Original Article

Improving Effect of MnO₂ Addition on TiO₂-Photocatalytic Removal of Lead Ion from Water

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ABSTRACT

Removal of Pb (II) ions from water was carried out by a coupling approach of adsorption and photoelectrodeposition over a porous TiO₂ photocatalyst loaded with MnO₂. The addition of MnO₂ onto the porous TiO₂ accelerated the photocatalytic oxidation of Pb (II) ions, which was caused by a strong interaction between MnO₂ and Pb (II) ions. Since the same effect was not observed on the photocatalytic degradation of methylene blue over MnO₂/TiO₂ photocatalysts, the photoelectrodeposition reaction rate appears to be determined by the amount of Pb (II) ions adsorbed on the surface of porous TiO₂ loaded with MnO₂.

Keywords: titanium dioxide, manganese dioxide, adsorption, photodeposition, lead ion removal

INTRODUCTION

Lead is one of the poisonous heavy metals released from various industrial processes, such as mining and processing plants. Because the toxicity causes serious damage to human body as well as environment, the technology of Pb (II) ion removal from wastewater is urgently required in accordance with more and more stringent environmental regulations in each country. Commonly, many effective techniques have been proposed for heavy metal ion removal from water, such as chemical precipitations using hydroxide, sulfide and chelating agents; ion exchange processes; and adsorption [1,2]. Among them, adsorption seems to be the most attractive approach due to its recovery merit and easy handling. However, it is difficult to remove the total ions by sole adsorption due to an accompanying desorption process. In order to compensate for the drawback, subsequent photoelectrodeposition of adsorbed Pb (II) ions has been attempted by TiO₂-photocatalytic oxidation [3,4] or reduction [5–9]. According to thermodynamic constraints, photocatalytic reduction of Pb (II) ions is a minor route and requires a hole scavenger for the reaction to proceed, whereas Pb (II) ions are mainly oxidized to PbO₂ by TiO₂-photocatalysis under O₂ or O₃ [3,4]. Chen and Ray [3]

reported that a P25 TiO₂ (Degussa) shows a higher oxidative removal than Hombikat UV 100 under ultraviolet (UV) light irradiation. In addition, Murrini *et al.* [4] reported that addition of platinum on P25 further improves the photocatalytic activity.

The objective of this study is to develop a TiO₂ photocatalyst possessing a high removal capacity of Pb (II) ions from water by a coupling method of adsorption and photoelectrodeposition. Improvement in the adsorption capacity is attempted by synthesizing high surface area of TiO₂ photocatalysts and adding MnO₂ particles on them. According to Pb (II) ion adsorption mechanism on TiO₂ reported by Yang and Zhang [10], the main driving force is electrostatic interaction between the ion and hydroxyl groups on TiO₂ surface about 5 sites per nm². The adsorption capacity improvement is expected by increasing the site number by preparing porous TiO₂. For further improvement of the adsorption capacity, MnO₂ is then loaded on the porous sample. Actually, MnO₂ itself has a strong interaction with Pb (II) ions, and the superior performance as adsorbents or additives has already been reported by some studies [11–13]. However, it has also been reported that MnO₂ addition to TiO₂ induces less UV light absorption of TiO₂ [14,15]. Thus, the influence of MnO₂

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Fig. 1 Flow chart of the synthesis of $\text{MnO}_2/\text{TiO}_2$ photocatalysts.

addition on Pb (II) ion removal by coupling adsorption and photocatalysis was discussed.

MATERIALS AND METHODS

Sample preparation

Porous TiO_2 was prepared by soft-templating method, following a procedure similar to that reported by Kobayashi *et al.* [16]. The flow chart is shown in **Fig. 1**. Approximately 1.0 g $(\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20}$ triblock copolymer (Pluronic P123 from BASF, Ludwigshafen, Germany) was dissolved in 10.0 ml of 99.5% ethanol (Wako Pure Chemical Industries, Osaka, Japan), and the solution was magnetically stirred for 4 hours. After that, an appropriate amount of 97% titanium (IV) isopropoxide (Sigma-Aldrich, St. Louis, USA) was dissolved in the solution with the addition of 1.6 mL 60% nitric acid (Wako Pure Chemical Industries, Osaka, Japan), and the solution was stirred for another 5 hours. After 2-day drying in an oven at 80°C , obtained precursor was again heated at increasing temperature rate of $1^\circ\text{C}/\text{min}$ to 400°C and then kept at 400°C for 4 hours. The final product was denoted as m-TiO_2 .

For MnO_2 loading m-TiO_2 photocatalysts, manganese species were loaded by impregnation method. Prepared titanium oxide (m-TiO_2) was impregnated in ethanol solution of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Osaka, Ja-

pan). Added amounts of the nitrate were adjusted according to MnO_2 weight percentage of 20 – 70% in the final products. After evaporation of ethanol, the precursor was calcinated at 400°C for 3 hours.

For comparison, TiO_2 (JRC-TIO-4 (2), supplied by Japan Reference Catalyst Society) was used in activity tests, which is actually identical to Degussa P25 commonly used as the standard photocatalyst.

Activity test

Experiments for lead ion removal were carried out under two different UV light sources: weak scattered UV light in Exp. (1) and high-power spot UV light in Exp. (2). The former was selected to evaluate the removal capacity in view of the actual applicable condition, while the latter was used to confirm the substantial capacity for a short period. Chosen Pb (II) ion concentration was over the range of 100 – 1000 ppm in order to evaluate the removal capacity of prepared catalysts under high concentration Pb (II) ion solution. All experiments were performed in closed test tubes or cells in air at room temperature ($23 \pm 3^\circ\text{C}$).

In Exp. (1), two 6W UV lamps (UVL-56 Handheld UV lamp, $2 \mu\text{W}/\text{cm}^2$ each, wavelength 365 nm, UVP LLC) without filters were placed 4 cm away from both sides of the test tube containing 0.1 g catalyst and 20 mL solution stirred at room temperature for 6 or 48 hours. Regularly used solution of 500 ppm Pb (II) ions was prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ (Wako Pure Chemical Industries, Osaka, Japan) in ion-exchange water. The pH value of solution was 4.9. After the experiments, the suspension was centrifuged at 15,000 rpm for 1 hour to separate solid and liquid. The resulting supernatant was used for the measurement of concentration of remaining ions by an inductively coupled plasma atomic emission spectroscopy (ICP-AES, PS7800, Hitachi) to examine the removal amount of lead ion in the solution. Experimental errors were calculated by conducting some experiments there times. Obtained coefficient of variation (CV) was 0.7 – 0.9% which indicated a good repeatability of experiments, so each experimental data shown in the figures was taken without repeated experiments.

In Exp. (2), a 200 W Hg-Xe lamp (Hamamatsu Photonics K. K., L5662-02, $4500 \text{ mW}/\text{cm}^2$, wavelength 200 nm) was used for a UV light source. The light was irradiated to a quartz cell of 50 mg sample and 30 mL solution of 209 ppm Pb (II) ions for 3 hours. After the experiment, Pb (II) ion concentration in the filtrate, which was obtained by vacuum filtration with $0.2 \mu\text{m}$ membrane filters (Merck Millipore, Darmstadt, Germany), was analyzed by ICP-AES (ICP-7510,

SHIMADZU). Detailed experimental procedures were described in the previous study [17]. In Exp. (2), the experimental errors were separately calculated by conducting each experiment in triplicate.

Experiments for photocatalytic degradation of methylene blue (MB) were carried out in a batch reactor. At first, 1 ml solution of 10 ppm MB (Wako Pure Chemical Industries, Osaka, Japan) and 5 mg sample powder were put together in a glass test tube, and then a UV LED lamp (NSPU510CS, NICHIA Corporation, 75 mW, wavelength 375 nm) was placed 5 cm away from the solution surface to irradiate UV light to the suspension for 20 minutes. Each solution was then centrifuged at 15,000 rpm for 10 minutes for solid-liquid separation. Finally, the remaining MB amount in each filtrate was examined by a UV-Vis spectrophotometer (U0080D, HITACHI). The experimental errors were separately calculated by conducting each experiment in triplicate.

Sample characterization

Phase identification was made with an X-ray diffractometer (XRD, D8ADVANCE, Bruker AXS) operated at 40 kV and 40 mA using monochromated Cu-K α radiation. Diffraction intensities were recorded from 20° to 80° at the rate of 2.000°/min with 0.020° step. Brunauer-Emmett-Teller (BET) surface area of the porous sample was measured by nitrogen adsorption experiments (Flowsorb III, Shimadzu Corporation). After the heat pretreatment of sample at 120°C for 30 minutes under the flow of 30% N₂/70% Ar mixture, adsorbed amount of nitrogen on the sample was measured at liquid nitrogen temperature. Morphology observation and surface elemental analysis of the samples used for the adsorption experiment were performed with a field emission scanning electron microscope and energy dispersive X-ray (FE-SEM/EDX, SU8000, Hitachi).

RESULTS AND DISCUSSION

Figure 2 (a) indicates the XRD pattern of m-TiO₂ prepared, where clear peaks were observed corresponding to anatase phase. In order to identify the loaded manganese species, XRD patterns were measured of several m-TiO₂ loaded with ~40wt% manganese species in the form of MnO₂, where no specific peaks were observed except anatase TiO₂ (**Fig. 2 (b)**). However, main peaks ascribable to MnO₂ were finally visible at 37.3° and 56.6° in a sample with an excess loading of 70wt% as shown in **Fig. 2 (c)**. Since XRD cannot detect the crystal structure of too small particles dispersed within samples, the results suggested that the particle size of MnO₂

existed on m-TiO₂ surface could be < 5 nm in the case of loading of less than or equal to 40wt% MnO₂/m-TiO₂.

Adsorption experiments were conducted without UV light irradiation at room temperature. As shown in **Fig. 3**, adsorption equilibrium was quickly achieved within 10 minutes in each experiment. **Figure 4 (a)** shows adsorption isotherms of Pb (II) ions measured at room temperature. Since it is reported that Pb (II) ions primarily adsorb on hydroxyl groups of TiO₂ surface [10], solution pH significantly affects the adsorption amounts. In our experiments, in order to correctly evaluate each adsorption capacity, final pH values of solution were measured as indicated in **Fig. 4 (b)** and it was confirmed that the differences were negligible for the comparison. Langmuir parameters were then taken by curve-fitting of the model equation shown in equation (1) [18], and the parameters and BET surface areas are summarized in **Table 1**.

$$C = C_{\max} \frac{bC_{eq}}{1 + bC_{eq}} \quad (1)$$

where C [mg/g] is the amount adsorbed, $C_{\max}$ [mg/g] is the saturation amount, C_{eq} [mg/g] is the equilibrium concentration of liquid phase and b [L/mg] is the affinity constant.

As clearly seen in **Fig. 4 (a)**, Langmuir model gave good correlation to the isotherms, which indicated that Pb (II) ion adsorption occurred on TiO₂ in accordance with Langmuir type adsorption where one adsorbate adsorbs on one specific site existing on adsorbent surface. Comparing the values of $C_{\max}$, adsorption capacity followed an order of 20wt%

Fig. 2 XRD patterns of (a) m-TiO₂, and (b) 40wt% MnO₂/m-TiO₂ and (c) 70wt% MnO₂/m-TiO₂.

Fig. 3 Adsorption amounts of Pb (II) ions at room temperature with m-TiO₂ (●) and P25 (▲) in Exp. (1) condition without UV light as a function of time.

MnO₂/m-TiO₂ > m-TiO₂ > P25. Taking the BET surface areas into consideration, the capacity difference between m-TiO₂ and P25 is probably derived from the difference of surface area that was indicating the adsorption site number on the surface. It is therefore indicated that the potential improvement in Pb (II) ion adsorption by TiO₂ could be achieved by fabricating high surface area TiO₂. As for MnO₂-loaded sample, the addition of MnO₂ further improved the adsorption capacity by approximately twice compared to the case

of m-TiO₂ only, regardless of the decrease in the BET surface area. Since McKenzie [11] has reported that manganese dioxides give 40 times as high capacity of Pb (II) ion adsorption as iron oxides, it was suggested that MnO₂ particles themselves had a strong interaction with Pb (II) ions in water.

Experiments of UV light irradiation were performed in order to examine the photocatalytic removal of Pb (II) ions. **Figure 5** shows the photocatalytic removal with two different UV light sources. In both Exp. (1) and Exp. (2) conditions, extra Pb (II) ions were removed by irradiating UV light for any samples of 20wt% MnO₂/m-TiO₂, m-TiO₂ and P25. After the UV light irradiation experiments, the color of TiO₂ suspension changed from white to brown. The morphology change of MnO₂/m-TiO₂ catalyst before and after the UV light irradiation experiment was examined by SEM (**Fig. 6**). From the EDX analysis, the existence of Pb species on catalyst surface was confirmed after the reaction, but distinct morphology change of the sample was not observed. In addition, other than anatase, no corresponding peaks were observed in XRD measurements (not shown here). Therefore, it was speculated that Pb species could disperse on surface as microscopic form. According to the report by Murrini *et al.* [4], photocatalytic oxidation of Pb (II) ions into PbO₂ or PbO_{1.37} was verified in the experiments with TiO₂ (P25) under O₃ and Pt-loaded TiO₂ under O₂ or O₃. Chen and Ray [3] proposed the mechanism of photocatalytic removal of Pb (II) ions from water in accordance with equations (2) and (3).

Fig. 4 (a) Adsorption isotherms and (b) pH changes of 20wt% MnO₂/m-TiO₂ (●), m-TiO₂ (▲) and P25 (■) at room temperature in Exp. (1) condition without UV light, together with curve-fit results denoted by lines in (a).

Table 1 Summary of BET surface areas and Langmuir parameters.

Catalyst	BET surface area [m ² /g]	Langmuir parameters		
		C _{max} [mg/g]	b [L/mg]	R ²
P25	50.0	12.1	0.0115	0.983
m-TiO ₂	151.2	24.6	0.0147	0.994
20wt% MnO ₂ /m-TiO ₂	110.2	48.0	0.0177	0.994

Fig. 5 Removed amounts of Pb (II) ions in the absence (□) or presence (■) of UV light irradiation performed at two different conditions (Plots (○) indicate the differences between the removed amounts with and without UV light. Error bars on the right figure were made using CV values).

Fig. 6 SEM images of 20wt% MnO₂/m-TiO₂ catalyst (a) before and (b) after a 48-hour UV light irradiation experiment in Exp. (1) condition with the EDX spectra.

Fig. 7 Reaction rates of photoelectrodeposition per unit surface area over MnO₂/m-TiO₂ photocatalyst estimated from data taken after 6-hour UV light irradiation in Exp. (1) condition.

The valence band holes (h^+) were produced on TiO₂ surface by irradiating UV light on it, and the holes effectively worked to oxidize Pb (II) ions previously adsorbed on the surface. It is therefore implied in this study that extra Pb (II) ions were removed probably due to the photocatalytic oxidation into lead oxides. The deposition of lead oxides is an irreversible reaction that is not restricted by chemical equilibrium, so that the Pb (II) ion removal under UV light irradiation has more advantages than that of adsorption alone. In terms of recycling the photocatalyst, since the lead oxides are easily dissolved by weak acid solution, such as acetic acid, deposited lead oxides can be removed from the used catalyst after the acid treatment.

Figure 7 indicates the reaction rates of photocatalytic oxidation of Pb (II) ions per unit surface area, which were estimated by subtracting adsorbed amounts from total removed amounts under 6-hour UV light irradiation in Exp. (1) condition. Since the rate of photocatalytic oxidation linearly increased in accordance with the increase of MnO₂ loading, up to 20wt%, it was suggested that MnO₂ addition was effective for the rate improvement of photocatalytic oxidation. In the case of more than 20wt% MnO₂ loading, the rate became slower than the rate of 20wt% MnO₂/m-TiO₂ photocatalyst. This is probably because a number of photocatalytic active sites that were physically covered by excess MnO₂ particles

Fig. 8 Removed amounts of MB in the absence (□) or presence (■) of UV light irradiation performed Plots (○) indicate the differences between them (Shown pH values were measured after the reactions. Error bars were made using CV values).

occupied the TiO₂ surface to be deactivated.

In order to examine the photocatalytic activity of MnO₂/m-TiO₂, MB degradation experiments were then carried out under UV light irradiation. **Figure 8** shows the results of activity tests with 20wt% MnO₂-loaded/unloaded m-TiO₂ photocatalysts. As a result, MnO₂/m-TiO₂ gave less removal amount of MB mainly due to the decrease in adsorption capacity of TiO₂, but it should be noted here that the extra removal by photocatalysis of MnO₂/m-TiO₂ was almost the same or a little bit less than m-TiO₂ alone. This inhibition effect of MnO₂ on the photocatalytic activity of TiO₂ is also previously reported by Li *et al.* [14]. Thus, it can be concluded that MnO₂ actually did not improve the TiO₂-photocatalysis, or possibly deactivated it.

Considering the results discussed above, Pb (II) ion removal under UV light irradiation seems to proceed over MnO₂/m-TiO₂ according to the two processes of adsorption and subsequent photocatalytic oxidation as shown in **Fig. 9**. Adsorption capacity of TiO₂ was improved by adding MnO₂ particles on it as well as synthesizing high surface area TiO₂ by a P123-templating method (**Fig. 4**). Added MnO₂ worked to attract Pb ions onto the TiO₂ surface more closely and some adsorbed Pb (II) ions that were approachable to UV light could undergo the subsequent photocatalytic oxidation more smoothly (**Figs. 5 and 7**). As a result, a faster rate of reaction was given to show extra removal amount of Pb (II) ions. Thus, it is concluded that adsorbed amount of Pb (II)

Fig. 9 Expected Pb (II) ion removal mechanism over MnO₂/m-TiO₂. (a) Reversible adsorption process and (b) irreversible photocatalytic oxidation process.

ions could determine the rate of subsequent photocatalytic oxidation reaction on TiO₂.

CONCLUSIONS

Removal of Pb (II) ions from water was performed by the coupling method of adsorption and photocatalysis over porous TiO₂ loaded with MnO₂. Regardless of the decrease in BET surface area, addition of MnO₂ on porous TiO₂ improved the adsorption capacity, resulting from the strong interaction between MnO₂ and Pb (II) ions. The addition of MnO₂ further promoted the reaction rate of photocatalytic oxidation of adsorbed Pb (II) ions. Since photocatalytic degradation of methylene blue was not improved by MnO₂ addition, it was suggested that MnO₂ substantially did not improve the TiO₂-photocatalysis and only functioned to attract Pb (II) ions more closely to TiO₂ surface. In such situation, much Pb (II) ions might adsorb on TiO₂ more tightly, and it was suggested that the adsorbed amount could determine the reaction rate of the subsequent photoelectrodeposition.

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REFERENCES

- [1] Bailey SE, Olin TJ, Bricka RM, Adrian DD: A review of potentially low-cost sorbents for heavy metals. *Water Res.*, **33**(11), 2469–2479, 1999. doi: 10.1016/S0043-1354(98)00475-8
- [2] Fu F, Wang Q: Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manage.*, **92**(3), 407–418, 2011. doi: 10.1016/j.jenvman.2010.11.011
- [3] Chen D, Ray AK: Removal of toxic metal ions from wastewater by semiconductor photocatalysis. *Chem. Eng. Sci.*, **56**(4), 1561–1570, 2001. doi: 10.1016/S0009-2509(00)00383-3
- [4] Murrini L, Leyva G, Litter MI: Photocatalytic removal of Pb(II) over TiO₂ and Pt–TiO₂ powders. *Catal. Today*, **129**(1–2), 127–135, 2007. doi: 10.1016/j.cattod.2007.06.058
- [5] Mishra T, Hait J, Aman RK, Chakravarty JS: Effect of UV and visible light on photocatalytic reduction of lead and cadmium over titania based binary oxide materials. *J. Colloid Interface Sci.*, **316**(1), 80–84, 2007. doi: 10.1016/j.jcis.2007.08.037
- [6] Kabra K, Chaudhary R, Sawhney RL: Effect of pH on solar photocatalytic reduction and deposition of Cu(II), Ni(II), Pb(II) and Zn(II): Speciation modeling and reaction kinetics. *J. Hazard. Mater.*, **149**(3), 680–685, 2007. doi: 10.1016/j.jhazmat.2007.04.028
- [7] Murrini L, Conde F, Leyva G, Litter MI: Photocatalytic reduction of Pb(II) over TiO₂: New insights on the effect of different electron donors. *Appl. Catal. B*, **84**(3–4), 563–569, 2008. doi: 10.1016/j.apcatb.2008.05.012
- [8] Kabra K, Chaudhary R, Sawhney RL: Solar photocatalytic removal of Cu(II), Ni(II), Zn(II) and Pb(II): Speciation modeling of metal-citric acid complexes. *J. Hazard. Mater.*, **155**(3), 424–432, 2008. doi: 10.1016/j.jhazmat.2007.11.083
- [9] Yang ZP, Zhang C: Kinetics of photocatalytic reduction of Pb(II) on nanocrystalline TiO₂ coatings: A quartz crystal microbalance study. *Thin Solid Films*, **518**(21), 6006–6009, 2010. doi: 10.1016/j.tsf.2010.06.041
- [10] Yang ZP, Zhang C: Mechanism and kinetics of Pb(II) adsorption on ultrathin nanocrystalline titania coatings. *J. Hazard. Mater.*, **172**(2–3), 1082–1086, 2009. doi: 10.1016/j.jhazmat.2009.07.114
- [11] McKenzie RM: The adsorption of lead and other heavy metals on oxides of manganese and iron. *Aust. J. Soil Res.*, **18**(1), 61–73, 1980. doi: 10.1071/SR9800061

- [12] Han R, Zou W, Li H, Li Y, Shi J: Copper(II) and lead(II) removal from aqueous solution in fixed-bed columns by manganese oxide coated zeolite. *J. Hazard. Mater.*, **137**(2), 934–942, 2006.
- [13] Wang SG, Gong WX, Liu XW, Yao YW, Gao BY, Yue QY: Removal of lead(II) from aqueous solution by adsorption onto manganese oxide-coated carbon nanotubes. *Separ. Purif. Tech.*, **58**(1), 17–23, 2007. doi: [10.1016/j.seppur.2007.07.006](https://doi.org/10.1016/j.seppur.2007.07.006)
- [14] Li SJ, Ma ZC, Wang L, Liu JZ: Influence of MnO₂ on the photocatalytic activity of P-25 TiO₂ in the degradation of methyl orange. *Sci. China Ser. B*, **51**(2), 179–185, 2008. doi: [10.1007/s11426-007-0100-2](https://doi.org/10.1007/s11426-007-0100-2)
- [15] Xu X, Zhou X, Li X, Yang F, Jin B, Xu T, Li G, Li M: Electrodeposition synthesis of MnO₂/TiO₂ nanotube arrays nanocomposites and their visible light photocatalytic activity. *Mater. Res. Bull.*, **59**, 32–36, 2014. doi: [10.1016/j.materresbull.2014.06.025](https://doi.org/10.1016/j.materresbull.2014.06.025)
- [16] Kobayashi Y, Horiguchi J, Kobayashi S, Yamazaki Y, Omata K, Nagao D, Konno M, Yamada M: Effect of NiO content in mesoporous NiO–Al₂O₃ catalysts for high pressure partial oxidation of methane to syngas. *Appl. Catal. A Gen.*, **395**(1–2), 129–137, 2011. doi: [10.1016/j.apcata.2011.01.034](https://doi.org/10.1016/j.apcata.2011.01.034)
- [17] Ayawanna J, Teoh WT, Niratisairak S, Sato K: Gadolinia-modified ceria photocatalyst for removal of lead (II) ions from aqueous solutions. *Mater. Sci. Semicond. Process.*, **40**, 136–139, 2015. doi: [10.1016/j.mssp.2015.06.058](https://doi.org/10.1016/j.mssp.2015.06.058)
- [18] Do DD: Adsorption analysis: Equilibria and kinetics. Imperial College Press, London, 1998.