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Heavy-metal extraction from aqueous medium with an immobilized TiO_2 photocatalyst and a solid sacrificial agent

K. Tennakone *, K.G.U. Wijayantha

Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka

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Abstract

A system consisting of a layer of calcium oxalate coated on paper followed by a layer of TiO_2 above calcium oxalate is found to extract heavy metals (Pb, Hg) from an aqueous medium under solar irradiation. The mechanism involves the transfer of photogenerated electrons to metal ions in the solution with consumption of holes by calcium oxalate. It is suggested that dangling carboxylate bonds on the surface of calcium oxalate facilitate hole transfer towards calcium oxalate.

Keywords: Heavy metal removal; Photocatalysis; Titanium dioxide; Sacrificial agent

1. Introduction

The application of semiconductor photocatalysis as a means of decontaminating heavy-metal (Pb, Hg) polluted water has been discussed by several authors [1–4]. In addition to heavy metal depollution, this technique is also a promising method for extracting heavy metals from the aqueous medium. TiO_2 powder, the photocatalyst used for the above purpose, is inert and shows sufficient sensitivity to sunlight. Most studies on photocatalytic extraction of heavy metals are based on dispersions of TiO_2 powder in water, which involves the energy-consuming operation separating TiO_2 from the liquid phase [5–12]. To avoid this major drawback, methods of deposition of TiO_2 on glass, polythene, etc., have been proposed, and the results obtained seems to be promising [13]. Another problem associated with photocatalytic heavy metal extraction with TiO_2 is the necessity of using hole-consuming sacrificial agents to enhance the rate of reduction of metal ions. Examples of sacrificial agents used are water-soluble substances such as formaldehyde or citric acid [13,14]. The removal of the excess sacrificial agent and supplementing large bulks of solution with the same are problems that restrict the adoptability of semiconductor photocatalysis for heavy-metal extraction. An ideal technique would be to incorporate a solid sacrificial agent together with the catalyst onto a suitable substrate. We have succeeded in accomplishing this goal by fabricating a system where calcium oxalate (hole-consuming sacrificial agent) is coated on paper, and above which a layer of TiO_2 is deposited. In this composite system having solid ingredients, the light incident on the top layer of TiO_2 is photoactive. Of the photogenerated carriers, electrons are transferred to the solution reducing heavy-metal ions in solution, while holes are consumed by calcium oxalate lying beneath the TiO_2 particles coated on the upper surface. Experiments indicated that this system is capable of extracting lead from aqueous solution under solar irradiation.

2. Experimental

Calcium oxalate was prepared by mixing aqueous solutions of ammonium oxalate (0.5 M) and calcium chloride (0.5 M). The precipitate of calcium oxalate formed in the double decomposition is filtered, washed with water and dried in air at 110°C. Dried precipitate is grounded and made into a paste by addition of water and further grinding. The paste is evenly spread on a sheet of paper (thickness ~0.5 mm) to form a layer of thickness ~0.2 mm and dried at 90°C. The outer surface of calcium oxalate layer is then painted with a suspension of the anatase form of TiO_2 (Aldrich 99.9%, specific surface area ~3.8 $m^2\ g^{-1}$ as measured by Horiba particle size distribution analyzer (CAPA 700)) in water (0.05 g in ml of H_2O) and dried again. Irradiation experiments were conducted in sunlight, as well as in a photochemical reactor. Experiments under sunlight were performed as follows: A solution (100 ml) containing lead nitrate (400 ppm of Pb^{2+}

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* Corresponding author.

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at pH ~6) was placed in a cylindrical glass vessel (diameter = 12.2 cm, height = 6.5 cm). A paper disc coated with calcium oxalate/TiO_2 (approximately the same diameter as the glass vessel) was kept immersed just below the surface of the solution (which is magnetically stirred) and exposed to sunlight (average solar intensity as measured by an Eko Pyranometer Model MS-801 being 680 w/m^2). The depletion of lead in the solution was monitored by atomic absorption spectroscopy, and the black deposit on the surface was collected and tested for Pb using X-ray diffractometer (Shimadzu XD-D1). To determine the rates of CO_2 evolution during irradiation, experiments were also conducted in a 500-ml water-cooled (26°C) photochemical reactor (Applied Photophysics) with a quartz inner jacket (diameter ~5.7 cm). In these experiments, the calcium oxalate/TiO_2-coated paper was loosely wrapped around the inner quartz cylinder of the reactor, and the solution containing 400 ppm of Pb^{2+} was placed in the annular region (~0.65 cm) between the quartz cylinder and the double-walled pyrex jacket. The light source (400 W medium pressure mercury lamp of photon flux $\sim 5 \times 10^{19}$ photons s^{-1}) was mounted at the central axis of the quartz cylinder. The solution was kept purged with pure nitrogen (15 ml min^{-1}), and carbon dioxide in the outgoing gas was determined by gas chromatography (Shimadzu GC 9AM gas chromatograph, activated charcoal column, thermal conductivity detector). To ascertain the role of oxygen in the photochemical reaction, experiments were also conducted when the solution is kept purged with air (15 ml min^{-1}). In both sets of experiments (i.e., in sunlight and with the UV lamp), lead depletion and CO_2 evolution were also examined in the absence of one ingredient TiO_2 or calcium oxalate.

The following procedure was used to test for the presence of $CaCO_3$ in the final residual. Photolysis was continued until evolution of CO_2 from the photochemical reactor reached its minimum. Five millilitres of concentrated HCl was then added to the solution and the gas phase examined for CO_2.

3. Results and discussion

Results of the experiment conducted in sunlight are illustrated in Fig. 1. When the paper coated with calcium oxalate/TiO_2 is used, nearly complete removal of lead from the solution occurs in about 4 h (Fig. 1, curve 1) and in the absence of sunlight, depletion of lead in the solution was not observed (Fig. 1, curve 4). A detectable but very small decrease in Pb^{2+} concentration is observed when paper is coated with one of the ingredients calcium oxalate or TiO_2 (Fig. 1 curves 2 and 3). X-ray diffractometry revealed that the black deposit on paper coated with calcium oxalate/TiO_2 is metallic lead. Fig. 2 shows the rate of CO_2 evolution ($R[CO_2]$) in experiments with the photochemical reactor, when the solution is purged with N_2. As the rate of hole

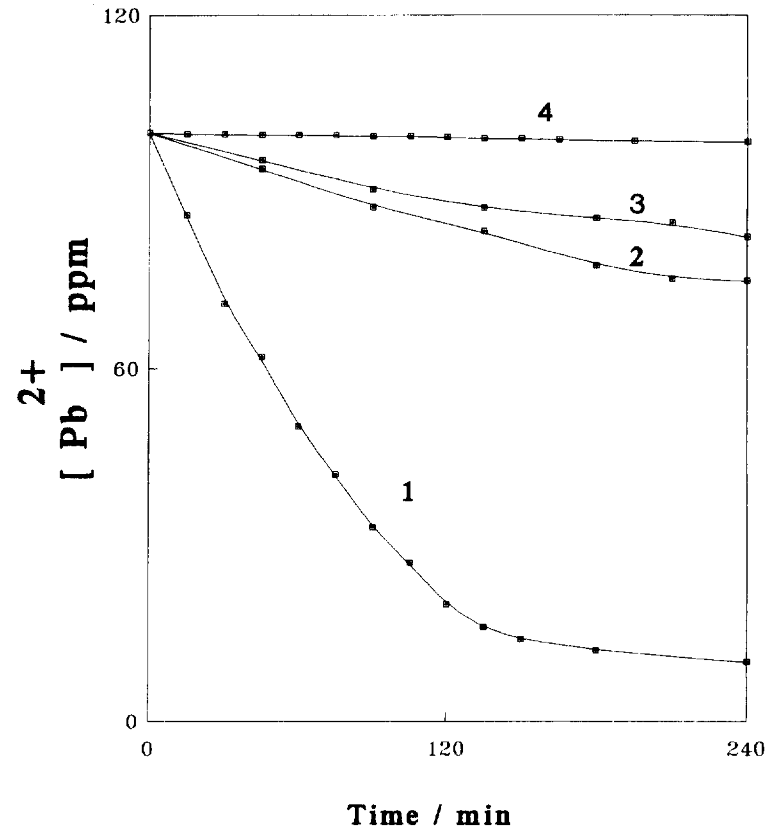

Fig. 1. Depletion of lead in the solution under the sunlight in the presence of (1) calcium oxalate/TiO_2-coated paper, (2) TiO_2-coated paper, (3) calcium oxalate-coated paper (4) in the dark.

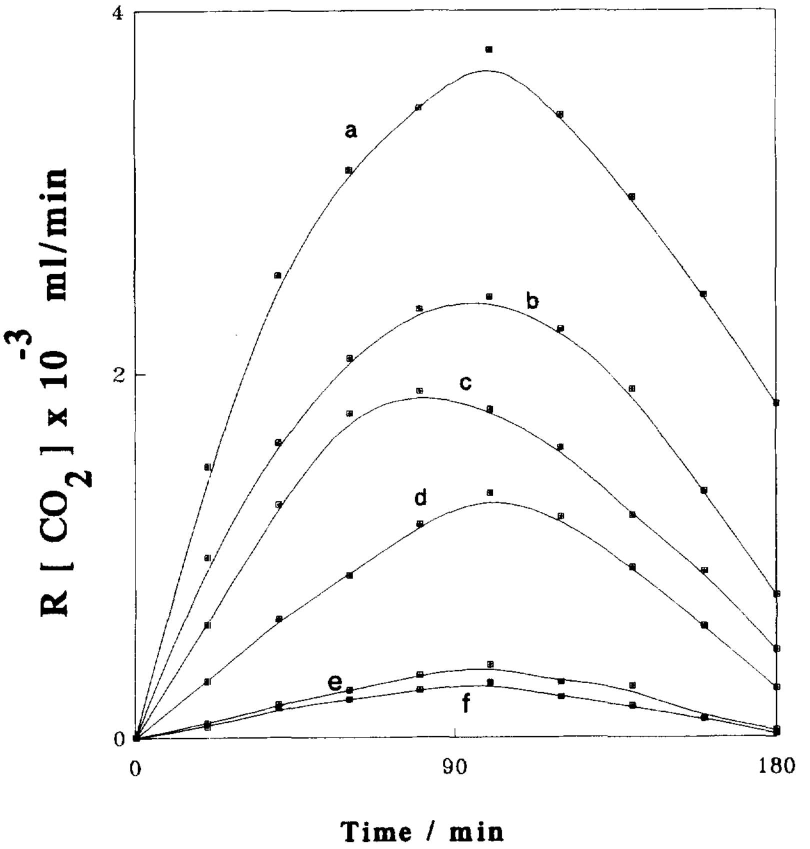

Fig. 2. Plot of carbon dioxide evolution rate ($R[CO_2]$) vs. time in the absence of oxygen (nitrogen-purged solution) with calcium oxalate/TiO_2 paper in reactor experiment at Pb concentrations of (a) 400 ppm, (b) 200 ppm, (c) 100 ppm, (d) 50 ppm, (e) 400 ppm with calcium oxalate coated paper, (f) 400 ppm with TiO_2-coated paper.

consumption by calcium oxalate is dependent upon the rate of electron acceptance by Pb^{2+}, the initial valve of $R[CO_2]$ increases with the increase of the concentration of Pb^{2+} in the solution. Fig. 3 shows the time development of $R[CO_2]$ when the solution is kept purged with air. Lead deposition with CO_2 evolution is still noticed, slightly higher value $R[CO_2]$ (for 100 ppm, compare curve c of Fig. 2 and curve a of Fig. 3) in the air-purged experiment is presumably due to direct interaction between $O_2^{\bullet -}$ and calcium oxalate (the superoxide ion $O_2^{\bullet -}$ is formed when photogenerated electrons in TiO_2 are transferred to molecular oxygen).

The effective reaction steps involved in the system can be summarized as follows: Bandgap radiation incident on TiO_2 generates electron-hole pairs of which the electrons tunnel into the solution reducing Pb^{2+} to metallic Pb, i.e.,

$$h\nu \xrightarrow{TiO_2} e^- + h^+ \qquad (1)$$

$$2e^- + Pb^{2+} \rightarrow Pb \qquad (2)$$

Holes react with hydroxyl ions producing highly oxidative hydroxyl free radicals $OH^\bullet$, which reacts with calcium oxalate yielding carbon dioxide.

$$OH^- + h^+ \rightarrow OH^\bullet \qquad (3)$$

$$2OH^\bullet + Ca(COO)_2 \rightarrow CaCO_3 + CO_2 + H_2O \qquad (4)$$

It is known that carboxylate bonds strongly interact with the TiO_2 surface and facilitate transfer of electrons into TiO_2 (alternatively holes from TiO_2) across the carboxylate bonds. Perhaps the dangling carboxylate bonds on the surface of calcium oxalate are instrumental in transferring holes towards calcium oxalate. A schematic diagram depicting the proposed mechanism is shown in Fig. 4.

The acidified final residual was examined for CO_2 evolution. The increase of CO_2 observed after acidification revealed that the final product contained $CaCO_3$.

4. Conclusion

The above experiments demonstrate the feasibility of using a solid hole-consuming agent to promote reductive photocatalytic action of TiO_2. The efficiency of the system depends on the ability of the sacrificial agent to attract holes. Calcium oxalate is an insulator; we believe that dangling carboxylate bonds on calcium oxalate plays an important role. An alternative is to look for a sacrificial material that is a p-type semiconductor that accumulate holes. It may be possible to improve the performance of the system by improving the TiO_2 layer deposited on calcium oxalate. The particle size and thickness of this layer are crucial for efficient charge

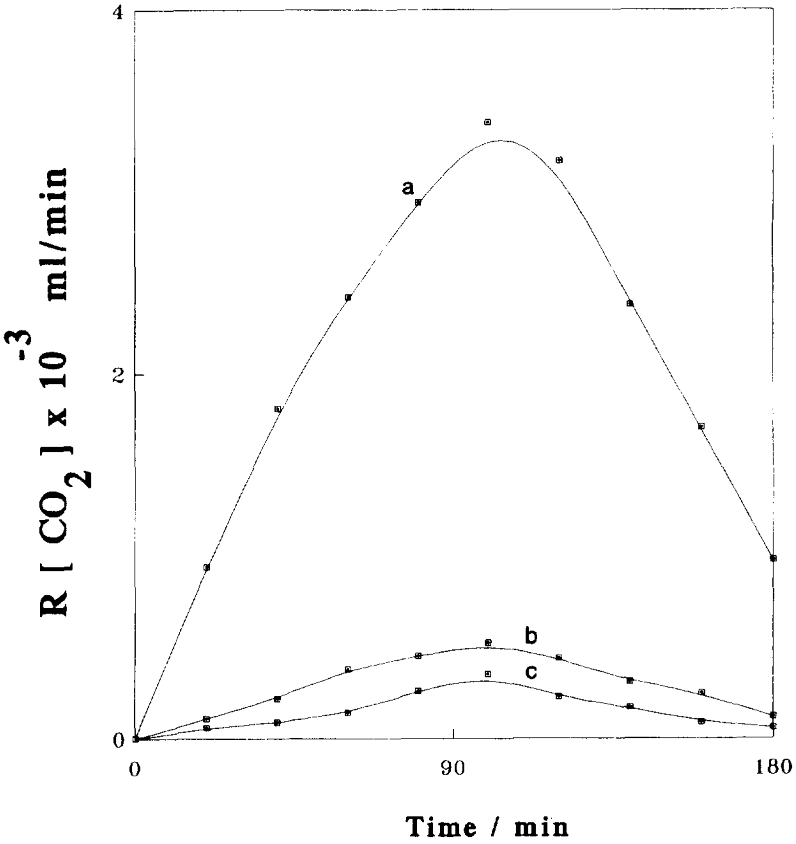

Fig. 3. Plot of carbon dioxide evolution rate (R[CO_2]) vs. time in the experiments with the photochemical reactor (air-purged solution) when Pb^{2+} concentration is 100 ppm (a) calcium oxalate/TiO_2-coated paper, (b) calcium oxalate-coated paper, (c) TiO_2-coated paper.

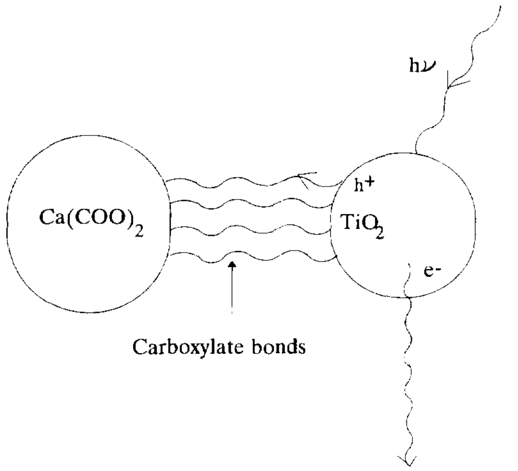

Fig. 4. Schematic diagram showing carboxylate bonds on the surface of calcium oxalate interacting with the TiO_2 surface, acting as bridges that facilitate hole transfer from TiO_2 to calcium oxalate.

transfer. The system is also capable of extracting Hg, Ag, and to a lesser extent Cd and Cu.

Acknowledgements

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