

Preparation of Heterogeneous Ferrite Catalysts and Their Application for Fenton-Like Oxidation of Radioactive Organic Wastewater

Hsien T. Hsieh, Chao R. Chen, Li C. Chuang, Chin C. Shen

Abstract—Fenton oxidation technology is the general strategy for the treatment of organic compounds-contained wastewater. However, a considerable amount of ferric sludge was produced during the Fenton process as secondary wastes, which were needed to be further removed from the effluent and treated. In this study, heterogeneous catalysts based on ferrite oxide (Cu-Fe-Ce-O) were synthesized and characterized, and their application for Fenton-like oxidation of simulated and actual radioactive organic wastewater was investigated. The results of TOC decomposition efficiency around 54% ~ 99% were obtained when the catalyst loading, H₂O₂ loading, pH, temperature, and reaction time were controlled. In this case, no secondary wastes formed and the given catalysts were able to be separated by magnetic devices and reused again.

Keywords—Fenton, oxidation, heterogeneous catalyst, wastewater.

I. INTRODUCTION

WITH the stricter tendency of environmental and safety requirements, the treatments of radioactive liquid waste containing organic compounds have become one of the most important issues in the field of nuclear facility. The organic components are toxic and flammable so that the destruction of the unstable organic components may provide a feasible way for further treatment and disposal.

Small producers' radioactive waste of small quantity produced from medical, agricultural, industrial, education and research organizations are currently collected, transported and stored by the Institute of Nuclear Energy Research (INER) in Taiwan. INER have also received low-level radioactive liquid wastes generated from domestic hospitals and research institutions. The received liquid wastes were temporarily stored in the stainless T61 tanks with capacity of 50m³. In order to reduce the risk of those hazardous radioactive liquid wastes, we have studied a series of treatment methods for these liquid wastes and determine its propriety treatment technology to handle those radioactive wastes.

The mixture of liquid wastes stored in T61 tank has been separated into oil (upper layer) and aqueous layer (lower layer) by natural sedimentation for decades. In our previous study [1],

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the oil phase of radioactive liquid waste was solidified by utilizing Nochar Petrobond® N910 as oil absorbents. In order to evaluate the performance of solidification, various oil/N910 ratios were tested to observe the optimal experimental parameters, and the oil retention tests and exudation tests were also carried out to demonstrate the oil absorbency of the polymers. It was found the weight ratio of oil to N910 was suggested as 1:1 due to the results of excellent oil retention under thermal heating or external loading. The oil/N910 mixtures were then incinerated by a thermal furnace for volume reduction. However, in the case of aqueous layer of T61, absorbent-based technology is not acceptable as result of excess amount of the wastewater and inefficient economics by burning water-loading absorbents.

Fenton reagent, developed by H. J. H. Fenton in 1890s, has still attracted much attention in the application of the treatment of wastewater containing organic pollutants. Taking account of the ferric sludge formed by homogeneous Fenton reaction, heterogeneous catalysts based on iron oxide were studied [2]-[4], and their magnetic properties allow their easy, fast and inexpensive separation from the treated medium [5], [6]. The degradation of wastewater pollutants in heterogeneous catalytic Fenton system were developed as a feasible and environmentally benign process [7]-[9]. Therefore, the heterogeneous catalysts of ferrite oxide (Cu-Fe-Ce-O) were prepared and utilized in Fenton-like reaction in this study, and the effect of TOC degradation of the simulated solutions with organic compounds and radioactive aqueous layer in T61 tank were investigated, respectively.

II. MATERIALS AND METHODS

A. Materials

Metal salts with reagent grade including copper acetate (Cu(CH₃COO)₂·H₂O), ferric nitrate nonahydrate (Fe(NO₃)₃·9H₂O), ferrous chloride tetrahydrate (FeCl₂·4H₂O), cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O), ferrous sulfate heptahydrate (FeSO₄·7H₂O), ferrous oxalate dehydrate (Fe(C₂O₄)·2H₂O) and copper ferrite (CuFe₂O₄) were purchased from Merck Ltd. and used as received without further purification. Iron powders (Fe-200) were obtained by Alfa Aesar, Thermo Fisher Scientific Ltd. Triply distilled water (resistivity greater than 18 M cm) was produced by Millipore Milli-Q system. Methanol and isopropanol (IPA) with reagent grade were provided by Aldrich Ltd.

B. Synthesis of Catalysts Based on Ferrite Oxide

Firstly, copper acetate, ferric nitrate nonahydrate, ferrous chloride tetrahydrate, and cerium nitrate hexahydrate with specific weight percentages are mixed in deionized water in a fixed ratio. After mixing the above materials in deionized water, stir uniformly to make them dissolved in the water completely to get the homogeneous solution. Then, the pH value of the homogeneous solution is adjusted by adding sodium hydroxide to the range between 9 and 11. Thereby, a precipitate will be produced. The precipitate is separated by a centrifuge and flushed using deionized water for several times. The dried precipitate is then ground and sifted. Afterwards, the precipitate is calcined in a furnace at the temperature of 850°C for three hours. Finally, the calcined precipitate is cooled to the room temperature to give the magnetic catalyst.

C. Characterization

The X-ray diffraction (XRD) pattern was recorded by a Bruker D8 advance X-ray diffractometer using Cu K α radiation operated at 40 kV and 200 mA. The 2 θ angle was measured from 4 to 20 with a resolution of 0.05. SEM image was performed on a Hitachi S4800 field emission scanning electron microscope at 15 kV. For the determination of TOC in treated solution, Spectroquant® TR 620 thermoreactor and NOVA 60 purchased from Merck Ltd. were utilized with reagent test kits. It was capable of simultaneously digesting samples at the different temperatures required, yielding the TOC results after just 120 minutes.

III. RESULTS AND DISCUSSION

A. Characterization of Radioactive Wastewater in T61 Tank

The liquid mixture stored in T61 tank has been separated into oil layers and aqueous layer as result of natural sedimentation for decades. The brown-colored oil phase of radioactive liquid wastes is present at the upper layers as shown in Fig. 1, however aqueous wastes are light yellow liquids in the lower layer. The dried residues of aqueous wastes were analyzed by SEM/EDX to evaluate the chlorine content. From the specific character of chlorine spectrum, the obvious peaks at 2.6 KeV were found in EDS energy position analysis, thus it was verified chlorine ion was found in aqueous sample as shown in Fig. 1. In addition, radioactive wastewater was composed of miscellaneous organic compounds, such as organic solvents, detergents, couple agents, and so on. Thus, large amounts of carbon from organic spices in aqueous wastes was found, and the total organic carbon (TOC) of the wastewater is near to 22,000 ppm as shown in Table I. Moreover, it was found Cs-137 and H-3 nuclei in the wastewater according to the results of radiochemical analysis. In general, the oil phase wastes were solidified by polymer-based absorbents, such as Nochar Petrobond® N910, and followed by the thermal degradation through incineration in a furnace to achieve the volume reduction. On the other hand, the aqueous wastes with high TOC were needed to be pretreated before entering the evaporator system to avoid the accumulation of bubbles.

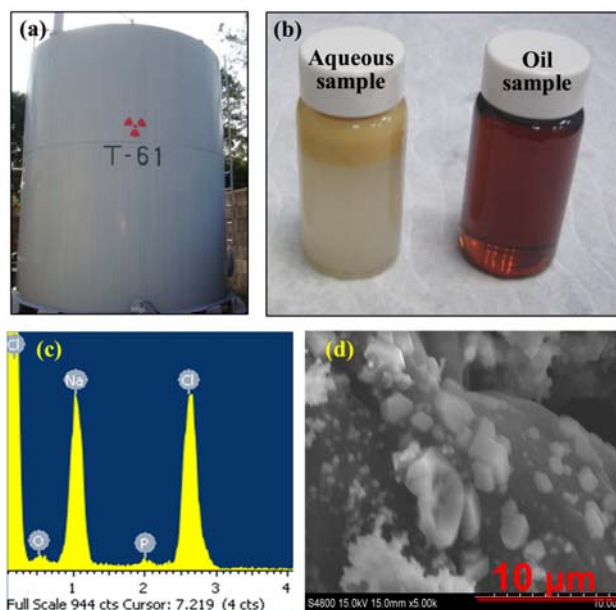


Fig. 1 (a) The appearance of T61 tank with 50 m3, (b) the samples of brown-colored oil layer and light yellow aqueous layer, (c) the EDS analysis of dried residual of aqueous sample, and (d) SEM of dried residual of aqueous sample

TABLE I
PROPERTIES OF AQUEOUS WASTE IN T61 TANK

Liquid Wastes in T61	Description
Aqueous phase	The aqueous phase is the lower layer of radioactive liquid wastes stored in T61 tank. Radioactive wastewater was composed of miscellaneous organic compounds, such as organic solvents, detergents, couple agents, and so on.
Volume (m3)	~40
Chloride content	0.7wt% of NaCl were detected
TOC (ppm)	21,600 mg/L
Radiological characterization	1.86 Bq/ml of Gross β 1.57 $\times 10^1$ Bq/ml of Cs-137 1.81 $\times 10^3$ Bq/ml of H-3

B. Synthesis and Characterization of Heterogeneous Catalysts

By mixing with various metal salts (copper acetate, ferric nitrate nonahydrate, ferrous chloride tetrahydrate, and cerium nitrate hexahydrate) in deionized water with pH around 10, the precipitates are formed in the solution under various controlled temperature at 30, 60, and 90°C for 2 hours. The precipitate samples were analyzed by XRD and their pattern was shown in Fig. 2. The XRD pattern revealed that the crystal phases of these samples were the same, thus there were no effect of temperature on the formation of crystal of precipitates. In this report, the metal oxide-based CFCO precipitates (Cu-Fe-Ce-O) were utilized as heterogeneous catalysts to perform the degradation of TOC in aqueous wastes stored in the lower layer of T61 tank.

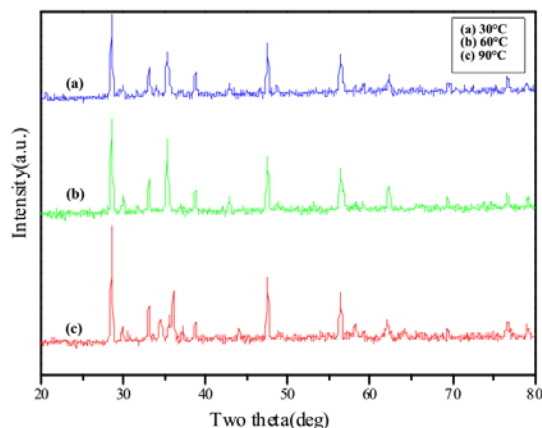


Fig. 2 The XRD pattern of prepared CFCO precipitates in (a) 30°C, (b) 60°C, and (c) 90°C

C. Fenton-like Oxidation of Simulated Wastewater by Using Heterogeneous Catalyst

In this section, as shown in Table II, three parts of simulated wastewater containing organic solvent, such as methanol and IPA, were utilized to test the heterogeneous catalysts. The simulated solution of 100 ml was mixed and stirred mechanically in a glass vial with CFCO catalysts of 2 g at 95 °C for 2 hours.

TABLE II
TOC DEGRADATION OF SIMULATED SOLUTION

	RUN 1	RUN 2	RUN 3
Simulated wastewater	10% IPA	10% MeOH	20% MeOH
W_{TOCi} (mg) ^a	4712	2968	5936
W_{TOCf} (mg) ^b	789	1	2729
C_{TOC} (mg/L)	4933	7	16438
DRE (%)	83.25	99.97	54.03
pH	3.25	6.93	2.09

Volume of simulated solution: 100 ml

50% H_2O_2 : 80 ml at adding rate of 2.5ml/min

Amount of CFCO catalysts: 2g

Reaction condition: 95°C for 120 min

^a W_{TOCi} : initial weight of TOC before Fenton-like oxidation reaction

^b W_{TOCf} : final weight of TOC after Fenton-like oxidation reaction

In order to perform the Fenton-like oxidation reaction, H_2O_2 solution (50%) of 80 ml was added by drops at rate of 2.5 ml/min. In order to calculate the destruction efficiency of TOC in organic waste liquid quantitatively, the destruction and removal efficiency (DRE) is defined according to (1) below. Because the final volume of the sample after each experiment cannot be controlled identically, the final volume of the sample is measured and multiplied by the concentration of the sample under analysis to give the total mass of TOC as the basis for quantitative analysis. Then, the variation in mass is used for calculating the DRE.

$$DRE (\%) = \frac{TOC_i - TOC_f}{TOC_i} \times 100\% \quad (1)$$

In the case of RUN 1, DRE of IPA solution (10%) was about 83%. However, DRE of MeOH (10%) could be achieved to nearly 100%. These results revealed that various organic

compounds may have different efficiency of Fenton-like oxidation reaction. The possible reasons for the difference were probably due to the rates and mechanisms of degradation of specific organic species. Moreover, it should be noted that higher concentration of MeOH (20%) led to lower DRE at 54% than that of MeOH (10%). Therefore, it needed to increase the amount of H_2O_2 to perform the oxidation reaction to degrade the redundant MeOH molecules in solution.

In order to compare the homogeneous catalysts with heterogeneous catalysts, water-soluble iron salts including ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and ferrous oxalate dehydrate ($Fe(C_2O_4) \cdot 2H_2O$) were selected to perform homogeneous Fenton reactions. In addition, commercial ferric-based powders, such as Fe-200 and $CuFe_2O_4$, were also utilized to check the efficiency of TOC degradation. Table III illustrated the results of RUN 4~ RUN 8. In the case of RUN 4 and RUN 5 by homogeneous catalysts, DRE could both achieve more than 99%, however, the results of RUN 6 ~ RUN 8 only have much lower DRE of 54.96% ~ 78.98%. This suggested that Fenton reactions were preceded efficiently as the catalysts were soluble into homogeneous state in the simulated solution. However, the soluble iron salts would produce large amount of suspensions and sludge in basic condition. Thus, the sequential process of separation was needed, and the secondary wet wastes were formed to be further treated. In comparison with homogeneous catalysts, heterogeneous catalysts would not produce sludge or secondary wastes and provided the cost economically treatments of organic liquid waste. In Table III, it was also demonstrated Cu or Ce contained catalysts performed well than Fe-200 powders, which means Cu/Ce metal could improve the efficiency of Fenton oxidation reaction.

TABLE III
TOC DEGRADATION BY DIFFERENT CATALYSTS

Catalyst	RUN 4	RUN 5	RUN 6	RUN 7	RUN 8
	Homogeneous catalyst		Heterogeneous catalyst		
	$FeSO_4 \cdot 7H_2O$	$Fe(C_2O_4) \cdot 2H_2O$	Fe-200	$CuFe_2O_4$	CFCO
W_{TOCi} (mg) ^a			2968		
W_{TOCf} (mg) ^b	13	20	1337	624	791
C_{TOC} (mg/L)	115	175	10780	5625	6590
DRE (%)	99.56	99.33	54.96	78.98	73.35
pH	1.91	5.25	2.02	2.29	2.40

Volume of MeOH solution (10%): 100 ml (TOC = 29682 mg/L)

50% H_2O_2 : 50 ml at adding rate of 2.5ml/min

Amount of CFCO catalysts: 2g

Reaction condition: 95°C for 60 min

^a W_{TOCi} : initial weight of TOC before Fenton-like oxidation reaction

^b W_{TOCf} : final weight of TOC after Fenton-like oxidation reaction

D. Fenton-Like Oxidation of Radioactive Liquid Wastes by Using Heterogeneous Catalyst

Aqueous phase stored in T61 was selected as radioactive liquid waste for the investigation of Fenton-like oxidation reaction, and CFCO precipitates were utilized as heterogeneous catalysts. The catalytic oxidation process was proceeded by adding 2 g of CFCO precipitates into aqueous wastes of 100 ml under thermal condition at 95°C. In addition to mechanical agitation, the solution of H_2O_2 (50%) was also added by drops

at the rate of 2.5 ml/min. The digital images of aqueous waste sample from T61 tank, as-prepared CFCO catalysts, experimental apparatus, and treated sample were shown in Fig. 3. The experimental conditions of catalytic oxidation of aqueous wastes were also illustrated in Table IV.

TABLE IV
TOC DEGRADATION OF AQUEOUS WASTE SAMPLES FROM T61

	RUN 9	RUN 10	RUN 11	RUN 12	RUN 13
C_{TOCi} (mg/L) ^a			21600		
CFCO catalyst (g)	0	0	2	2	2
H ₂ O ₂ (ml)	0	80	20	40	80
C_{TOCf} (mg/L) ^b	9162	491	151	109	3

Volume of aqueous waste from T61: 100 ml

50% H₂O₂: adding rate of 2.5 ml/min by drops

Reaction condition: 95°C for 120 min

^a C_{TOCi} : initial concentration of TOC before Fenton-like oxidation reaction

^b C_{TOCf} : final concentration of TOC after Fenton-like oxidation reaction

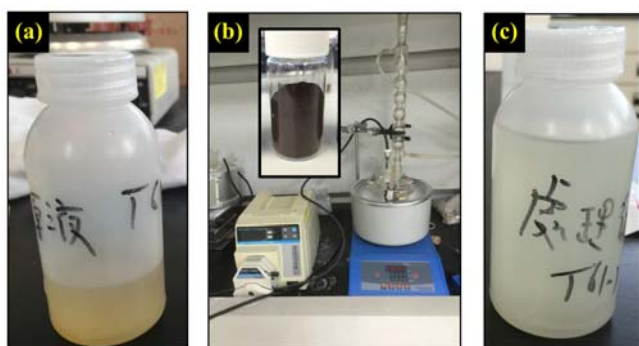


Fig. 3 The digital images of (a) aqueous waste sample, (b) apparatus and CFCO catalysts, and (c) treated sample

The apparatus was combined with glass reactor, liquid transport tube, condenser, liquid transport pump, oil bath and hotplate. As aqueous wastes were heating in the reactor, the produced vapor and steam were partly condensed and reflux into the reactor. However, the organic component with low boil point could not trapped by the condenser. Thus, the organic vapor would transfer into the ambient, which leading to the reduction of TOC concentration in aqueous waste samples, as shown in result of RUN 9. In the case of RUN 9, neither CFCO catalysts nor H₂O₂ were added and it was also found the reduction of TOC concentration from 21600 to 9162 ppm. This illustrated the apparatus was similar to the distillatory, which separate the light component (with low boil point) from the liquid mixtures. In order to investigate the role of H₂O₂ in the distillatory apparatus, 80 ml H₂O₂ solution was added in RUN 10. It was found the TOC concentration was reduced from 9162 to 491 ppm. The results revealed that the aqueous wastes were degraded in the presence of H₂O₂ even without catalysts. It was known that H₂O₂ was reactive and unstable reagent under thermal or light condition, which leading to the production of •OH radicals for the oxidation and degradation of organic components. However, the residual TOC in wastewater was still too high for further vaporization process due to the accumulation of bubbles. Thus, it was necessary to improve the degradation of aqueous waste through catalytic oxidation. In

the case of RUN 11 ~ RUN 13, the results demonstrated the amounts of H₂O₂ was benefit for the TOC degradation from 151 to 3 ppm by using 20 to 80 ml of H₂O₂. According to the results of RUN 9 ~ RUN 13, it was clear that the performance of Fenton-like oxidation of aqueous waste was depend on the presence of CFCO catalysts and the amount of H₂O₂ added.

IV. CONCLUSION

In this work, ferrite-based catalysts were prepared and applied in the Fenton-like oxidation reaction by comparison with homogeneous water-soluble catalysts and commercial available catalysts. According to the results of catalytic oxidation, the TOC concentration of either simulated solution or aqueous radioactive wastes were reduced obviously without forming sludge or wet secondary wastes. It was also found that the amounts of H₂O₂ were indeed helpful for the improvement of TOC degradation.

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