough ^{60}Co dosage. It was further proven by weight lose and TOC determination. The variation of organics content in water was determined by TOC using Spectroquant NOVA 60 TOC analyzer. Simultaneously, collection of dried mixture of resin residues and photocatalyst was weighting after a period of reaction time. Resin of 1, 3 and 5 g were also decomposition by an identical photocatalyst to demonstrate its stability and durability.

3. Results and discussion

3.1. Characterization of photo-catalyst

It is interesting to investigate the alternation of surface area as well as pore size of the prepared composite materials. As exhibited in Table 2, the TiO_2 and BaF_2 modified ceramic was significantly increasing in surface area and decreasing in pore size, which meant that both nanoparticles were embedded in

the cavities of ceramic substrates after the synthesis. Those data shown represent the average quantity by three times measurement repeatedly ($n = 3$).

Fig. 1 shows the SEM diagram of $TiO_2/BaF_2/ceramic$. In Fig. 1(a), a nearly thirty microns ceramic particle is chosen as a host to immobilize the nanophase TiO_2 as well as BaF_2 and to provide the site for photo-catalytic reaction. Fig. 1(b) exhibits an optimized magnification to clarify the co-existence of both TiO_2 and BaF_2 nano-crystalline. The cubic shape of deposited BaF_2 ,

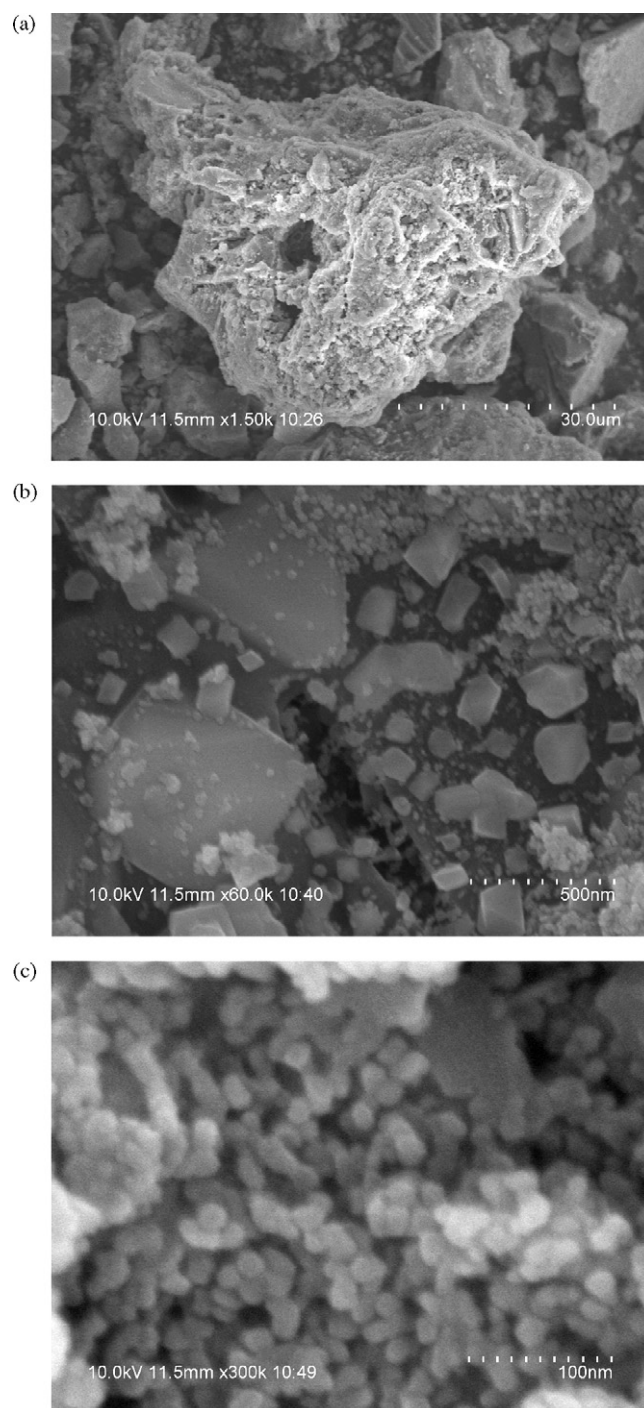


Fig. 1. SEM diagram of $TiO_2/BaF_2/ceramic$ composite at different magnification: (a) 1.5k; (b) 60k; (c) 300k.

Table 2
BET results for ceramic and photocatalyst ($n = 3$)

Product	Ceramic	TiO ₂ /ceramic	BaF ₂ /ceramic	TiO ₂ /BaF ₂ /ceramic
Specific surface area (m ² /g)	4.10 ± 0.21	27.3 ± 1.6	20.1 ± 1.2	26.9 ± 1.4
Pore size (nm)	68.9 ± 2.8	16.5 ± 1.0	18.5 ± 1.3	17.9 ± 0.8

which is similar to the result of Singh et al. [15], can be easily distinguished from the adjacent nano-sized TiO₂ spherical particles. The estimated size of a BaF₂ particle is about 100–500 nm. Fig. 1(c) further illustrates the distribution of sphere-like TiO₂ nano-particles with a magnification of 300,000 times. A number of 10–20 nm TiO₂ grains are coagulated on the substrate.

It is important but difficult to examine the co-existence of TiO₂ and BaF₂ nanoparticles by using XRD [13]. The difficulty is originating from the complex peak of ceramic on XRD spectrum, such as gahnite (JCPDS 05-0669), which inherently interfere with the TiO₂ and BaF₂ signals. Nevertheless, by synthesizing on simple graphite substrate (JCPDS 41-1487) using same prepared method, the crystalline of TiO₂ anatase phase (JCPDS 21-1272) and BaF₂ frankdicksonite phase (JCPDS 04-0452) were showed on spectrum. It is worthy to emphasize that the same preparation procedure can be applied to various substrates such as ceramic and zeolite; it is possible to confirm the co-formation of pure anatase TiO₂ phase separated from BaF₂ on the ceramic.

Table 1 presents the elemental concentrations of ceramic powder and composite material determined by ICP–AES. Those data represent the average quantity by three times measurement repeatedly ($n = 3$). Some of preparing work has been performed in which several similar concentrations of Ti and Ba in composite was selected in order to recognize the radiocatalytic activity under UV and ⁶⁰Co. As indicated in the Table, the concentrations of Ti and Ba in the substrate raised, respectively from 8.50 ± 0.24 and 0.50 ± 0.01 mg/g to 41.1 ± 2.3 and 140 ± 5 mg/g after the synthesis. In other words, a significant amount of Ti and Ba were embedded on the surface of ceramic substrates.

3.2. Photocatalytic decomposition of MB

The validation of prepared composite materials was first proved by photo-catalytically decomposing MB in aqueous solution with the irradiation of UV and ⁶⁰Co sources. Literature [16,17] has pointed out that the adsorption rate of MB on the porous surface becomes significant under alkaline condition. To reduce the influence of adsorption, photo-catalytic decomposition of MB was thus performed at neutral condition (pH 7).

The extent of MB decomposition is revealed through the measured absorbance value shown in Fig. 2, which depicts the variation of UV–vis absorbance of 0.3 g sample in 10 ppm MB solution at various UV irradiation time. The decomposition of MB is also confirmed visually through the gradual de-colorization of solution. A pre-adsorption process with MB saturating the adsorption of composites was performed before the irradiation. As shown in this figure, MB was a little degraded only by UV photolysis at ceramic and BaF₂/ceramic sample, wherein the UV energy was invalid to excite BaF₂. However,

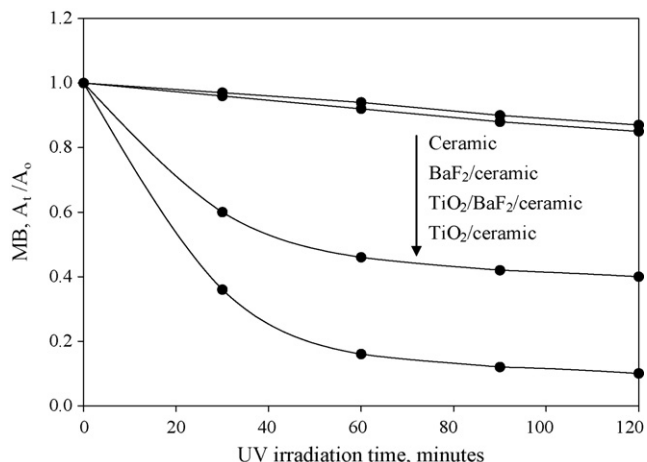


Fig. 2. 10 ppm MB decomposed by 0.3 g composite at UV irradiation.

the MB concentration was obviously decreases rapidly at first and then levels off gradually after a period of irradiation time if TiO₂ photocatalytic reaction was happened. It was inferred that a heterogeneous photo-catalytic reaction occurs on/or near the surface of TiO₂. Composite TiO₂/BaF₂/ceramic and TiO₂/ceramic were similar in Ti content, but former revealed a worsen decomposition efficiency than later, which may be attributed to the effect of BaF₂ pile-up on the surface of TiO₂. This is due to weak penetrating ability of UV light, only outer core of TiO₂ layer on the ceramic powder can be excited and used as the MB photo-catalytic degradation site. The kinetic rate constant κ_{app} is estimated at 0.019 min⁻¹ for TiO₂/ceramic and at 0.004 min⁻¹ for TiO₂/BaF₂/ceramic. Furthermore, it was noticeable that only less than 10 mg of TiO₂ was involved in this heterogeneous decomposition reaction, which validates an excellent photo-catalytic capability of the prepared composite materials.

Fig. 3 showed that MB could not be decomposed by ceramic and TiO₂/ceramic even BaF₂/ceramic, which excluded the possibility of MB dye might be decomposed by the direct absorption of UV light at 220 or 310 nm emitted from BaF₂ under the gamma radiation. It was also exhibited an interesting phenomenon that MB organics can also be radio-catalytically decomposed by a TiO₂/BaF₂/ceramic sample under ⁶⁰Co irradiation with kinetic rate constant κ_{app} estimated at 0.239 h⁻¹. Literature [18,19] pointed out that semiconductor nanoparticle such as TiO₂ and Al₂O₃ could be triggered to enhance decomposition of organics by at least 10,000 Gy of ⁶⁰Co. Those experiments should be performed by a high strength ⁶⁰Co irradiation facility. In our work, total radiation dose employed for the radio-catalysis was about 0.04 Gy only. On the other hand, the decomposition of MB by radio-catalysis of TiO₂ free of BaF₂ was found inefficiently, that meant not only TiO₂ but also BaF₂

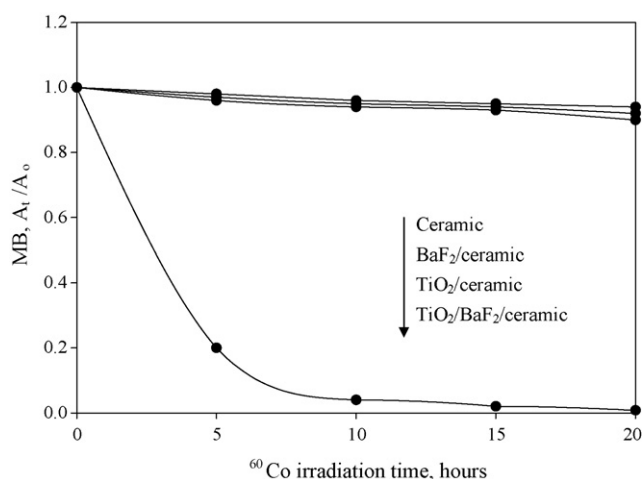


Fig. 3. 10 ppm MB decomposed by 0.3 g composite at ^{60}Co irradiation.

playing a key role to initiate the radio-decomposition of MB organics in the solution. Higher TiO_2 content exhibited better decomposition efficiency with both UV and irradiation. On the other hand, higher BaF_2 content may deteriorate the decomposition efficiency of UV light but enhances that of γ -radiation.

It assured that nanophase TiO_2 deposited on the composite surface is an effective photo-catalyst for an oxidation–reduction reaction. BaF_2 crystal absorbs high energy radiation even in dark and emits appropriate UV photons to excite the TiO_2 surrounding BaF_2 . This synergic effect may be a key factor to facilitate a heterogeneous radio-catalytic reaction to destruct organic solid wastes such as spent resin.

3.3. Radio-catalytic degradation of resin

Purolite resin sample was decomposed by using the prepared composite materials with a ^{60}Co source. Some of SEM experiments were proceed to support the evidence of decomposition of resin. As shown in Fig. 4, the smoothly surface of resin with some of tiny channel which providing a reaction site for hydroxyl radical. In this Fig., resin was first swelling then defects and cracks appeared after 15 h reaction that providing a direct demonstration of resin bead decomposition under SEM inspection.

Physical and chemical properties of Purolite resin has been described elsewhere [20], wherein the properties of spherical shape and particle size of bead resin can be visually examined about its exterior destruction. Preliminary experiment has demonstrated that this resin material has a high resistance toward direct radiolysis in a high-level radiation environment. However, cross-linking matrix of polystyrene and divinyl benzene might be photo-catalytically decomposed into soluble organic products such as linear polystyrene, benzyl anions [1]. Information such as TOC level in the aqueous solution and weight loss of resin during the degradation process was thus studied to understand the destruction route.

Fig. 5 coherently shows the time course of degradation of organic resin measured by TOC and weight loss against the ^{60}Co irradiation time, which were determined with about one gram resin and one gram composite materials in 70 ml aqueous

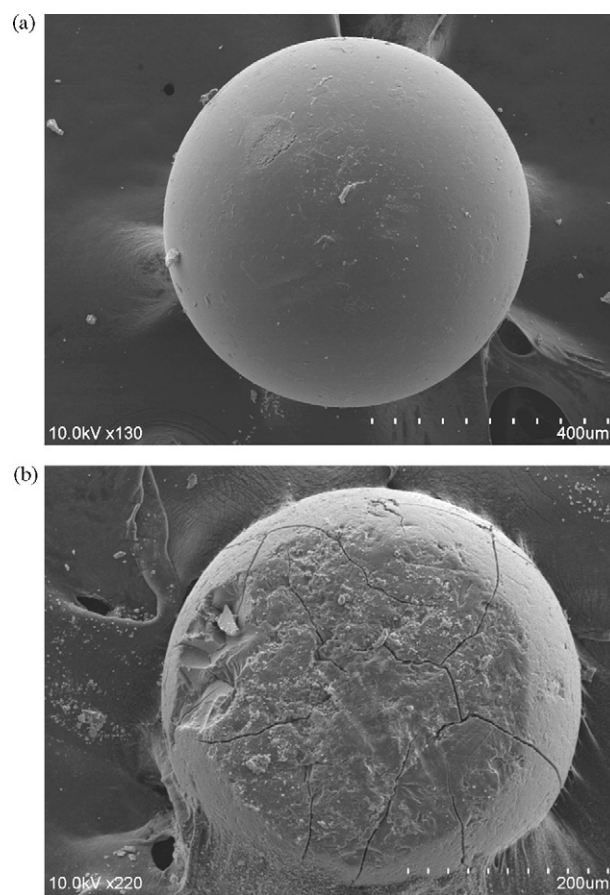


Fig. 4. SEM diagram of resin (a) before and (b) 15 h reaction performed by $\text{TiO}_2/\text{BaF}_2/\text{ceramic}$ under ^{60}Co irradiation.

solution. It was observed that the TOC level increases rapidly at first, and then decreases after reaching the maximum. The bulk bead resin in the solution gradually disappears while the TOC increases, which implies its decomposition into resin scraps and further into soluble organic molecules. As shown in Fig. 5, the solid resin would be completely decomposed into soluble organics at the maxima of TOC curves. It is believed that both radio-decomposition and radio-mineralization occur during the irradiation. The photo-generated hydroxyl radical diffused in the solution will attack the cross-linking molecules to expose more resin surface as heterogeneous reaction sites. High moisture content of Purolite resin may provide extra hydroxyl radical source during the decomposition of resin. In consideration of mobility, the degradation of dissolved organic molecules is superior to that of partially collapsed resin scraps, and radio-mineralization becomes more and more significant with TOC level increased in the solution. After reaching the maxima, soluble organics will continue to be radio-degraded into CO_2 , SO_4^{2-} and H_2O by ^{60}Co irradiation. The TOC level will eventually be annihilated with enough radiation dosage.

The influence of pH value has always been a critical factor for the TiO_2 based photocatalyst. Dionysiou et al. [21] mentioned that the reaction of OH_{ads}^- with valance band hole h^+ on the TiO_2 surface will be accelerated in the alkaline solution. As indicated in Fig. 5, the radio-degradation rate of resin increases

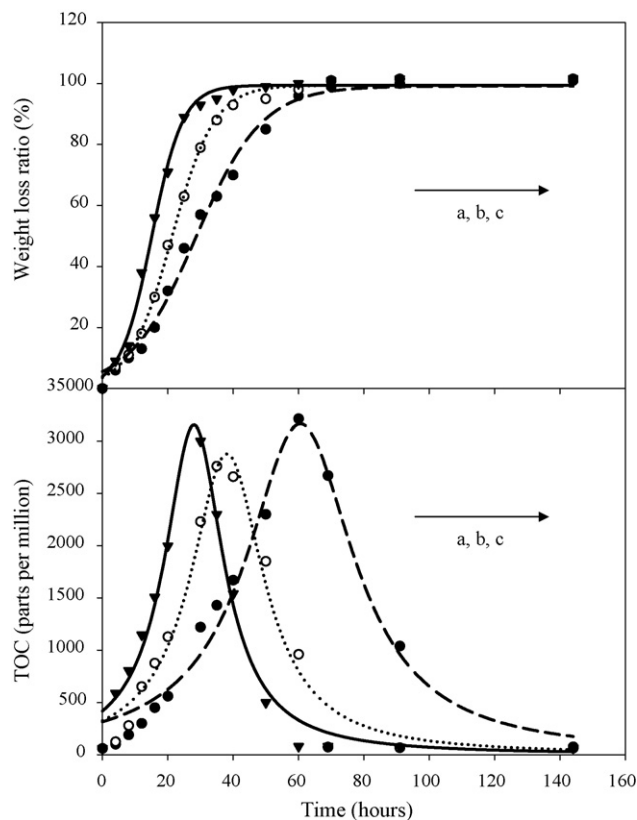


Fig. 5. The variations of TOC and weight loss % of resin under ^{60}Co irradiation (photocatalyst: 1 g; resin: 1 g; a: pH 11; b: pH 9; c: pH 7).

as pH value increases. At natural condition (pH 7, curve 5c), one gram of resin would not be completely decomposed until going through 65 h of irradiation. However, in a much more alkaline condition, only 30 h of irradiation is required to decompose them (pH 11, curve 5a).

The stability of $\text{TiO}_2/\text{BaF}_2/\text{ceramic}$ photocatalyst after decomposition of resin was examined by ICP–AES and SEM. It was doubt that if photocatalyst was collapsed due to collision with resin beads at long time. We found that SEM diagram of $\text{TiO}_2/\text{BaF}_2/\text{ceramic}$ after reaction was still unchanged with co-existence of BaF_2 and TiO_2 as similar to Fig. 1(b). After radio-decomposition of resin, some of solution samples were filtered and taken to determine dissolved Ti and Ba element concentration. The ICP result showed that Ti and Ba contents lost in solution were only 0.01–0.05% in comparison to those elements amount in $\text{TiO}_2/\text{BaF}_2/\text{ceramic}$, which implied constant photo-generation of e^- and hole after radio-excited of TiO_2 . The MB photo-degradation ratio performed repeatedly three times at 20 h induced by ^{60}Co was found to keep in 98–100%.

In the Fig. 6, it was shown that prepared $\text{TiO}_2/\text{BaF}_2/\text{ceramic}$ could be well used to decompose 1, 3 and 5 g resin in an experiment. It was found that TOC in solution should be maximal at fully diminishing of all resin beads even the competition of mineralization and decomposition. In the x axis, T_{max} indicated that all resin beads were decomposed and meant highest TOC (y axis) in the solution. Actually the bar a in Fig. 6 is identical to Fig. 5(b) for 1 g photocatalyst treating 1 g resin with T_{max} of 40 h. The T_{max} was approximately corresponding to resin weight in

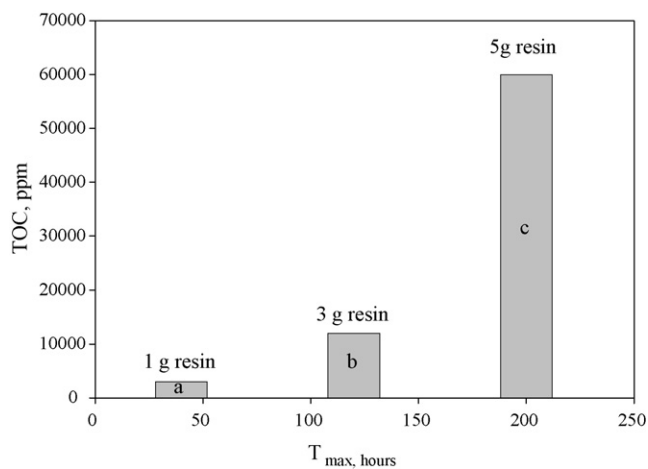


Fig. 6. Diagram of radio-catalytic decomposition of 1, 3 and 5 g resin by 1 g photocatalyst under 1×10^6 Bq ^{60}Co irradiation (pH 9).

which 40, 120 and 200 h stood for 1, 3 and 5 g resin, respectively. However it was unfortunately that TOC of 3000, 12,000 and 60,000 ppm mismatched to resin weight as shown in this figure.

4. Conclusions

By naked-eye observation, the feasibility of the photo-catalytic elimination of organic resin by ^{60}Co has been accomplished. A synergic effect of combining photo-catalyst (TiO_2) and scintillator (BaF_2) on the ceramic powder provides a simple way to facilitate a heterogeneous photo-catalytic reaction induced by high energy radiation. This is an efficient and environment-friendly method to decompose organics especially for spent resin by radio-sensitive photocatalyst instead of pollutants and cost produced by chemical oxidation. It was found that 1 g of purolite resin was gradually diminished within 60 h and mineralizes within 6 days with simple stirring, air supply and 1×10^6 Bq ^{60}Co when mixed with the prepared composites. Basic environment enable further facilitation in the decomposition and mineralization of resin. The technique developed is especially applicable to the volume reduction of spent resin produced by nuclear facilities. With spent resin itself acting as the radiation source that facilitates the photo-catalytic decomposition and mineralization of resin, the application of prepared composites to spent resin would result in self-degradation of it. Therefore, no extra energy is needed and the radio-catalytic decomposition of spent resin can be self-proceed in a remote area for the concern of radiation safety.

Acknowledgement

The authors wish to thank the Instrument Center at National Tsing Hua University in Taiwan for the ICP–AES support in this work.

References

- [1] X.C. Jian, T.B. Wu, G.C. Yun, Nucl. Safety 37 (1996) 149–157.
- [2] R.S. Juang, T.S. Lee, J. Hazard. Mater. B92 (2002) 301–314.

- [3] U.K. Chun, K. Choi, K.H. Yang, J.K. Park, M.J. Song, *Waste Manage.* 18 (1998) 183–196.
- [4] N.D. Hutson, C.L. Crawford, D.O. Russo, M.E. Sterba, *WSRC-TR-2001-00368*, 28, 2002.
- [5] Y.J. Huang, H.P. Wang, C.T. Li, Y.C. Chien, *Chemosphere* 40 (2000) 347–349.
- [6] P.A. Taylor, Destruction of Ion-Exchange Resin in Waste from the HFIR, T1, and T2 Tanks Using Fenton's Reagent, ORNL/TM-2002/197, 2002.
- [7] J.C. D'Oliveira, G.A. Sayyed, P. Pichat, *Environ. Sci. Technol.* 24 (1990) 990–996.
- [8] K. Tanaka, K. Padermpole, T. Hisanaga, *Water Res.* 34 (2000) 327–333.
- [9] R.L. Ziolli, W.F. Jardim, *J. Photochem. Photobiol. A: Chem.* 5887 (2001) 1–8.
- [10] IAEA-TECDOC-1336, Combined methods for liquid radioactive waste treatment, 2003.
- [11] M.A. Henderson, Ionizing Radiation Induced Catalysis on Metal Oxide Particles, US Department of Energy Final Report, 1996.
- [12] S. Seino, T.A. Yamamoto, K. Hashimoto, S. Okuda, N. Chitose, S. Ueta, K. Okitsu, *Rev. Adv. Mater. Sci.* 4 (2003) 70–74.
- [13] C.F. Wang, C.T. Yu, B.H. Lin, J.H. Lee, *J. Photochem. Photobiol. A: Chem.*, in press.
- [14] J.C. Yu, Y.L. Chan, *J. Chem. Educ.* 75 (1998) 750–751.
- [15] R. Singh, S. Sinha, P. Chou, N.J. Hsu, F. Radpour, *J. Appl. Phys.* 66 (1989) 6179–6181.
- [16] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Herrmann, *Appl. Catal. B: Environ.* 31 (2001) 145–157.
- [17] S. Lakshmi, R. Renganathan, S. Fujita, *J. Photochem. Photobiol. A: Chem.* 88 (1995) 163–167.
- [18] J.C. Gonzalez-Juarez, J. Jimenez-Becerril, *Rad. Phys. Chem.* 75 (2006) 768–772.
- [19] A.Z. George, A.G. Kimberly, V.K. Prashant, *J. Phys. Chem. B* 105 (2001) 4715–4720.
- [20] R.S. Juang, T.S. Lee, *J. Hazard. Mater.* B92 (2002) 301–314.
- [21] D.D. Dionysiou, M.T. Suidan, I. Baudin, J.M. Laine, *Appl. Catal. B: Environ.* 45 (2003) 293–300.