Chemical Engineering Journal 333 (2018) 613–620

Contents lists available at ScienceDirect

Chemical Engineering Journal

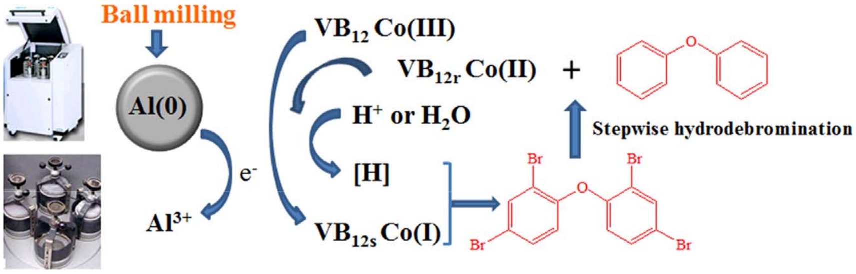
journal homepage: www.elsevier.com/locate/cej

Synergistic effect of ball-milled Al micro-scale particles with vitamin B_{12} on the degradation of 2,2′,4,4′-tetrabromodiphenyl ether in liquid system

Bo Yang[a,e,*], Jianping Deng[a], Liyan Wei[a], Yanni Han[a], Gang Yu[b], Shubo Deng[b], Caizhen Zhu[a,*], Huabo Duan[c], Qiongfang Zhuo[d]

[a] *College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, PR China*
[b] *School of Environment, POPs Research Center, Tsinghua University, Beijing 100084, PR China*
[c] *Smart City Research Institute, College of Civil Engineering, Shenzhen University, 518060 Shenzhen, PR China*
[d] *South China Institute of Environmental Sciences, The Ministry of Environment Protection, Guangzhou 510655, PR China*
[e] *Shenzhen Key Laboratory of Environmental Chemistry and Ecological Remediation, Shenzhen University, Shenzhen 518060, PR China*

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Al particles
Vitamin B_{12}
Ball milling
BDE47
Catalytic debromination

ABSTRACT

2,2′,4,4′-Tetrabromodiphenyl ether (BDE47) is known as a recalcitrant bromated organic pollutant with the significant persistence, toxicity, and bioaccumulation. In this study, a synergistic effect of ball-milled Al particles with vitamin B_{12} on the degradation of BDE47 was found according to the coordinated catalytic reduction process. The micro-scale Al particles prepared by ball milling and vitamin B_{12} as common pharmaceutical composed a new combination reagent for hydrodebromination with low-cost and high reactivity. The degradation conditions were optimized by the addition of 2.0 g/L BM Al particles and 0.3 mM VB_{12} using the solvent of methanol/H_2O (v:v = 40:60) at pH 4.0. More than 97% of 25 mg/L BDE47 was debrominated into lower-brominated diphenyl ethers in a sequential pattern and finally into diphenyl ethers within a 120-min reaction. UV/Visible spectra showed that vitamin B_{12} (Co(III)) was reduced to vitamin B_{12s} (Co(II)) by the ball-milled Al particles, which possesses super nucleophilic property to associate the carbon atom on C—Br bond and then facilitates the hydrodebromination process of brominated diphenyl ethers. The experimental results can provide basic understanding to identify a reaction process of vitamin B_{12}/vitamin B_{12s} for the enhanced reductive debromination of polybrominated diphenyl ethers by ball-milled Al particles, which would be possibly applied to treat soil washing solvent in the field of soil remediation.

---

[*] Corresponding authors at: College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, PR China (B. Yang).
E-mail addresses: boyang@szu.edu.cn (B. Yang), czzhu@szu.edu.cn (C. Zhu).

http://dx.doi.org/10.1016/j.cej.2017.09.183
Received 22 June 2017; Received in revised form 28 September 2017; Accepted 28 September 2017

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants in various applications, including textiles, plastics, wire insulation, and automobiles since the 1970s [1]. However, many reports indicated that they are persistent and the bioaccumulative industrial chemicals that cause numerous diseases including cancer, thyroid problems, and neurodevelopmental disorder [2]. Therefore, the industrial production of some PBDEs was restricted as Persistent Organic Pollutants (POPs) under the Stockholm Convention in 2009 [3]. Although the production of PBDEs was restricted or even ceased, the harmful exposure can continue for decades due to the big “reservoir” of existing PBDEs. This highlights the need to eliminate the spread and accumulation of these chemicals. In addition, PBDEs are classified in terms of the average number of bromine atoms in the molecule. PBDEs molecule containing 1–5 bromine atoms are more harmful because they are more efficiently bioaccumulative [4,5]. Lower-brominated PBDEs have been known to affect hormone levels in the thyroid gland. So the low brominated congeners such as 2,2′,4,4′-tetrabromodiphenyl ether (BDE47) was appropriately chosen as a target contaminant to conduct the study related to their degradation due to its environmental abundance and high recalcitrance to natural degradation [6,7].

In fact, some chemical methods have been applied for the effective removal of PBDEs from contaminated liquids [3]. Photolysis, reductive dehalogenation by zero-valent iron (ZVI), and photocatalysis of TiO_2 mainly constitute the reported degradation methodologies [5,8,9]. Photolysis treatment performed the decomposition of PBDEs at μg/L concentration level, which often adopts the organic solvents of high hydrogen donor including hexane and tetrahydrofuran or photosensitizers such as toluene. Moreover, hydroxylated PBDEs derivatives are likely to be generated, which present significantly higher thyroid hormone activities than PBDEs and even possibly photogenerated polybromodibenzo-*p*-dioxins [3]. Although ZVI has shown its availability of removing PBDEs slowly with reductive debromination, the reactive surface of ZVI was easily oxidized by forming passive iron oxide and/or hydroxide layers via surface complexation and precipitation. TiO_2-mediated photocatalysis can accomplish the oxidative degradation of PBDEs because the ether oxygen is an electron donor through resonance, which increases the electron density of the C atoms directly linking ether oxygen and makes the C atoms favorable to the electrophilic attack by h^+_{VB}/HO· species. But it is inconvenient to separate TiO_2 catalyst from the solution after reaction. Additionally, biodegradation processes of PBDEs have been known to be generally slow, which require more complicated environmental conditions for the growth of microorganisms [10].

On the other hand, vitamin B_{12} (VB_{12}) as transition metal coenzyme is the only vitamin containing metallic element, which could be produced naturally by anaerobic bacteria and synthesized largely by pharmaceutical industry [11]. It contains a corrin ring coordinated with cobalt atom as redox-active metal centers which can achieve their biological versatility [12]. In all stable VB_{12} forms, the central cobalt cation presents an oxidation state of +3; however, the unique function of VB_{12} stems from the performance of reduced cobalt species including **r**adical Co^{2+} (VB_{12r}) and “**s**upernucleophile” Co^{1+} (VB_{12s}) with various reductants (e.g., titanium(III) citrate, $NaBH_4$, 1-thioglycerol, and acetoin) [11–13]. Therefore, VB_{12} could act as coenzyme that catalysed a range of biological processes including isomerisation, methyltransfers, and dehalogenation [13]. As for environmental application, the reduced VB_{12} species could promote the reductive dechlorination of short-chain chlorinated hydrocarbons such as chloromethane and chloroethylene in liquids by facilitating the electron transferring to the target organics [14–17]. In these reports, nano-sized materials including Fe and mackinawite (FeS) as well as Cu/Al bimetallic particles were prepared as solid reductants for the sake of environmental remediation. However, to our knowledge, no study has been conducted to investigate the dehalogenation of any halogenated aromatics as environmental pollutants by coupling VB_{12} with solid electron donor. Moreover, except for nano-materials, more easily prepared solid reductants, which are convenient for VB_{12} application, should be further developed to enhance the practicality of the combined reagents with low cost and high efficiency.

In this study, a new method that combines ball-milled Al particles with VB_{12} for the enhanced reductive debromination of the toxic and recalcitrant BDE47 was investigated. Such combination only using metal electron donor to directly degrade halogenated aromatics has not been reported. Moreover, the novel Al micro-scale particles were prepared by mechanochemical method, which has been widely used as industrial synthesis of granular material [18,19]. Additionally, BDE47 was a representative as highly hydrophobic halogenated aromatics; thus mixed solution of methanol and water was used to increase its aqueous solubility in this system. Its application can simulate soil washing solution as potential remediation technique for PBDE-contaminated soil in these dismantling sites of electronic wastes [20]. The effect of influential factors on the degradation efficiencies of BDE47 were investigated including concentrations of VB_{12} and Al particles, solvent ratio, and initial suspension pH. VB_{12} species was identified by UV/vis analysis during the reaction; and distinct reaction mechanism was proposed according to the evolution of VB_{12} species and the analysis of intermediates using the ball-milled Al as electron donor. This work can provide basic knowledge to reveal the enhanced degradation process of PBDEs by biomimetic reactions.

2. Materials and methods

2.1. Materials

BDE47 (95%) was obtained from Wuhan Chemical Technology Co., Ltd. VB_{12} (cyanocobalamin, 98%) was obtained from Aladdin, Inc. Al powder (> 99%, 100–200 mesh) was supplied by Sinopharm Chemical Reagent Co., Ltd. Analytical-grade quartz sand (SiO_2, > 99%, 10–20 mesh), NaOH (98.0%), and HCl (36–38%) were purchased from Tianjing Tianli Chemical Reagent Co., Ltd., Tianjin Guangfu Technology Development Co., Ltd., and Dongguan Dongjiang Chemical Reagent Co., Ltd., respectively. Diphenyl ether (DE, 99%), dichloromethane, and HPLC grade methanol were provided by J & K Scientific Ltd. (Guangzhou, China). BDE1, BDE3, BDE7, BDE15, BDE17, BDE28 and BDE47 at 50 μg/mL in isooctane were obtained from AccuStandard. Water was distilled and then deionized with a Millipore-Q purification system.

2.2. Batch experiments

Micro-scale Al particles were firstly prepared by ordinary Al powder using a planetary ball mill (QM-3SP04, Nanjing Univ.) at a rotation rate of 240 rpm. Stainless pots (100 mL) as grinding container loaded two sizes of stainless steel balls including 10 mm and 6 mm with the numbers of 16 and 100, respectively, as our previous reports [21,22]. During each ball-milling (BM), the materials loaded into the pot included 156 g of steel balls and 5 g of Al and SiO_2 mixture. The weight ratio of Al powder to quartz sand was 9:1 with 0.3 mL of ethanol as process control agent. To prevent self-ignition of the active powder, after 3-h BM, the pot was cooled down to room temperature before opening its lid.

Batch experiments were performed in a 50 mL three-neck flask under strict exclusion of light containing BDE47 (25 mg/L) in methanol/water solution (v/v: 40/60, 100 mL). Each flask was loaded with ball-milled Al particles and various dosages of VB_{12}. Subsequently, the pH value of solution was adjusted by NaOH or HCl before the addition of BDE47. The flasks were then sealed with PTFE coated butyl rubber septa. Batch reactors were continuously stirred at 220 rpm with agitator. The experiments were conducted in triplicate; and average data were obtained.