Fabrication and Photocatalytic Activity of Fishbone-like PbMoO$_4$ via Separation-assembly Coupling Technique Based on a Supported Liquid Membrane System

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Abstract. Self-assembly fishbone-like PbMoO$_4$ were fabricated via separation of Pb^{2+} from plumbeous solution and combining with MoO$_4^{2-}$ in another solution containing organic dye, based on a supported liquid membrane (SLM) system. The photocatalytic activity of PbMoO$_4$ to degrade the organic dye was measured, which revealed that the PbMoO$_4$ was efficient and stable photocatalyst for degradation of both Rhodamine B (RhB) and Methylene Blue (MB) under the irradiation of ultraviolet light. The PbMoO$_4$ after photocatalytic measurement were collected and characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and UV-vis spectroscopy (UV-vis). A possible formation mechanism of fishbone-like PbMoO$_4$ was discussed. This separation-assembly coupling technique (SACT) is a novel way to combine separation of heavy metal ions in wastewater, preparation of self-assembly functional nanomaterials and degradation of organic contaminations, based on an SLM system.

Introduction

It is so often that high concentration of heavy metals are contained in many industrial wastewaters produced by metal plating, metal finishing, mining, automotive, aerospace, battery and general chemical plants[1]. Thus, water pollution with heavy metal ions is a serious problem due to their serious toxicity to human beings and other living organisms[2,3]. Lead(II) is a toxic metal ion frequently found in wastewater coming from industrial effluents. Maximum contaminant level(MCL), which is the highest permissible level of a contaminant in drinking water, has been established by the United States Environmental Protection Agency(USEPA) in 0.015mg L^{-1}, while the maximum contaminant level goal (MCLG, i.e., the level of a contaminant in drinking water below which there is not known or expected health risk) has been set by USEPA at zero, indicating the extreme potential toxicity of lead [4].

To remove lead ions from industrial wastewater, some conventional heavy metal removal processes such as biosorption [5–9], chemical precipitation [10], coagulation, complexing, solvent extraction [11–13], electro-membrane processes[14–16], ion exchange[17,18], and ion exchange/adsorption on solid surfaces [19] have been developed. However, there are some inherent shortcomings such as requiring a large area of land, a sludge dewatering facility, skillful operators, high capital and regeneration costs and multiple basin configurations [10]. Recently, some novel methods [20-23] have been reported for the removal of lead ions.

For the first time, to the best of our knowledge, a separation-assembly coupling technique (SACT) was employed to separate Pb^{2+} from plumbeous solution and combine with MoO$_4^{2-}$ to self-assemble fishbone-like PbMoO$_4$ in another solution containing organic dye, based on a supported liquid membrane (SLM). Sequently, the fishbone-like PbMoO$_4$ was utilized to degrade organic dye under irradiation of ultraviolet light and collected after degradation to be characterized. This SLM-based technique is of basis of theory and practice. On one hand, SLM is one of liquid membrane types and one of the most efficient membrane based methods of separation [24]. In SLM, usually organic liquid is imbedded in small pores of a polymer support and is kept there by capillary forces. If the organic

liquid is immiscible with the aqueous feed and strip streams, SLM can be used to separate the two aqueous phases. It may also contain an extractant, a diluent which is generally an inert organic solvent to adjust viscosity and sometimes also a modifier to avoid so-called third phase formation. Relatively small volume of organic components in the membrane and simultaneous extraction and reextraction in one technological step offers the advantages of possible usage of expensive carriers, high separation factors, easy scale-up, low energy requirements, low capital and operating costs, etc. On the other hand, since the year of 2004, one research group have synthesized sulfides(Cu_7S_4, ZnS) [25-26], carbonates($CaCO_3$, $MnCO_3$, $SrCO_3$) [27-30], tungstates($SrWO_4$, $BaWO_4$) [31,32] and bunched $PbMoO_4$ nanobelts [33] via biomimetic supported liquid membrane (SLM) system. Additionally, Bi et al. have studied the photocatalytic activity of $PbMoO_4$ particles prepared via a simple solvothermal process [34]. Therefore, it is practicable and significative to couple separation technique and fabrication of nanomaterials for environment protection.

Experimental

Separation of Pb^{2+} and assembly of $PbMoO_4$. All chemicals used were analytical grade, purchased from Shanghai Chemical Co. and used without further purification. In a typical procedure, 0.2 g o-phenanthroline (Phen), as mobile carrier, was added into 80 mL chloroform under vigorous stirring at 3000 rpm for 15 min to form an oil phase. Then a dried polymer membrane was immersed into the oil phase for 48 h to form SLM. The polymer membrane, a kind of commercial product, is a micro-pore film made by esterified fibrin and the pore diameter is about 200–250 nm. The SLM was treated with filter paper to eliminate remnant oil on the surface. Then the SLM was solidified in a reactor to separate it into two horizontal compartments, which were respectively filled with a mixture of 30 mL of 20 mgL-1 organic dye (Rhodamine B(RhB) or Methylene Blue (MB)) and 0.35 mL of 0.1 M Na_2MoO_4 and 10 mL of 0.01 M $Pb(Ac)_2$ solutions, both of solutions with same height. White precipitation was generated in the mixture of organic dye and Na_2MoO_4 side and the mixture solution with precipitation were irradiated under ultraviolet light to evaluate the photocatalytic activity of the precipitation to degrade the organic dye after 50 hours reaction. After the measurement of photolysis, the precipitation was collected and washed by distilled water, acetone, and absolute ethanol in turn. The obtained white product was kept in absolute ethanol to be characterized.

Photocatalytic activity of the as-obtained $PbMoO_4$ to degrade organic dyes. The photocatalytic reactions were carried out in a glass cell containing the reaction mixture irradiated by a 300 W medium pressure mercury lamp. The reaction temperature was maintained at room temperature by water cycling. Prior to light illumination, the reaction mixtures were sonicated for 5 min to obtain a homogeneous suspension and set in the dark for 120 min to achieve adsorption equilibrium. In each experiment, the generated white precipitation ($PbMoO_4$, theoretical product weight 12.85 mg) was catalysts and the organic dye (RhB or MB) was 30 mL of 20 mgL^{-1}. The degradation of organic dye during the photocatalytic experiments was monitored by UV-vis spectroscopy.

Characterizations

The collected white precipitation were characterized using X-ray powder diffraction (XRD) (Bruker D8-advance, Cu Ka, k = 0.154056 nm), scanning electron microscopy (SEM) (Philips XL-30E), transmission electron microscopy (TEM) (Hitachi Model 800) and UV-vis spectroscopy.

Results and discussion

Fig. 1 shows the RhB dye (a) and MB dye (b) decomposition on the precipitation under ultraviolet light irradiation as a function of time. It was found that after 120 min and 150 min, respectively, of irradiation, the degradation percentages of RhB dye and MB dye was both approximately 100%, while those of the RhB photolysis and MB photolysis without catalyst were about 0% and less than 50%, respectively. Thus, the precipitation generated in the mixture of organic dye and Na_2MoO_4 side

was an efficient photocatalyst under the irradiation of ultraviolet light. The XRD results shows that the precipitation was $PbMoO_4$, and its theoretical output is 12.85 mg, therefore, the degradation rates of RhB and MB were at least 0.39 mg/(min·gcat) and 0.31 mg/(min·gcat), respectively.
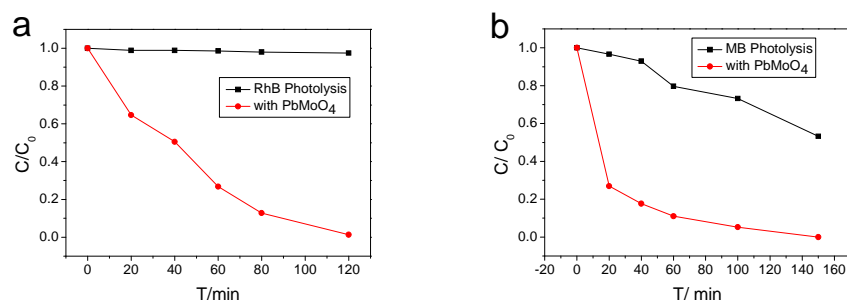

Fig.1. (a) Photodegradation curves of RhB and (b) Photodegradation curves of MB by the precipitation ($PbMoO_4$) upon ultraviolet light irradiation.

After the experiment of photocatalytic activity, the precipitation generated through SLM system was collected and washed by distilled water, acetone, and absolute ethanol in turn. XRD, SEM, TEM and UV-vis were employed to characterize the as-obtained precipitation.

Fig.2 shows the characterization results of the product generated in the mixture of RhB dye and Na_2MoO_4 side after photocatalytic experiment. Fig.2(c) presents the XRD pattern of the product. All peaks in the pattern are well indexed to tetragonal phases of $PbMoO_4$, and the corresponding JCPDS number is 44-1486. The cell lattice constants of product are calculated and corrected by MDI Jade (5.0 Edition) software. SEM and TEM were used to examine the size and morphology of the product. The results (Fig.2 (a) and (b)) reveal that the product is of fishbone-like morphology. Fig.2 (d) is UV-vis absorption spectrum of the fishbone-like $PbMoO_4$ in the medium of ethanol. It is clear that there are two absorption peaks at about 281 nm and 371 nm, respectively.
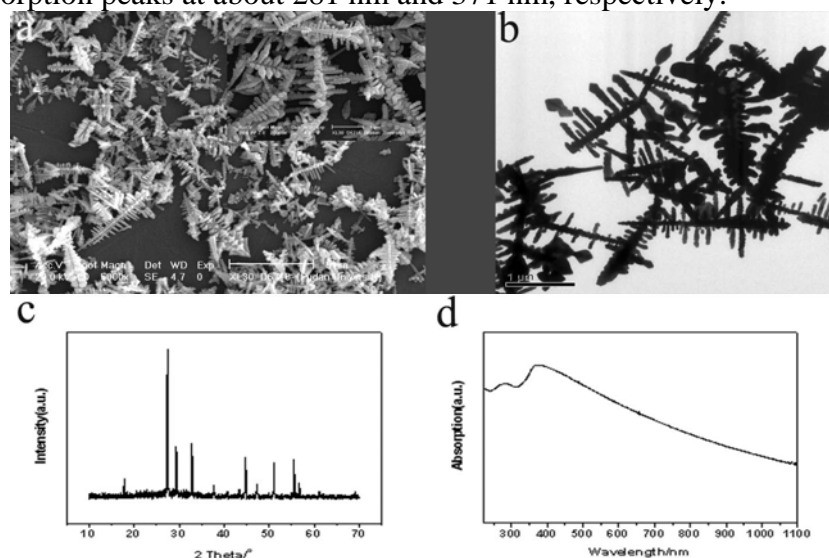

Fig.2. (a) SEM image(scale bar: 5 μm; inset scale bar: 2μm), (b) TEM image(scale bar: 1 μm), (c) XRD pattern, and (d) UV-vis spectrum of $PbMoO_4$ after photodegradation of RhB.
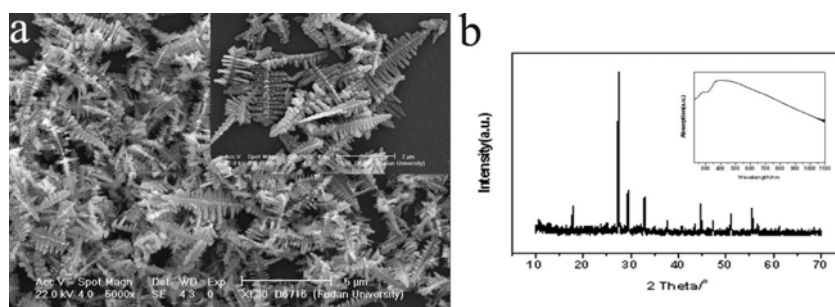
Fig.3. (a) SEM image ((scale bar: 5 µm; inset scale bar: 2µm), (b) XRD pattern (inset: UV-vis spectrum) of PbMoO$_4$ after photodegradation of MB.

Fig.3 shows the characterization results of the product generated in the mixture of MB dye and Na$_2$MoO$_4$ side after photocatalytic experiment. The results of XRD, SEM and UV-vis are the same to those of the product generated in the mixture of RhB dye and Na$_2$MoO$_4$ side. It is confirmed that precipitation (PbMoO$_4$) with fishbone-like morphology can be generated by separation-assembly coupling technique (SACT) based on supported liquid membrane (SLM) system which RhB dye or MB dye was mixed with Na$_2$MoO$_4$ as one of the sides.

To investigate the effect of SLM on the formation of the products, chemical precipitation method was employed to prepare PbMoO$_4$. Fig.4 shows the size and morphology (a: SEM image; b: TEM image.) of PbMoO$_4$ obtained by direct precipitation. It can be observed that the particles (20 nm-70 nm) agglomerate, while fishbone-like PbMoO$_4$ is not found. And the XRD pattern (not shown here) of the product revealed that the peaks at 17.88, 27.58, 29.58, 37.88, 40.88, 43.58, 44.98, 47.48, 51.28, 55.68, 56.88 match well with the (1 0 1), (1 1 2), (0 0 4), (1 1 4), (1 0 5), (1 2 3), (2 0 4), (2 2 0), (1 1 6), (3 1 2), (2 2 4) crystal planes of wulfenite PbMoO4.
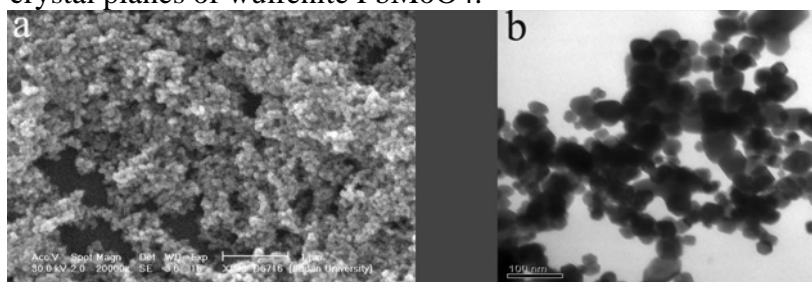

Fig.4. (a) SEM image (scale bar: 1µm) and (b) TEM image (scale bar: 100 nm) of PbMoO$_4$ obtained by direct precipitation.

Based on above-obtained SEM, TEM and XRD results, it is clear that Pb^{2+} can be separated from plumbeous solution and self-assembled fishbone-like PbMoO$_4$ can be obtained through the combination between Pb^{2+} and MoO$_4^{2-}$ in another side of membrane via SLM system. Consulting previous reference [35], a formation mechanism about fishbone-like PbMoO$_4$ is proposed as follows: First, Pb^{2+} ions combined with Phen and were carried and collected to other side of SLM system by the selective transportation. Thus, the concentration of Pb^{2+} was rather high on the surface of membrane, which provided a large supersaturation favoring the formation of PbMoO$_4$ nuclei. Furthermore, the high concentration of Pb^{2+} ions around a PbMoO$_4$ nucleus also favors kinetic crystal growth. However, the concentration of MoO$_4^{2-}$ ions was relatively low around the PbMoO4 nucleus and also low in the regions far from the nucleation centers. Thus, the concentration gradient was small for MoO$_4^{2-}$ ions. According to Fick's first law, the diffusion rate of ions is proportional to the concentration gradient of the ions. Thus, MoO$_4^{2-}$ ions diffused only slowly into the PbMoO$_4$ nucleation regions, which limited the crystal growth rate. Therefore, the nanoparticles self-assembled into fishbone-like PbMoO$_4$.

As known for the people, there are many heavy metal ions in industrial wastewater. SACT as a novel method can be employed to separate metal ions from wastewater and prepare various functional nanomaterials simultaneously.

Conclusions

Based on a supported liquid membrane (SLM) system, Pb^{2+} was separated from plumbeous solution and was self-assembled into fishbone-like $PbMoO_4$ through combining with MoO_4^{2-} in another solutioncontaining organic dye. The photocatalytic activity of the obtained $PbMoO_4$ to degrade the organic dyewas measured, which revealed that the product was efficient and stable photocatalyst for degradation ofboth Rhodamine B (RhB) and Methylene Blue (MB) under the irradiation of ultraviolet light. The $PbMoO_4$ after photocatalytic measurement were collected and characterized by a series of moderntechniques. A possible formation mechanism of fishbone-like $PbMoO_4$ was discussed. This separation-assembly coupling technique (SACT) is a novel way to combine separation of heavy metal ions in wastewater, preparation of self-assembly functional nanomaterials and degradation of organic contaminations.

Acknowledgements

References

[1] P. Canizares, A. Perez and R. Camarillo: Desalination, Vol. 144 (2002), p. 279

[2] J.O. Nriagu and Pacyna J.M.: Nature, Vol. 333 (1988), p. 134

[3] G. Mance: Elsevier Science, New York, 1987.

[4] http://epa.gov/safewater/mcl.html#8.

[5] A. Vecchio, C. Finoli, and Di Simine D.: J. Anal. Chem., Vol. 361 (1998), p. 338

[6] M.L. Merroun, N. Ben Omar, M.T. and Gonzalez Munoz,: Int. Biodet. Biodeg. Vol. 37 (3-4) (1996), p. 241

[7] M. Bustard, and A.P. McHale: Bioprocess Eng., Vol. 19 (5) 1998, p. 351

[8] A.A. Pradhan, and A.D. Levine: Sci. Total Environ. Vol. 170 (1995), p. 209

[9] J.M. Brady, and J.M. Tobin: Enzyme Microb. Technol., Vol.17 (1995), p. 791

[10] P. Zhou, J.C. Huang, and Li A.W.F.,: Water Res., Vol. 33 (8) (1999), p. 1918

[11] S.R. E1-Hasani, S.M. AI-Dhaheri, and M.S. EI-Maazawi: Water Sci. Technol., Vol. 40 (7) (1999), p. 67

[12] E. Rodryguez, J.C. Aguilar, and M.T.J. Rodryguez: Hydrometallurgy, Vol. 57 (2000), p. 151

[13] A.R.K. Dapaah, N. Takano, and A. Ayame: Anal. Chim. Acta Vol. 386 (1999), p. 281

[14] V. Gopal, G.C. April, and V.N. Schrodt: Sep. Purif. Technol., Vol. 14 (1998), p. 85

[15] K. Basta, A. Aliane, and A. Lounis: Desalination, Vol.120 (1998), p. 175

[16] R.S. Juang, and S.W. Wang: Water Res., Vol. 34(15) (2001), p. 3795

[17] V.J. Inglezakis, and M.D. Loizidou: Water Res., Vol. 36(11) (2002), p. 2784

[18] M.V. Mier, R.L.P. Callejas, and R. Gehr: Water Res., Vol. 35(2) (2001), p. 373

[19] G. Banerjee, and S. Sarker: Bioproc. Biosyst. Eng., Vol. 17 (1997), p. 295

[20] M. Sadrzadeha, T. Mohammadia, and J. Ivakpourb: Chem. Eng. Process., Vol. 48 (2009), p. 1371

[21] X.J. Ju, Sh.B. Zhang, and M.Y. Zhou: J. Hazard. Mater., Vol.167 (2009), p. 114

[22] J.S. Liu, Y. Ma, and Y.P. Zhang: J. Hazard. Mater., Vol. 173 (2010), p. 438

[23] M. Sadrzadeha, T. Mohammadia, and J. Ivakpourb: Chem. Eng. J., Vol.144 (2008), p. 431

[24] N.M. Kocherginsky, Q. Yang, and L. Seelam: Sep. Purif. Technol., Vol. 53 (2007), p. 171

[25] D.M. Sun, Q.S. Wu, and Y.P. Ding: J. Inorg. Mater., Vol. 19(3) (2004), p. 487

[26] D.M. Sun, Q.S. Wu, and Y. Zhu: Acta Chim Sinica., Vol. 63(16) (2005), p. 1479

[27] Q.S. Wu, D.M. Sun, and H.J. Liu: Cryst. Growth. Des., Vol. 4(4) (2004), p. 717

[28] D.M. Sun, and Q.S. Wu: Chinese J. Chem., Vol. 22(10) (2004), p. 1067

[29] D.M. Sun, D.Z. Zhu, and Q.S. Wu: J. Chem. Crystallogr., Vol. 38(12) (2008), p. 949

[30] D.M. Sun, Q.S. Wu, and Y.P. Ding: J. Appl. Crystallogr., Vol.39 (2006), p. 544

[31] F.Q. Dong, Q.S. Wu, and D.M. Sun: J. Mater. Sci., Vol. 43(2) (2008), p. 641

[32] F.Q. Dong, Q.S. Wu, and Y.P. Ding: J. Alloy. Compd., Vol. 476(1-2) (2009), p. 571

[33] F.Q. Dong, and Q.S. Wu: Appl. Phys. A-Mater., Vol.91(1) (2008), p. 161

[34] J.H. Bi, L. Wu, and Y.F. Zhang: Appl. Catal. B-Environ., Vol. 91(1-2) (2009), p. 135

[35] H.B. Chu, X.M. Li, and G.D. Chen: Nano Res., Vol. 1 (2008), p. 213