Catalytic ozonation of PCE by clay from tidal flat sediments

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Clay from tidal flat sediments showed an efficient catalytic activity in the decomposition of PCE by ozonation where the thermal treatment of clay enhanced the catalytic activity. No changes in XRD patterns of clays by the thermal treatment were observed, while EPR spectra were significantly changed. The intensity of the EPR signal that arises from natural radiation defect was decreased with increasing thermal treatment temperature, which enhanced the PCE removal efficiency. Contrary to ozonation alone, superoxide radicals were detected from ozonation in the presence of clay. This suggests that the superoxide radicals further increase PCE decomposition.

KEY WORDS: catalyst; clay; EPR; ozonation; PCE

1. Introduction

The widespread use of chlorinated organic compounds, including perchloroethylene (PCE) as cleansing solvents and their accidental and illegal emission into the environment has led to the serious pollution of groundwater resources all over the world [1]. Hence, many technologies such as aeration, conventional oxidation (commonly ozonation alone), activated carbon absorption and advanced oxidation technology have been attempted and effective methods have been desired to treat these chlorinated organic contaminants [2–4]. Among them, ozonation is a common process of water treatment used for the oxidation of pollutants [5]. However, as it was shown [6], ozonation alone is not sufficient for effective degradation of chlorinated pollutants in water. Therefore, seeking some apt promoters such as a catalyst to increase the efficiency of ozonation seems to be one of the most pressing tasks. Thus, we investigated the ozonation of PCE using clay from tidal flat sediments as catalyst in this study. The effect of thermal treatment temperature of clay on the PCE removal was characterized by X-ray diffraction (XRD) and electron paramagnetic resonance (EPR) spectroscopy. EPR is a powerful tool to characterize paramagnetic metal ions and defects in oxide catalysts [7]. Moreover, the catalytic activity of clay was evaluated in terms of radical production by the EPR/spin trapping method that is a useful tool to detect unstable radicals [8].

2. Experimental

2.1. Clay treatment and characterization

The clay used in this work was taken from tidal flat sediments at Yeosu, South Korea. It contains, expressed as a wt% mass, silicon 29%, aluminum 10%, iron 3.8% and potassium 2.3% analyzed using an energy dispersive X-ray spectrometer (EDS) [9].

The clay was washed with a 15% H_2O_2 solution (clay 1 g for 50 cm^3 of solution) at 50 °C for 24 h in order to eliminate the organic impurities [10], and the residual H_2O_2 was removed by several washings with water. The clay was then dried at 110 °C after sedimentation and filtration. After this treatment, the thermal treatments of clay were carried out in air at 300, 500 and 700 °C for 2 h. EPR spectra of clays before and after the thermal treatment were recorded in the X-band on a Bruker EMX spectrometer at 77 K. The thermal transformation and the formation of clay were also observed with X-ray diffraction (model PW-1710, Philips Co.).

2.2. Catalytic ozonation and solution analyses

Experiments were performed at room temperature (around 20 °C) in 50 ml pyrex glass bottle reactors that were filled up to full with ozone-saturated water (about 5.8 ppm) in the presence of 0.8 wt% thermally treated clays. The ozone-saturated water was prepared by bubbling with ozone gas, which was made by a laboratory ozonizer (Won Jeon Technical Development Co. Ltd., Korea) with 99.99% dioxygen. PCE was purchased from Aldrich and PCE decomposition experiments were performed with 0.03 mM PCE solution.

For PCE analyses, 2 ml of sample were withdrawn from the reactor into 2 ml of an aqueous solution of 0.2 M $Na_2S_2O_3$, in order to remove the excess ozone [1]. PCE contents were measured by a Younglin M600D gas chromatograph equipped with a ^{63}Ni-electron capture detector. The concentration of residual ozone was measured by the spectrophotometric indigo carmine method immediately after sampling [11].

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2.3. Radical measurements

A nitro spin-trapping reagent DMPO (5,5-dimethyl-pyrroline-N-oxide) was used to detect radicals. Ozone solutions were prepared by purging ozone gas through phosphate buffer (0.1 M, pH 7.4) for two hours and the DMPO (100 mM) in phosphate buffer and/or clays were added then further purged with ozone gas for 10 min. 25 μl of sample solution were transferred into a capillary tube, and then EPR spectra were recorded in the X-band on a Bruker EMX spectrometer.

3. Results and discussion

Figure 1 shows the PCE removal by ozonation with and without clays. The PCE removal for ozonation alone and in the presence of the thermally treated clays at 110, 300, 500 and 700 °C after 10 min of ozonation was 60.6, 77.8, 78.8, 84.3 and 93.9%, respectively. The PCE removal efficiency in the presence of thermally treated clays was much better than that of ozonation alone and increased with thermal treatment temperature of clay.

In order to evaluate ozone consumption in ozonation with and without clays, the content of the residual ozone is shown in figure 2. The rate of ozone consumption in the presence of thermally treated clays was much faster than that of ozonation alone and increased with thermal treatment temperature of the clay. This is quite similar to the tendency of the PCE removal. In presence of the clay treated at 700 °C, especially, ozone is completely consumed after only 10 min. The above results indicate that clay catalyzes ozone consumption and thus enhances PCE removal efficiency.

XRD was used to identify the thermal transformation and the formation of clays by thermal treatment. Figure 3 shows XRD patterns of clays thermally treated at from 110 to 700 °C. The result of the XRD analyses shows that the clays are composed of illite, quartz and albite and the thermal treatment dose not change XRD patterns. This indicates that the enhanced PCE decomposition in the presence of clay is not caused by the thermal transformation and the formation of clays.

EPR spectroscopy was used to characterize the change of clay that was not detected by XRD and to evaluate the change of the PCE removal efficiency. Figure 4 shows EPR

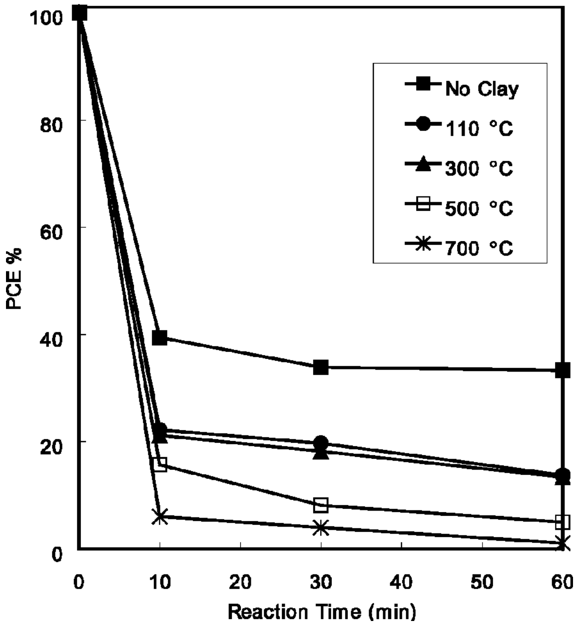

Figure 1. PCE decomposition by ozonation with and without clays.

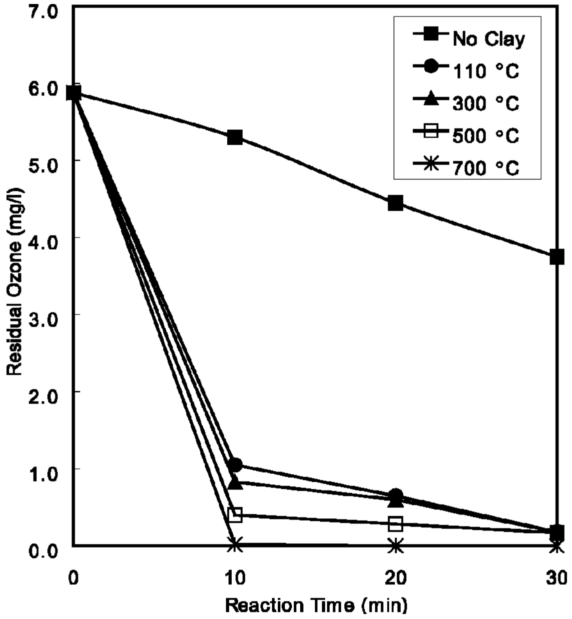

Figure 2. Ozone consumption with and without clays.

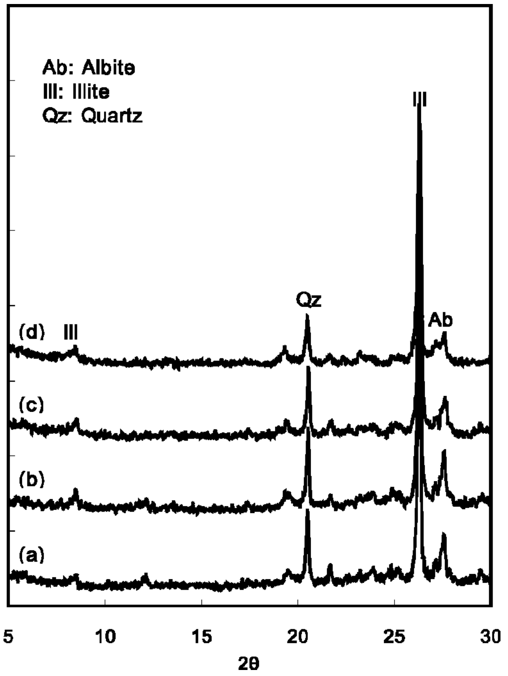

Figure 3. XRD patterns of clays thermally treated at (a) 110, (b) 300, (c) 500 and (d) 700 °C.

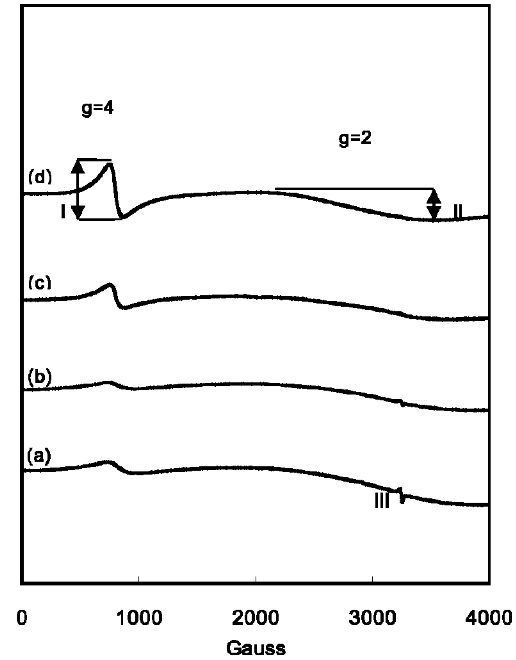

Figure 4. EPR spectra of clays thermally treated at (a) 110, (b) 300, (c) 500 and (d) 700 °C.

spectra of clays that were thermally treated at from 110 to 700 °C [9]. They showed three distinct signals. Signal I at $g = 4$ comes from localized Fe^{3+} in the structure, broad signal II at $g = 2$ is attributable to Fe(III) oxy/hydroxide species on the surface and narrow signal III at $g = 2$ is assigned as natural radiation defect that induces the formation of radicals [10,12].

The intensity of the signal I increased while the intensity of the signal III decreased with increasing thermal treatment temperature. In particular, signal III disappeared according to increasing thermal treatment temperature. This indicates that natural defect of clay is deeply related to the PCE removal efficiency, that is, the intensity of signal III is inversely proportional to the PCE removal by ozonation. The relationship between the signal I and the PCE removal efficiency has not been identified thus far; however this might not be important because the Fe^{3+} localized in the structure might not influence the catalytic reactions occurring on the surface.

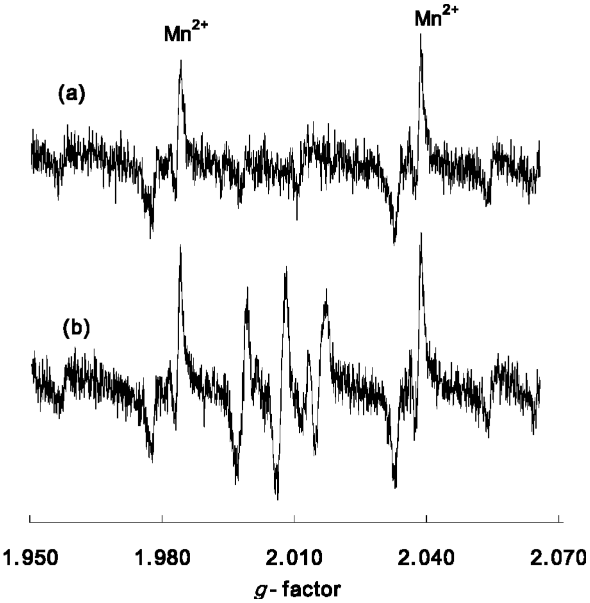

Figure 5. EPR spectra of DMPO-OH adduct obtained from (a) ozonation alone and (b) ozonation in the presence of the thermally treated clay at 700 °C.

It is widely known that ozone reacts with various organic and inorganic compounds in aqueous solution, either by a direct reaction of molecular ozone or through a radical type reaction induced by ozone decomposition in water [13]. EPR/spin-trapping was used to characterize the difference of ozonation with and without clay in terms of radical production. Figure 5 shows EPR spectra obtained from spin trapping experiments with DMPO. The triplet signals with $g = 2.006$ are observed from ozonation with clay, while no EPR signal is observed from ozonation without clay. The triplet signals can be assigned as the superoxide radicals [14] that are generally known to accelerate the oxidation of organic compound [15,16]. From this result, we carefully suggest that the clay catalyzes the ozone decomposition and thus increases the radical production to accelerate the PCE decomposition.

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