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Removal of AOX in Activated Sludge of Industrial Chemical Dyestuff with Bimetallic Pd/Fe Particles

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Abstract: Pd/Fe bimetallic particles were synthesized by chemical deposition and used to remove absorbable organic halogens (AOX) in the activated sludge of a chemical dyestuff wastewater treatment plant. Bath experiments demonstrated that the Pd/Fe bimetallic particles could effectively remove AOX. It indicated several factors, such as Pd loading, the amount of Pd/Fe used, initial activated sludge pH, and reaction time, which could affect the removal effect. The results showed that increasing the Pd content in Pd/Fe particles, from 0.01 to 0.05 wt %, significantly increased the removal efficiency of AOX in activated sludge. The Pd/Fe particles had a much higher removal efficiency of AOX in the activated sludge than bare Fe particles. A slightly acidic condition with a Pd content of 0.05% and 10 g/L of Pd/Fe was beneficial to the process of removing AOX in activated sludge. In detail, the removal efficiency of AOX in the activated sludge could reach 50.7% after 15 days of reaction with 10 g/L of Pd/Fe (Pd loading 0.05 wt %) and at an initial pH of 6.0 during the experiments. It also showed that the control samples without Fe⁰ and Fe/Pd additions only removed 7.9% of AOX under the same conditions. Meanwhile, the concentrations of AOX in the supernatant of activated sludge were lower than the initial AOX concentration in the supernatant during the activated sludge remediation with Pd/Fe bimetallic particles. The results indicated that the AOX removal from the activated sludge matrix might be mainly due to the Pd/Fe bimetallic particles, and not just by phase transfer.

Keywords: absorbable organic halogens (AOX); activated sludge; Pd/Fe bimetal; chemical dyestuff industry; catalytic reduction



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1. Introduction

Halogenated organic compounds have a wide range of industrial and domestic uses, and they are employed as industrial solvents or intermediates in the synthesis of other chemicals, dyestuffs, pesticides, lubricants, and dielectric [1]. Due to their physicochemical property, halogenated organic compounds are highly toxic, mutagenic, and possibly carcinogenic as well as bio-refractory in the natural environment. They are also persistent and tend to accumulate in animal tissues; once released into the environment, they can accumulate in the surroundings and cause a potential long-term threat to human health and ecosystem safety [2,3]. Thus, halogenated organic compounds must be removed from environmental media as well as from waste matrices.

Chloroanilines, chlorophenols, and chloronitrobenzenes are used in the chemical dyestuff industry as raw materials, and many of them are on the Priority Pollutant List of USEPA [4]. While dye production may generate wastewaters containing a large number of organochloride compounds, it is well known that biological processes are not necessarily effective at removing halogenated organic compounds. In the treatment plant, chloroanilines, chlorophenols, and chloronitrobenzenes can be assimilated or adsorbed and concentrated

on activated sludge, leading to the high halogenated organic compounds ratio in the activated sludge [5,6]. Moreover, some of the halogenated organic compounds present in activated sludge could be resistant to biodegradation [7,8]; a recent study indicated that carcinogenic and genotoxic responses were still detectable after 124 days of composting [9]. So, in this case, without proper treatment, the activated sludge from the chemical dyestuff industry may pose risks to ecosystems and human health. Unfortunately, studies regarding the removal of halogenated organic pollutants from the chemical dyestuff industry's activated sludge are somewhat limited.

The reductive dehalogenation of some bimetallic materials can be an effective method for detoxifying halogenated organic compounds and has started to be widely investigated by some researchers [10–15]. In these bimetallic materials, the first metal, which has a low standard redox potential (such as Fe, Mg, etc.), is an electron donor that reduces the halogenated organic compounds [11,13]; the second metal, which has a high standard redox potential (such as Ni, Cu, Pd, etc.), promotes the reactivity via hydrogenation and acceleration corrosion [10–12,16], acting as both catalyst and accelerator. Among them, Pd/Fe is the most investigated bimetal due to the low cost of Fe and excellent hydrogenation activity of Pd [14]. Previous studies mainly focused on halogenated organic compound transformation by bimetals in aqueous and soil systems [17,18]; little work describing the use of zero-valent iron or bimetallic materials to remediate halogenated organic compounds that have contaminated activated sludge was found in peer-viewed literature.

Since it is complicated to identify all of the halogenated organic contaminants in environmental samples, absorbable organic halogens (AOX) have become an increasingly important parameter in estimating the concentrations of organic halogen compounds in a variety of environmental samples. Therefore, this study focused on removing AOX found in the activated sludge of a chemical dyestuff wastewater treatment plant by Pd/Fe. The experimental parameters for the process—such as reaction time, Pd loading, the dosage of Pd/Fe, and initial activated sludge pH—were determined. Likewise, the changes of AOX content in supernatants during the activated sludge remediation with Pd/Fe bimetallic particles were also studied.

2. Materials and Methods

2.1. Activated Sludge and Chemical Reagents

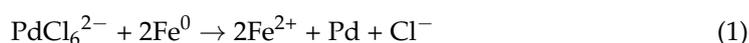
The activated sludge samples for this experiment were obtained from the secondary sedimentation tank of a chemical dyestuff wastewater treatment plant (Shangyu City, China), where the treating capacity is 10,000 m³/d using an anoxic/oxic (A/O) activated sludge process. The factory mainly produces azo dyes and intermediary products. The AOX concentration in the influent of the chemical dyestuff wastewater treatment plant was detected at 13.5 mg/L, and leaved AOX at 9.3 mg/L in the effluent. The activated sludge underwent gravity thickening, the supernatant was subsequently removed, and the thickened activated sludge was then suspended in the deionized water. The resuspended activated sludge samples were stored in a refrigerator at 4 °C for use. And the concentrations of total suspended solids (TSS) and volatile suspended solids (VSS) were about 15.62 and 7.61 g/L, respectively. In the resuspended activated sludge, the AOX concentration in activated sludge was 2279 mg/kg dry weight; the concentration of AOX in the supernatant was 1.93 mg/L.

Iron metal powder (Fe⁰, 400 mesh), potassium hexachloropalladate (K₂PdCl₆, 99%), and acetone of analytical reagent grade were purchased from Aladdin Industrial Corporation.

2.2. Pd/Fe Preparation and Characterization

Pd/Fe bimetallic particles were prepared using a slightly modified method of the version used by Grittini et al. [19]. Iron particles in a fine (400 mesh) powder were pretreated by washing with 0.1 mol/L H₂SO₄, and then rinsed successively with acetone and distilled water to remove most of the surface oxide layers and undesired organic compounds before palladization. An aqueous solution of potassium hexachloropalladate (0.001 mol/L) was

prepared with deoxygenated water and used to deposit enough elemental palladium onto the iron powder. An aqueous solution of potassium hexachloropalladate (0.001 mol/L) in the amounts of 9.4 mL, 28.2 mL, 47.0 mL, and 94.0 mL was slowly added to a 500 mL three-neck flask prefilled with 10 g zero valent iron (ZVI) and 100 mL deoxygenated water to give 0.01%, 0.03%, 0.05%, and 0.1% (*w/w*) Pd coverage, respectively. The palladium was deposited onto the iron surface by the redox reaction (1), in which an orange solution of K_2PdCl_6 was stirred with the iron powder until a pale-yellow solution was formed after 1.5 h. In this study, Pd loading (Pd content over Fe) was calculated theoretically by mass of palladium divided by mass of ZVI [17]. Following this, an excessive amount of Cl^- and K^+ ions on the Pd/Fe particles were removed with deoxygenated water several times. Subsequently, the Pd/Fe particles were washed with acetone three times. Finally, Pd/Fe particles were dried under a flow of N_2 and stored under N_2 protection.



Field emission scanning electron microscopy (FESEM, Hitachi S-4800) equipped with energy-dispersive X-ray spectroscopy (EDS) was used to characterize the morphology and elemental mapping of the Pd/Fe bimetal.

2.3. Batch Experiment Procedure

Experiments were conducted in a 100 mL glass vial containing 50 mL activated sludge. The Fe^0 or Pd/Fe was added into activated sludge samples before the vials were sealed with butyl rubber stoppers, after which the vials were shaken at 210 rpm at a constant temperature of 30 °C. The experimental variables were reaction time, Pd loading, the dosage of Pd/Fe, and initial activated sludge pH. The experiments were conducted under various pH conditions, which were adjusted by H_2SO_4 and NaOH aqueous solutions. All samples were conducted in duplicate, and control samples were carried out without Fe^0 and Pd/Fe addition. The control sample's pH was 7.02 (as pH = 7). The effect of Pd loading on the removal efficiency of AOX— Fe^0 (10 g/L), Pd/Fe powder 10 g/L (Pd content over Fe were 0.01 wt %, 0.03 wt %, 0.05 wt %, and 0.1 wt %), pH 6.0; reaction time was 15 days. The effect of initial pH on the removal efficiency of AOX—Pd/Fe powder (Pd loading 0.05 wt %) 10 g/L; reaction time was 15 days. The effect of reaction time on the removal efficiency of AOX—Pd/Fe powder 10 g/L (Pd loading 0.05 wt %), pH 6.0.

The effect of added amounts of Pd/Fe on the removal efficiency of AOX—Pd loading 0.05 wt %, pH 6.0; reaction time was 10 days.

2.4. Analytical Methods

The vials were transferred onto the magnetic stirrers (IKA C-MAG HS 4, 100 rpm) after the reaction, and a stirrer bar was added to each vial for 3 min to recover the ZVI or Pd/Fe particles that could attach to the stirrer bar by magnetic force. The attached particles were subsequently removed from the activated sludge along with the stirrer bar. The activated sludge sample was then centrifuged at 4000 r/min for 10 min and divided into two parts, i.e., liquid phase and solid phase. The liquid phase was used in AOX analysis, and the solid phase was freeze-dried to avoid volatilization after the reaction. The freeze-dried solid phase was then ground and homogenized in an agate mortar and sieved through a mesh with a mesh pore size of 100. The homogenized activated sludge was used in AOX analysis.

A halogen analyzer (Jena, Germany, model Multi X2500) was used for the AOX analyses according to the European Standard EN 1485 H14, 1996 [20]. The concentrations of TSS and VSS were measured according to Standard Methods (APHA, 2005) [21].

3. Results and Discussion

3.1. Characterization of Pd/Fe

The Pd/Fe bimetallic particles were formed by depositing the metal (Pd) separately onto the iron surface through a spontaneous redox process. The images of Pd/Fe bimetallic particles were observed using FESEM, as shown in Figure 1. The results showed that Pd particles aggregated on certain iron particles with a non-uniform distribution of gathered dots (Figure 1b). The dark core was ZVI, which was easily distinguished [22]. Since ZVI accounted for a major part of the Pd/Fe bimetallic particles, the peak of Fe was dominant, and the peaks of Pd were fairly small (Figure 1c).

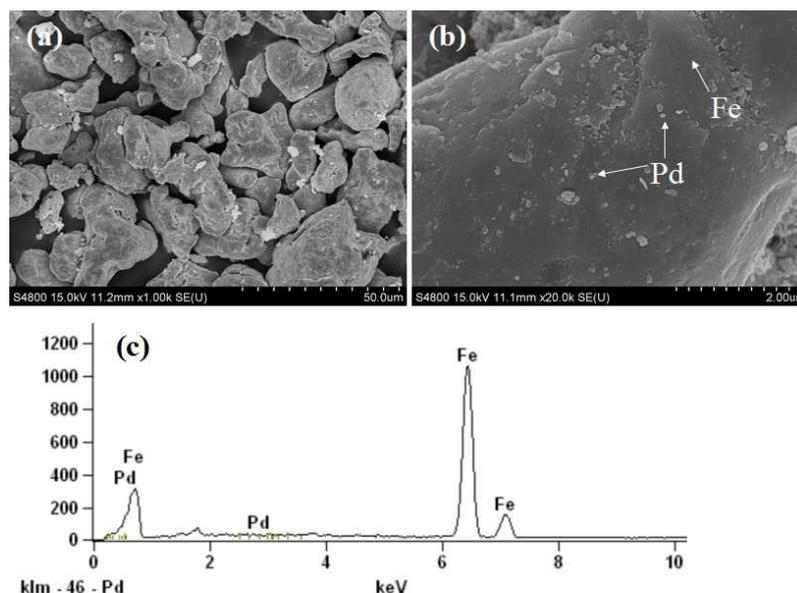


Figure 1. FESEM at different magnifications. (a–c) EDS of Pd/Fe (0.05% initial adding, *w/w*) bimetallic particles.

3.2. Effect of Some Experimental Parameters on the Removal of AOX in Activated Sludge

3.2.1. Effect of Pd Loading on the Removal of AOX

It is considered that Fe^0 can promote a hydrogenolysis reaction where a hydrogen atom can replace the halogen atom in halogenated organic compounds. Palladium is a well-known catalyst for hydrogenolysis [23]. Therefore, the Pd loading percentage on Pd/Fe bimetallic particles may be one of the important influential factors in reductive dehalogenation efficiency. In this study, Pd/Fe bimetallic particles with different palladium loadings were prepared and their Pd loadings (wt %) were 0.01%, 0.03%, 0.05%, and 0.1%. The variation of removal efficiency for the same reaction period under different Pd loadings in the bimetallic particles is presented in Figure 2. The final removal efficiencies of AOX corresponding to Pd loadings of 0.01%, 0.03%, 0.05%, and 0.1% were 26.6%, 45.3%, 50.7%, and 52.2%, respectively. With the increase of Pd loading, the removal efficiency of AOX increased correspondingly. The results demonstrated that higher Pd loading is favorable for the dehalogenation of AOX.

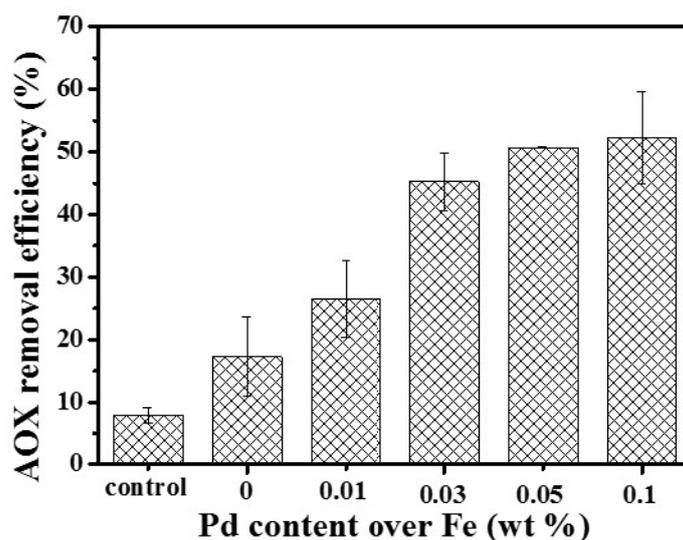


Figure 2. The effect of Pd loading on the removal efficiency of AOX (Fe powder = 10 g/L, Pd/Fe powder = 10 g/L, pH 6.0; reaction time was 15 days).

It was suggested that the promotion effect of palladium on the dehalogenation of AOX occurs for two reasons—the catalytic functions of palladium’s surface and the galvanic cell effects of the bimetallic system. Palladium could promote dehalogenation reactions by forming strong Pd–X bonds ($X = \text{Cl}, \text{Br}, \text{I}$), thereby accelerating the dissociation of halogenated hydrocarbons [17]. We can thus assume that the same process takes place for AOX. Furthermore, the hydrogen gas produced during the reaction process is adsorbed onto palladium and dissociated into atomic H, one of the strongest reductants for the dehalogenation reactions. The presence of the less active palladium on the iron surface certainly creates many galvanic cells, in which iron acts as the anode and palladium acts as the cathode [14]. The electrons transferred from iron to palladium are contributed to the halogen atoms to form halogen ions [14,24].

In this study, only 7.9% of AOX was removed in the control samples (without Fe^0 and Fe/Pd additions). The AOX removal from the activated sludge matrix in the control samples might be mainly due to phase transfer or the role of biology. The activated sludge was thought to have good pollutant degradation activity at 30 °C; consequently, this temperature was selected to examine the removal effect of activated sludge on AOX in this study. The experimental results showed that the biological processes were not effective for the removal of AOX in this study. Only 17.2% of AOX was removed by un-palladized iron particles under the same experimental conditions (Figure 2), which was much lower than with the Pd/Fe bimetal system. This experiment further proved that palladium plays a principal role in accelerating the catalytic dehalogenation reaction. As shown in Figure 2, the removal efficiency of AOX increased significantly as the Pd content increased progressively from 0.01 wt % to 0.05 wt %. Furthermore, increasing the Pd content from 0.05 wt % to 0.1 wt % caused only a slight improvement in the removal efficiency of AOX. The most likely explanation for this is that the maximum Pd coverage was less than one layer, and in this way, the loss of available catalytic reactive sites due to the overlapping of Pd atoms could be excluded. Nonetheless, the amount of hydrogen gas absorbed by Pd atoms increased with the addition of Pd content [19,25], and so did the efficiencies of AOX removal. The slight improvement of the removal efficiency at a Pd content of >0.05 wt % is that the accumulation of excessive hydrogen gas hinders the contact between the target pollutant and metal particles and reduces the surface area available for AOX dehalogenation. This phenomenon is consistent with previously reported studies [26,27]. Therefore, in order to promote the cost-effective use of Pd and the removal efficiency of AOX, a Pd loading of 0.05 wt % was employed in the following study.

3.2.2. Effect of Initial pH

The pH is considered a vital impact on the reductive dehalogenation rate using zero-valent iron [28]. The results are shown in Figure 3. From experimental data, the removal percentage of AOX was 50.7%, 43.8%, and 38.6% at the initial pH of 6.0, 7.0, and 9.0, respectively. The results showed that a slightly acid condition favors the removal of AOX. In a slightly acid condition such as pH 6.0, the amount of H^+ is sufficient for producing H_2 through the corrosion of iron; thus, the reduction of AOX progresses more readily. An alkaline condition was unfavorable because carbonate and hydroxide would precipitate on the Pd/Fe surface and eventually significantly inhibit further iron decomposition and electron transfer [29].

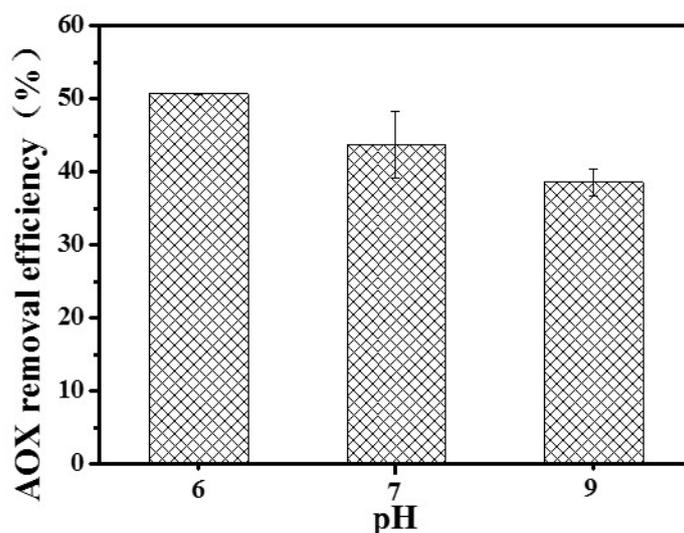


Figure 3. The effect of initial pH on the removal efficiency of AOX (Pd/Fe powder = 10 g/L, Pd loading = 0.05 wt %; reaction time was 15 days).

3.2.3. Effect of Reaction Time

From experimental data (Figure 4), the removal efficiency of AOX at different treatment times of 1 day, 3 days, 10 days, and 15 days reached 21.3%, 25%, 39.3%, and 50.7%, respectively. The removal efficiency of AOX increased with longer reaction times. The reductive dehalogenation of halogenated organic compounds by Pd/Fe bimetallic particles occurs on the surface of particles [30]. More AOX in solids might transfer into the supernatant of activated sludge with the extension of activated sludge remediation time. The removal percentage of AOX would then increase. The activated sludge contained humic acid and other organic matter. Humic acid might compete for reaction sites on the Pd/Fe bimetallic particles with halogenated organic matter [23], thus reducing the efficiency and rate of removal of AOX. Likewise, other matters in activated sludge might compete for reaction sites on the Pd/Fe bimetallic particles with halogenated organic matter. The longer reaction times therefore increased the removal efficiency of AOX.

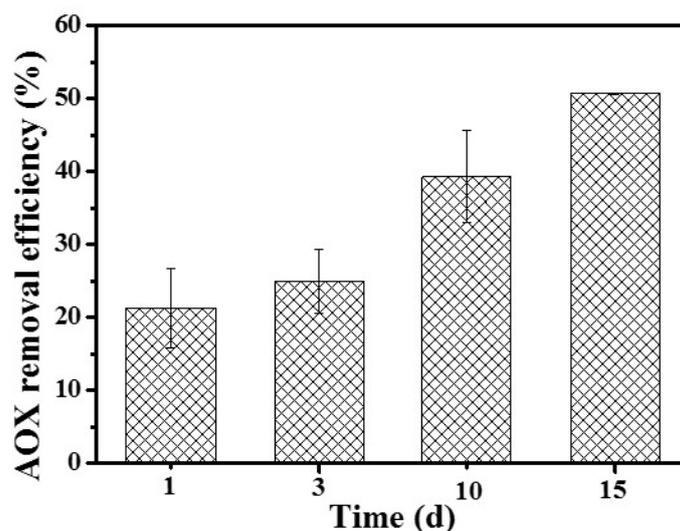


Figure 4. The effect of reaction time on the removal efficiency of AOX (Pd/Fe powder = 10 g/L, Pd loading = 0.05 wt %, pH 6.0).

3.2.4. Effect of Pd/Fe Bimetallic Particle Added Amounts

Different Pd/Fe particle dosages of 5, 10, 15, and 20 g/L were evaluated, as shown in Figure 5. From experimental data, the removal efficiency of AOX increased significantly as the Pd/Fe particle dosage was increased from 5 to 15 g/L, while the removal percentage of AOX increased from 30.1 to 52.2% after a reaction of 10 days. Since the reductive dehalogenation of halogenated organic compounds by Pd/Fe bimetallic particles occurs on the surface of particles [30], the Pd/Fe bimetallic particle amount is also a significant variable parameter. The amount of available surface area is among the most significant experimental variables affecting contaminant reduction. Increasing the concentration of Pd/Fe particles, though insignificant to the final removal efficiency in excess of Pd/Fe dosage, will accelerate the initial reaction rate and provide more active sites for the collision of Pd/Fe particles with AOX during the reduction. Increasing the dosage of Pd/Fe particles speeds up the initial reaction substantially, whereby AOX collides with the more significant number of active surface sites of iron particles and the greater area of adsorptive Pd sites. The larger amount of Pd/Fe particles relative to the amount of halogen to be removed allows for a more complete reaction before the passivation of the surface occurs.

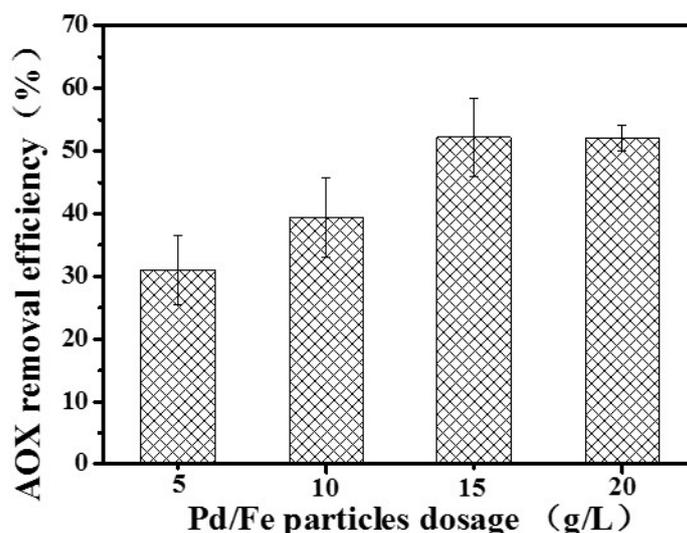


Figure 5. The effect of added amounts of Pd/Fe on the removal efficiency of AOX (Pd loading = 0.05 wt %, pH 6.0; reaction time was 10 days).

Furthermore, the removal percentage of AOX is similar for using a dosage of Pd/Fe particles of 15 or 20 g/L after a reaction of 10 days. Hence, Pd/Fe at 15 g/L was chosen as the appropriate dosage for AOX dehalogenation. From Figure 4, Pd/Fe (Pd loading = 0.05 wt %) bimetallic particle added amount was 10 g/L, while the removal rate of AOX increased from 39.3 to 50.7% when the reaction time increased from 10 days to 15 days. The 15-day removal efficiency of AOX under 10 g/L of added Pd/Fe was close to the 10-day removal efficiency of AOX under 15 g/L of added Pd/Fe. Therefore, the amount of Pd/Fe could be decreased by increasing the reaction time. However, 15 days is relatively long. A comparison of the cost of Pd/Fe preparation and the added dose in relation to the duration of the procedure would be advisable for future studies on possible practical applications.

3.2.5. Concentration Changes of AOX in Supernatant

Some contaminations in solid may partly transfer into the liquid of activated sludge during activated sludge remediation [21]. The concentration changes of AOX in the supernatant of activated sludge during activated sludge remediation with the Pd/Fe bimetallic particles are shown in Figure 6. The initial concentration AOX in the supernatant of resuspended activated sludge was 1.93 mg/L (Figure 6a). In the control sample, the AOX concentration in the supernatant increased slightly and reached to 2.15 mg/L after a reaction time of 15 days (Figure 6b). A part of AOX in activated sludge transferred into the supernatant, possibly due to shake or microbial activity. The concentrations of AOX in the supernatant at different treatment times of 1 day, 3 days, 10 days, and 15 days were 1.82, 1.92, 1.92, and 1.75 mg/L, respectively (Figure 6a). They were all lower than the initial AOX concentration in the supernatant. The concentrations of AOX in the supernatant at different Pd loading values of 0.01, 0.03, 0.05, and 0.1 wt % were 1.87, 1.78, 1.75, and 1.78 mg/L after a 15-day reaction time, respectively. They were all lower than the initial AOX concentration in the supernatant; in comparison, the AOX concentration was 2.02 mg/L after activated sludge remediation by un-palladized iron particles under the same experimental conditions, which was higher than with the Pd/Fe bimetal system (Figure 6b). The concentrations of AOX in the supernatant of activated sludge were lower than 1.93 mg/L in different initial pH conditions (Figure 6c). Moreover, the concentrations of AOX after a 10-day reaction time in the supernatant decreased from 1.92 to 1.33 mg/L following the increase of Pd/Fe particle dosage from 5 to 20 g/L (Figure 6d).

All the experimental data indicated that the concentrations of AOX in the supernatant of activated sludge were lower than the initial AOX concentration in the supernatant during activated sludge remediation with Pd/Fe bimetallic particles. The results indicated that the halogenated organic compound removal from the activated sludge matrix might be mainly due to the Pd/Fe bimetallic particles, not just by phase transfer.

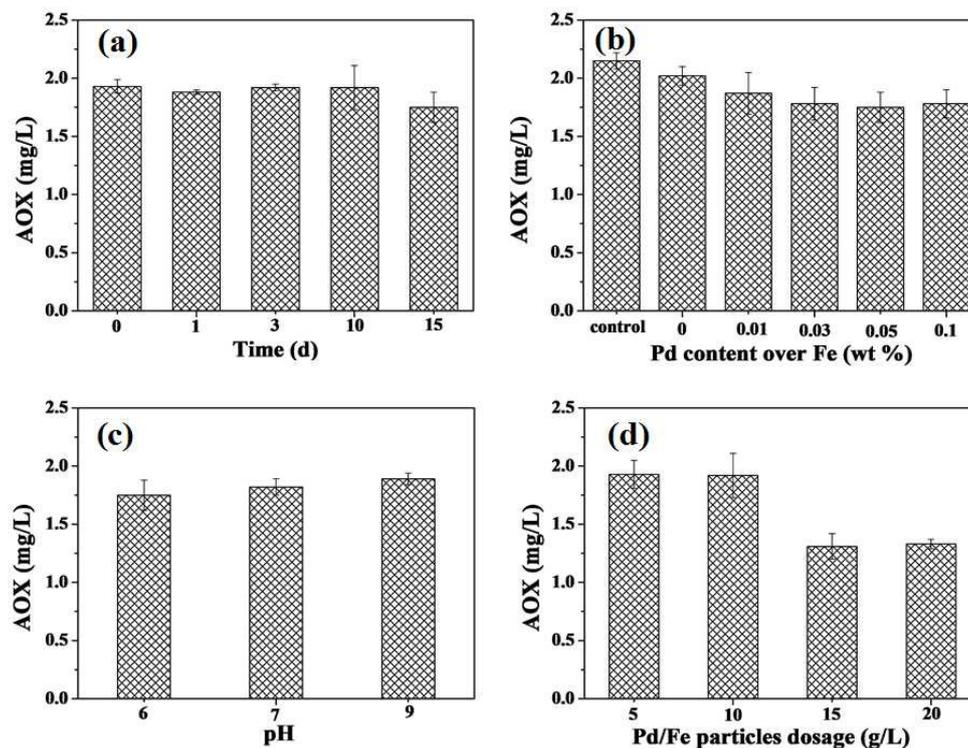


Figure 6. Concentration changes of AOX in supernatant: (a) effect of reaction time (Pd/Fe powder = 10 g/L, Pd loading = 0.05 wt %, pH 6.0), (b) effect of Pd loading (Fe powder = 10 g/L, Pd/Fe powder = 10 g/L, pH 6.0; reaction time was 15 days), (c) effect of initial pH (Pd/Fe powder = 10 g/L, Pd loading = 0.05 wt %; reaction time was 15 days), (d) effect of added amounts of Pd/Fe (Pd loading = 0.05 wt %, pH 6.0; reaction time was 10 days).

4. Conclusions

The Pd/Fe bimetallic particles were synthesized and found to be effective for the removal of AOX in the activated sludge of a chemical dyestuff wastewater treatment plant, at ambient pressure and 30 °C. The removal efficiency of AOX mainly depended on the relative amount of Pd/Fe, the loading of palladium onto the catalyst, the reaction time, and the initial pH of activated sludge. The Pd bulk loading was optimized at 0.05 wt %, and an initial weak acid condition was considered beneficial for removing AOX. It was found that the removal efficiency of AOX in activated sludge could reach 52.2% after 10 days of reaction with 15 g/L of Pd/Fe (Pd loading 0.05 wt %) and at an initial pH of 6.0, and the 15-day removal efficiency of AOX under 10 g/L Pd/Fe was 50.7% close to the 10 days removal efficiency of AOX under 15 g/L of Pd/Fe. The amount of Pd/Fe could be decreased by increasing the reaction time. All the experimental data indicated that the concentrations of AOX in the supernatant of activated sludge were lower than the initial AOX concentration in the supernatant during the activated sludge remediation with Pd/Fe bimetallic particles. The results indicated that the halogenated organic compound removal from the activated sludge matrix might be mainly due to the Pd/Fe bimetallic particles, not just by phase transfer. The experimental results obtained from the batch system may be expected to provide the additional possibility of application for full-scale site remediation operation or joint bioremediation to the remediation of halogenated organic compound-contaminated activated sludge.

Author Contributions: C.X. conducted the data analysis, data modeling, and wrote the paper; W.Z., R.L., and L.C. contributed to the writing of the paper; C.X. and L.L. obtained the experimental data. All authors have read and agreed to the published version of the manuscript.

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Institutional Review Board Statement: “Not applicable.” for this study did not involve humans or animals.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available on request from the corresponding author. The data presented in this study are not publicly available as they will be used for further research, thus requiring the maintenance privacy.

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