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A role for calcium hydroxide and dolomite in water: Acceleration of the reaction under ultraviolet light

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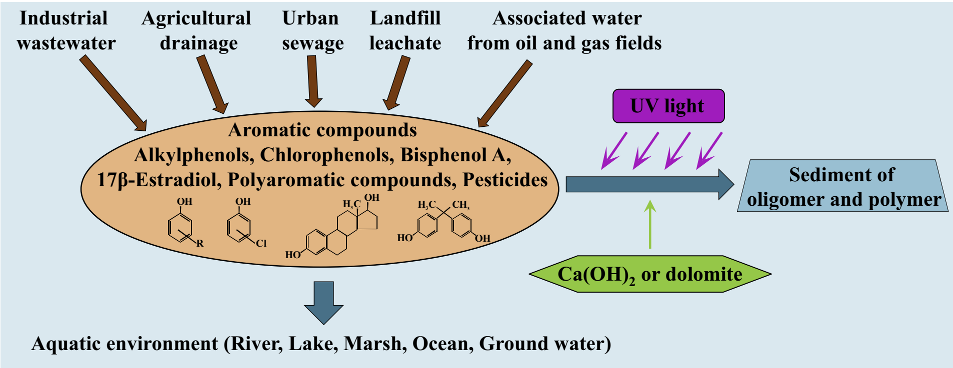
HIGHLIGHTS

- Organic environmental pollutants are removed from water under ultraviolet light.
- Addition of calcined dolomite can accelerate the reaction significantly.
- The major component of dolomite responsible for the removal was calcium hydroxide.
- The mechanism is not mineralization but polymerization.

GRAPHICAL ABSTRACT



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ABSTRACT

Organic environmental pollutants are now being detected with remarkably high frequency in the aquatic environment. Photodegradation by ultraviolet light is sometimes used as a method for removing organic chemicals from water; however, this method is relatively inefficient because of the low degradation rates involved, and more efficient methods are under development. Here we show that the removal of various organic pollutants can be assisted by calcined dolomite in aqueous solution under irradiation with ultraviolet light. It was possible to achieve substantial removal of bisphenol A, chlorophenols, alkylphenols, 1-naphthol and 17β-estradiol. The major component of dolomite responsible for the removal was calcium hydroxide. Our results demonstrate that the use of calcium hydroxide with ultraviolet light irradiation can be a very effective method of rapidly removing organic environmental pollutants from water. This is a new role for calcium hydroxide and dolomite in water treatment.

1. Introduction

Environmental pollutants, which have carcinogenic, mutagenic, teratogenic, endocrine-disrupting properties, or acute and chronic toxicity, are now being detected in rivers, lakes, marshes, oceans and groundwater (Giger et al., 1984; Colborn et al., 1996; Fukazawa et al., 2001; Yamamoto et al., 2001; Kashiwada et al., 2002; Ministry of the Environment, 2010). Especially, bisphenol

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A (BPA), chlorophenols, alkylphenols, and some kinds of pesticides have been detected with remarkably high frequency in the aquatic environment in Japan (Ministry of the Environment, 2010).

Phenols are widely used as a raw material in industry. BPA has been used in the manufacture of epoxy resin and polycarbonates. These plastic materials are finally disposed of in landfill and BPA can be extracted by rain water. BPA was often detected in high levels in leachate from landfill sites, which is one of the sources of BPA found in environmental water (Yamamoto et al., 2001). BPA is also produced in pulp wastewater during paper recycling (Fukazawa et al., 2001). Chlorophenols are used as raw materials in the production of pesticides and dyes. They may also be present in industrial wastewater resulting from the production of these materials. 2,4-Dichlorophenol is a decomposition product of 2,4-dichlorophenoxyacetic acid (2,4-D), which is a widely used herbicide in the world (Pattanasupong et al., 2004). Chlorophenols also occur in pulp wastewater as a by-product of chlorine bleaching. Alkylphenols are used in the manufacture of surfactants and are often found in the waste from sewage plants, even after the surfactant-containing sewage has been treated in an effluent treatment facility (Giger et al., 1984). Associated water, which is the ground water generated in producing oil and natural gas, contains various alkylphenols. It has also become clear that 17β-estradiol, a natural human and animal female sex hormone, is present in large quantities in sewage (Kashiwada et al., 2002).

For the removal of environmental pollutants in water, biological methods using microorganisms, such as bacteria, fungi and microalgae, have also been pursued. For example, microalgae can be effective in treating hazardous chemicals (Hirooka et al., 2003, 2005). However, it is generally difficult to find a single microorganism capable of breaking down multiple hazardous chemicals. Combination of microorganisms, such as soil microorganisms (Pattanasupong et al., 2004) and activated sludge, was also used for degrading multiple chemicals. However, it is sometimes difficult to degrade large numbers of different pollutants simultaneously using the microorganisms. Furthermore, these microbial methods take a comparatively long time to degrade some pollutants, which means that a large-scale treatment system is necessary. For these reasons, there are limitations in treating pollutants using only biological methods. On the other hand, water treatment using UV light is a well-known method for degrading organic compounds, and is used in water-purification systems. It is possible to degrade a large variety of environmental pollutants under the same conditions by irradiating them with UV light. However, because of the low degradation rates involved, in practical terms the method is not widely used for wastewater treatment. In order to accelerate the reaction speed of organic pollutants under UV irradiation, advanced oxidation processes (AOPs) were also reported using hydrogen peroxide (Rosenfeldt and Linden, 2004) or ozone (Rivas et al., 2009) as an oxidizing agent for BPA treatment. In these methods, produced OH radicals oxidize and mineralize organic compounds rapidly. However, the practical applications of AOPs have still been limited. One reason is the high cost of these oxidizing agents.

Calcium hydroxide ($Ca(OH)_2$) and dolomite are harmless to living things, and are widely used as a food additive, neutralizer of acidic water and soils, plaster, mortar, materials for pulp, steel and resin production. $Ca(OH)_2$ is produced by calcination and hydration of limestone. Dolomite is often produced with limestone. In this study, we found a new role for $Ca(OH)_2$ and dolomite in water treatment. The photochemical removal of various organic environmental pollutants from water was assisted by $Ca(OH)_2$ or calcined dolomite under irradiation with UV light. We showed the characteristics of this reaction using BPA, and discussed the mechanism through which it works.

2. Materials and methods

2.1. Material and reagents

The dolomite, which was calcined and hydrated, was produced in Tochigi Prefecture, Japan. The other chemicals were purchased from Nacalai Tesque (Kyoto, Japan).

2.2. Experimental procedure

As a base case, each organic compound was dissolved in 50 mL of milli-Q water in a 100-mL beaker. The concentration of BPA, 4-*tert*-butylphenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4-D, 3,5-dimethylphenol, 1-naphthol, 2-nitrophenol, 3-nitrophenol and 2,4,6-trinitrophenol was 100 μM. The concentration of 17β-estradiol and 4-octylohenol was set at 10 and 50 μM, respectively, because of the low solubility. Dolomite was added to the solutions at $1.0\ g\ L^{-1}$. UV light was produced from a low-pressure mercury lamp (peak = 254 nm; GL-15, Panasonic, Osaka, Japan) placed 12 cm above the surface of the solution (light intensity = $1.22\ mW\ cm^{-2}$). UV irradiation was performed for 60 min with mixing by a magnetic stirrer at 100 rpm. For comparison, solutions were also incubated under UV irradiation without dolomite. For the characterization of BPA removal, the dolomite concentration was varied in the range from 0.05 to $8.0\ g\ L^{-1}$, initial BPA concentrations from 25 to 200 μM, and light intensity from 0.53 to $2.18\ mW\ cm^{-2}$ at the surface of the solution, by varying the height of the lamp above the surface in the range 6–24 cm. 1 mL of each solution was sampled before and after irradiation.

2.3. Analytical methods

Concentrations of BPA and organic compounds were measured using a HPLC system (D-7000 series; Hitachi, Tokyo, Japan) with a UV detector (L-4500; Hitachi) at 280 nm. A Cosmosil 5C18-AR-II column (4.6 mm $\phi \times$ 150 mm; Nacalai Tesque) was used for the separation. For pretreatment, each HPLC sample (150 μL) was mixed with 15 μL of 5 M HCl, and 40 μL of this solution was then applied. Methanol/water (50/50, v/v) was used as the mobile phase at a flow rate of $1\ mL\ min^{-1}$.

Intermediate products of BPA were identified by a liquid chromatography mass spectrometry (LC-MS) analyses, which were performed on a HCTultra IonTrap-MS system (Bruker Daltonics, Kanagawa, Japan). A Xterra-C18 column (2 mm $\phi \times$ 150 mm; Waters, MA, USA) was used for the separation at 30 °C. Solvent A was 10 mM ammonium acetate, and solvent B was methanol. The initial composition of the binary solvent was 50% B and was kept for 5 min. Solvent B was increased from 50% to 90% over 5 min and remained for 5 min. Then, it was decreased to 50% and remained for 10 min. A flow rate was set at $0.2\ mL\ min^{-1}$. 50 μL of sample solution was applied. Mass spectrometer was operated using an electrospray ionization source in the negative mode.

Light intensity was measured with a UV photometer, UVX Digital Radiometer, with a radiometer sensor, UVX-25 (UVP, CA, USA).

Diffraction pattern of sample by X-ray diffraction (XRD) was measured from 2° to 80° of 2θ by RAD-C (Rigaku, Tokyo, Japan) using Cu Kα X-ray.

Metal contents of dolomite were analysed using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Optima 3000XL, Perkin Elmert, CT, USA). Dolomite was dried in an oven at 120 °C for 1 h. For measurement of Ca and Mg, 0.01076 g of dried dolomite was dissolved in 1 mL of HCl and diluted with pure water in a 100-mL volumetric flask. For the other metals, 0.19995 g of