Iranian Journal of Chemical Engineering
Vol. 11, No. 1 (Winter), 2014, IAChE

Research note

Photocatalytic Decomposition of Epichlorohydrin by TiO_2/Ag Coated Sintered Glass Filters

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Abstract

The sintered glass filters with 90–150 µm porosity were coated with titanium oxide/silver composite. For deposition of titanium oxide, the filter was deep coated in the titanium oxide sole. Subsequently the solution of silver nitrate in methanol was used for silver deposition. The ultra violet (UV) radiation with 254 nm wave length was used for reducing silver ions to metallic silver. The prepared filters were characterized by X-ray diffraction and scanning electron microscopy. The photo-catalytic efficiency of TiO_2 and TiO_2/Ag coated sintered glass filters was investigated for photocatalytic decomposition of epichlorohydrin. The 67% of 1 and 20 mg/lit of epichlorohydrin solution in ethanol was decomposed by TiO_2 /Ag coated filter after 3 hours UVA radiations.

Keywords: *TiO_2/Ag, Epichlorohydrin, Photocatalyst, Coated Sinter Glass Filter*

1. Introduction

Epichlorohydrin (1-chloro-2, 3-epoxypropane) is a raw material used in the manufacture of various resins (epoxy resins, ion exchangers, etc.) and elastomers. Epichlorohydrin-based polymers are used as a coagulant in the treatment of water supplies. The presence of epichlorohydrin in water is caused by its migration from various materials in contact with the water, into the water stream [1].

Epichlorohydrin in drinking water has the potential to negatively impact human health. Due to the presence of chlorine and an epoxy bridge in ECH (Fig. 1), it is a highly reactive molecule. ECH tends to hydrolyze in water at ambient temperature to form 3-MCPD (3-monochloropropane-1,2-diol or 3-chloro-1,2-propanediol), a carcinogen. The hydrolysis of ECH is accelerated in the presence of heat and acid [2].

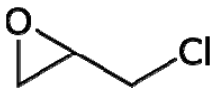

Figure 1. Epichlorohydrin molecule.

Titanium oxide TiO_2 is well known as a photocatalyst for decomposition of environmental pollutants. This photocatalyst

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absorbs photons of 380 nm wavelength then generates electron-hole which produces active oxygen species such as $O^{\cdot}$ and $OH^{\cdot}$ radicals and O_2^- ion by reaction with adsorbed H_2O and O_2 on the TiO_2 surface [3-6]. Additionally, in the photo-catalytic reactions, it is considered that the deposition of metals, such as platinum, gold, palladium and silver on TiO_2 increases the charge separation efficiency and inhibits recombination of electron and hole produced by UV absorption [3, 4, 7]. The increase in charge separation efficiency will enhance the formation of active oxygen species. In recent years, several studies have been reported on preparation of heterogeneous photo-catalyst on polymers and ceramics or quartz substrates [8-11]. An antibacterial thin film from silver, titanium oxide, polyvinyl-pyrrolidone and a macromolecule as stabilizer have been prepared by *Zhang et al.* for drinking water system [12]. Many researchers have observed enhanced degradation rates of dyes due to the deposition of silver on titanium oxide [13]. In this paper silver- deposited TiO_2 was prepared on a sintered glass filter substrate and the characteristics and photo-catalytic activities for degradation of epichlorohydrin were analyzed.

2. Experimental

2-1. Materials and equipment

The X-ray diffraction (XRD) investigation was performed on a Philips DW3710 using CuKα radiation at 50KV and 250 mA in the range of 5–70. The micro-structures were studied by a scanning electron microscope (SEM) from Cambridge Co. Stereo Scan 360. A commercial sinter glass filter with 90 – 150 μm porosity as substrate was chosen.

Epichlorohydrin (ECH) from Merck Company as a toxic volatile organic compound for investigation of photo-catalytic activity of filters and its photo-degradation was chosen. The reaction products were analyzed by gas chromatography–mass selective detector (GC-MS) from Agilent Technologies, GC 6890 N and MS- 5973 Model, with the column HP-5M (30m x 0.25 mm x 0.25 μm). The employed GC condition was: oven initial temperature 50°C, held for 3 min and increasing to 140°C with the ramp rate 8°C/min. The concentration of un-degraded ECH was obtained from integration of chromatography picks.

2-2. Cleaning of substrates

Sintered glass filter substrate was immersed in concentrated sulfuric acid overnight and was then rinsed with de-ionized water. After removing the sulfuric acid, the filter was dried in oven at 120°C.

2-3. Preparation titanium oxide sole and coating of sintered glass filter

For preparation of titanium oxide sole, acetic acid was added into the 2-propanol for the estrification reaction. Then, titanium tetra isopropoxide (TTIP) was added drop-wise under stirring condition. It was also further stirred for 1h after the addition of precursor at room temperature. The molar ratio of 2-propanol/ acetic acid/ TTIP was 45: 6: 1. This sole was stable for a few weeks.

Two clean filters were deep coated for 5 minutes in titanium oxide sole, the filter was dried at 120°C and annealed 1 h in 500°C. This coating process was repeated 3 times for

one of the filters and the prepared sample was named filter/TiO_2.

Another coated filter was dipped in a solution of 0.05 mol/lit silver nitrate in methanol for 5 minutes. The silver ions were reduced to elemental silver by irradiation under 40 W UV lamp with 254 nm wavelength for 30 minutes. The filter was previously white in color and changed to dark which indicates the formation of metal silver. This filter was coated with TiO_2 sol as in the above method, and subsequently coated with silver again 2 times and the sample was named filter/TiO_2/Ag.

2-4. Photo-degradation of ECH

Two solutions of ECH in ethanol with 1 and 20 mg/lit concentrations were prepared. Three segments from the filter, filter/TiO_2 and filter/ TiO_2/ Ag with an area 1 cm^2 were dipped in 50 ml of the above solutions. The solutions were irradiated under 32 W UVA and analyzed by GC-Mass at different times.

2-5. Characterization of coated filters

The X- ray diffraction (XRD) of filter/TiO_2/ Ag (Fig. 2) shows weak peaks of anatase TiO_2 on the amorphous glass. The measuring of silver by atomic absorption indicated that the amount of silver was 0.12 percent of filter, therefore the silver peak was not observed in XRD patterns.

In the scanning electron microscopy (SEM) study, the filter before (a) and after coating with titanium oxide (filter/TiO_2) was compared (Fig. 3). As seen in these images, the grains and the porosity of SiO_2 are thoroughly coated by titanium oxide. The forming of cracked layers increased the porosity and surface area of this filter and improved efficiency of the filter as a catalyst. The thickness of titanium oxide layer is about 1 μm after undergoing coating process three times.

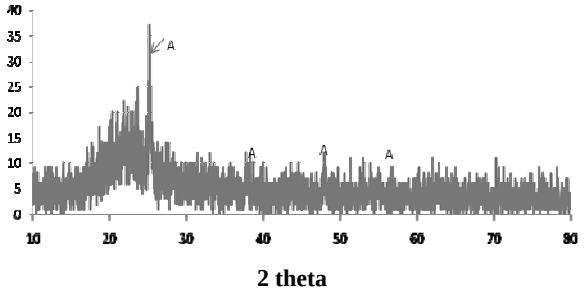


Figure 2. XRD pattern of filter /TiO_2 /Ag (A = Anatase titanium oxide).

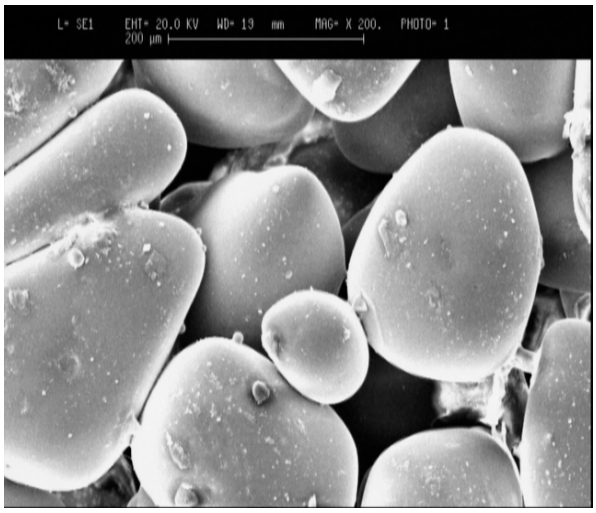
Fig. 4 shows the SEM micrographs of the filter/TiO_2/Ag. In Fig. 4 (a) the cracked TiO_2 layer is observed clearly and silver nanoparticles are observed in the higher magnitudes in Fig. 4 (b).

In this research work, the sintered glass filter without coating with TiO_2 was coated with silver nitrate and was later reduced to metal silver. The dark filter after shaking in water changed to white in color. This indicated that the silver particles were not fixed rigidly on SiO_2 substrate but were deposited only by the aid of TiO_2.

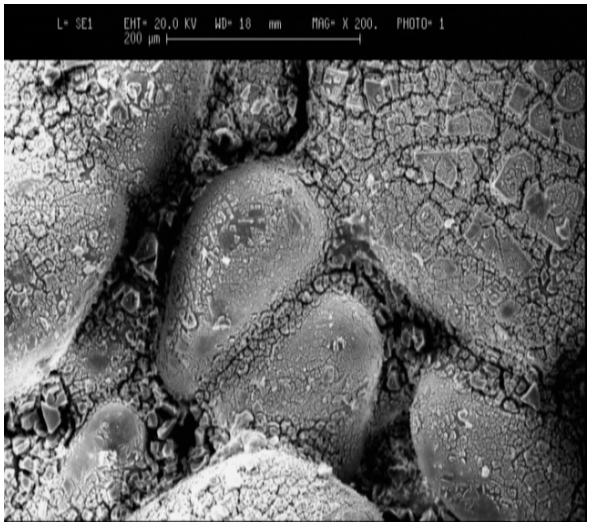
2-6. Photo degradation of ECH

Fig. 5 shows the chromatograms of the ECH solutions with the concentration of 20 mg/lit after UVA irradiation in 3h. The peak at the 2.73 min retention time corresponds to ECH. Integrating these peaks indicates the ECH was degraded only 7% in the presence of filter/TiO_2 while it was degraded 64% in the presence of filter/TiO_2/Ag. After 24 h of irradiation, photo-degradation in the presence of filter/TiO_2 increased to 46% and the other

filter increased to 67%. The results clearly show the silver deposited filter increased the rate of ECH photo-degradation and improved the photo-catalytic efficiency.



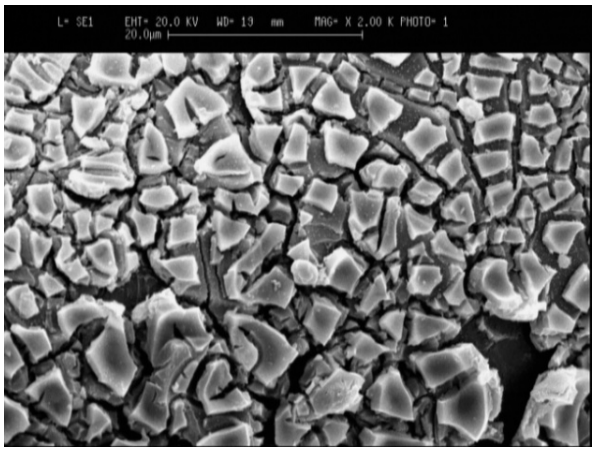
(a)



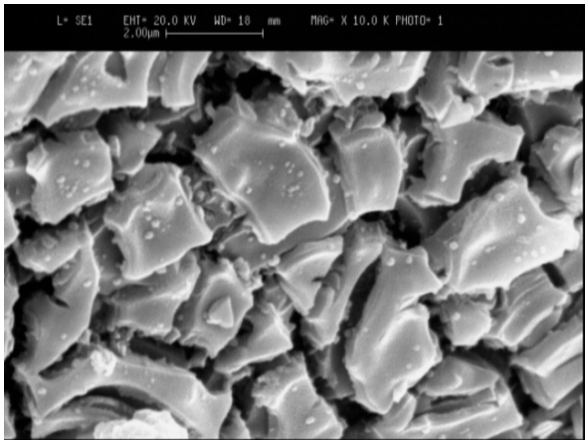
(b)

Figure 3. SEM images of sintered glass filter (a) and filter/TiO_2 (b).

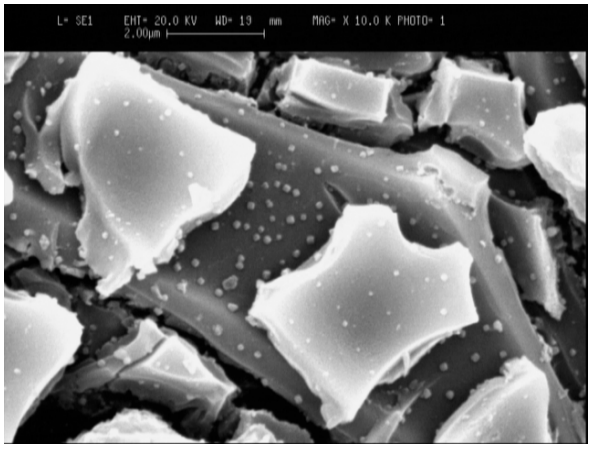
The other solutions of ECH with the concentration of 1mg/lit irradiated in the same conditions. In the lower concentration the rate of degradation was not changed by the filter/TiO_2/Ag, while ECH was degraded 46% by TiO_2 photo-catalyst after 3 hours radiation (Fig. 6).



(a)



(b)



(c)

Figure 4. SEM images of filter/TiO_2/Ag in different magnitude.

This study confirms that the deposited metal silver on TiO_2 increases the charge separation efficiency and inhibits recombination of electron and hole produced

by UV absorption. The silver is more efficient in primary hours and activity of catalyst decreased after 24 hours. It may be due to oxidation of silver by the active oxygen species in solution for a long time.

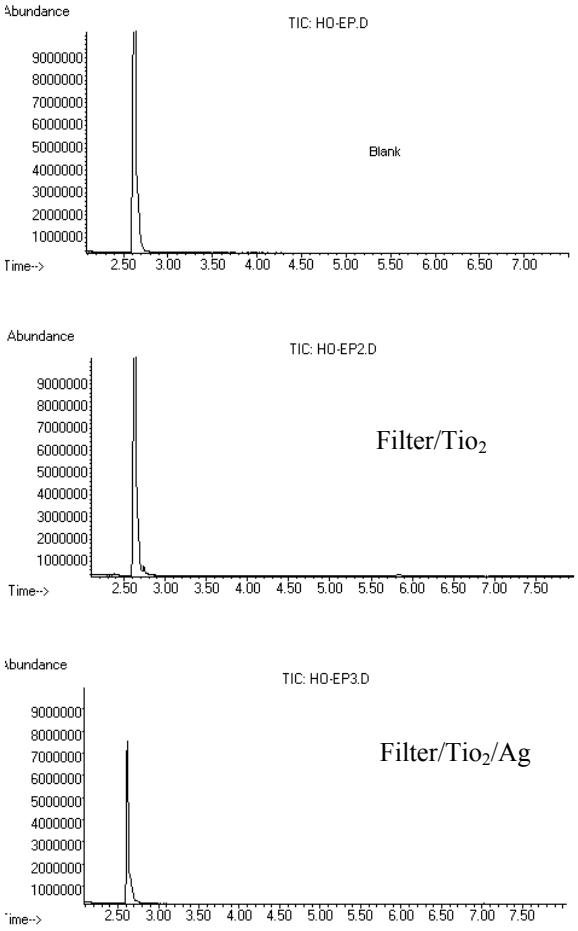


Figure 5. Chromatograms of ECH with primary concentration 20 mg /lit after 3h UVA irradiation.

3. Conclusions

For fixing silver particles on sintered glass filter a titanium oxide layer is needed. Both filter/TiO_2 and filter/TiO_2/Ag photo-degraded a part of the epichlorohydrin, but the filter/TiO_2/Ag is more efficient in primary hours. Although the metal silver on TiO_2 increases the charge separation efficiency in longer duration of (24 hours) irradiation, the silver may be oxidized by active oxygen, therefore reducing the efficiency of the catalyst.

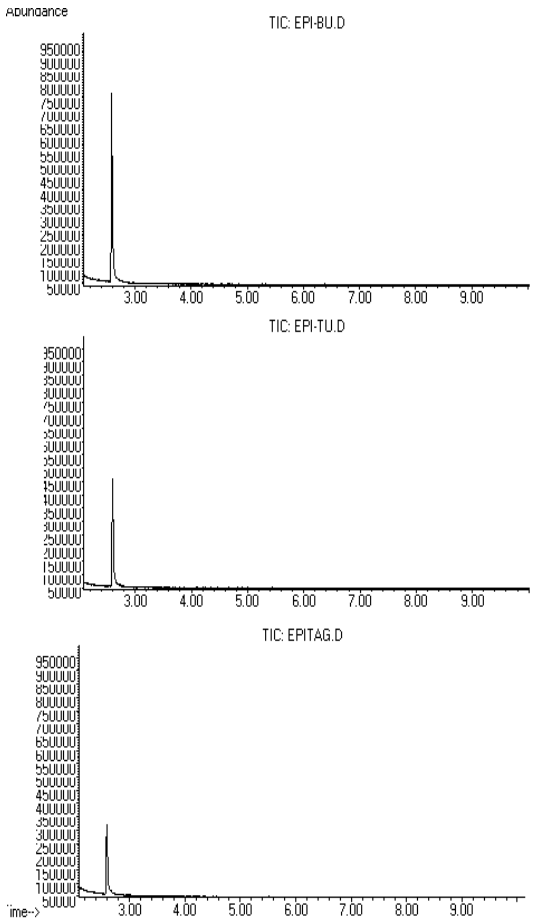


Figure 6. Chromatograms of ECH with primary concentration 1 mg /lit after 3h UVA irradiation.

References

[1] IPCS Epichlorohydrin, Geneva (World Health Organization), International Program on Chemical Safety (Environmental Health Criteria 33), (1984).

[2] IARC overall evaluation of carcinogenicity: An updating of IARC for research on cancer, pp. 202-203, (1987).

[3] Hoffmann, M.R., Martin, S.T., Choi, W. and Bahnemann, D.W., "Environmental applications of

semiconductor photocatalysis", Chem. Rev., 95, 69, (1995).

[4] Linsebigler, A.L., Lu, G. and Yates, J. I., "Photocatalysis on TiO_2 surfaces: principles, mechanisms and selected results", Chem. Rev., 95, 372, (1995).

[5] Ibusuki, T. and Takeuchi, K., "Removal of low concentration nitrogen oxides through photoassisted heterogeneous catalysis", J. Mol. Catal., 88, 93, (1994).

[6] Ishitani, O., Inoue, C., Suzuki, Y. and Ibusuki, T., "Photocatalytic reduction of carbon dioxide to methane and acetic acid by an aqueous suspension of metal-deposited TiO_2", J. Photochem. Photobiol. A: Chem., 72, 269, (1993).

[7] Dunnill, C.W., Page, K., Aiken, Z.A., Noimark, S., Hyett, G., Kafizas, A., Pratten, J., Wilson, M. and Parkin, I.P., "Nanoparticulate silver coated-titania thin films-photo-oxidative destruction of stearic acid under different light sources and antimicrobial effects under hospital lighting conditions", J. Photochem. Photobiol., A: Chem., 220, 113, (2011).

[8] Ubolchonlakate, K., Sikong, L. and Tontai, T., "Formaldehyde degradation by photocatalytic Ag-doped TiO_2 film of glass fiber roving", J. Nanoscience and Nanotechnology, 10, 7522, (2010).

[9] Kato, Sh., Hirano, Y., Iwata, M., Sano, T., Takeuchi, K. and Matsuzawa, S., "Photocatalytic degradation of gaseous sulfur compounds by silver-deposited titanium dioxide", Appl. Catal., B: Environ., 57, 109, (2005).

[10] Jin Choi, K. and Won Hong, S., "Preparation of TiO_2 nanofibers immobilized on quartz substrate by electrospinning for photocatalytic degradation of ranitidine", Res. Chem. Intermed., 38, 1161, (2012).

[11] Yu, B., Leung, K.M., Guo, Q., Lau, W.M. and Yang, J., "Synthesis of Ag–TiO_2 composite nano thin film for antimicrobial application", Nanotechnology, 22, 115603, (2011).

[12] Zhang, L., Bai, X., Tian, H., Zhong, L., Ma, C., Zhou, Y., Chen, Sh. and Li, D., "Synthesis of antibacterial film CTS/PVP/TiO_2/Ag for drinking water system", Carbohydrate Polymers, 89, 1060, (2012).

[13] Damm, C. and Israel, G., "Photoelectric properties and photocatalytic activity of silver-coated titanium dioxides", J. Dyes and Pigments, 75, 612, (2007).