Kinetics of 2,3-DCB dechlorination by Pd/Fe-MWCNTs-Fe$_3$O$_4$ nanoparticles synthesized under ultrasonic irradiation

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Abstract. Kinetics of 2,3-DCB dechlorination by Pd/Fe-MWCNTs-Fe$_3$O$_4$ composite nanoparticles synthesized under ultrasonic irradiation was investigated. The diameters and specific surface areas of most Pd/Fe-MWCNTs-Fe$_3$O$_4$ nanoparticles that prepared by liquid phase reduction method under 40 kHz and 150 W ultrasonic irradiation were obviously modified. The optimized experimental conditions were obtained and up to 95% of 2,3-DCB was removed in 300 min with mass fraction of Pd in Pd/Fe-MWCNTs-Fe$_3$O$_4$ nanoparticles 0.35%, initial pH value 3.0, initial 2,3-DCB concentration 10 mg·L$^{-1}$, reaction temperature 25 $^\circ$C, Pd/Fe nanoparticles 5.0 g·L$^{-1}$, Fe$_3$O$_4$ nanoparticles 2.0 g·L$^{-1}$, and MWCNTs dosage 0.25 g·L$^{-1}$. The dechlorination of 2,3-DCB followed pseudo-first-order kinetics reaction and the kinetics constants $k_1$ and $k_2$ were 0.025 min$^{-1}$ and 0.105 min$^{-1}$, respectively.

1. Introduction

Polychlorinated biphenyls (PCBs) are widely applied in electric power, chemical industry and other industries because of their stable chemical properties[1,2]. However, PCBs are also highly toxic and difficult to degrade pollutants, once PCBs released into the environment will produce persistent pollution, and PCBs have "carcinogenic, teratogenic, mutagenic" effects[3]. Therefore, the research on the treatment of PCBs has been paid more and more attention.

Nano-zero-valent iron (nZVI) has active chemical properties, high electronegativity and strong reduction ability. It can not only effectively remove chlorinated organic compounds from water and soil but also effectively adsorb heavy metals, azo dyes, nitro aromatic compounds, nitrates, perchlorates and other pollutants[4]. Although nZVI can effectively treat chlorine-containing organic compounds, it also has some defects that the nanoparticles are easy to agglomerate with the reaction proceeding, which reduces the activity of catalyst reaction. Meanwhile, the surface of nZVI will gradually form hydroxide, which will make it passivated, hinder the reaction and even produce more toxic byproducts. Pd/Fe-MWCNTs-Fe$_3$O$_4$ composite nanoparticles were prepared by introducing ultrasound irradiation[5], nFe$_3$O$_4$ particles[6,7]and MWCNTs[8], which can improve the nanoparticles stability, reductive dichlorination and recycling effects, and the above defects were all solved.

In this paper, the reductive dechlorination of 2,3-dichlorobiphenyl (2,3-DCB) in Pd/Fe-MWCNTs-Fe$_3$O$_4$ nanoparticles prepared by ultrasonic enhanced liquid-phase reduction method was explored. The effects of mass fraction of Pd in Pd/Fe-MWCNTs-Fe$_3$O$_4$ composite nanoparticles, Pd/Fe dosage, Fe$_3$O$_4$ dosage, the usage of MWCNTs, reaction temperature and initial pH value on the system were explored. The degradation mechanism and kinetics were established. It provides basic parameters for industrial application.
2. Experimental

2.1. Main reagents

2,3-DCB, 2-chlorobiphenyl and 3-chlorobiphenyl (standard), J&K Chemical Reagent Co. Ltd., China; NaBH₄ (98%, AR), Aladdin Chemicals Co. Ltd., China; FeCl₃·6H₂O (AR), Sinopharm Chemical Reagents Co. Ltd., China; K₂PdCl₆ (Pd 26.2%), Sigma Aldridge Trading Co. Ltd., China; methanol (≥99.8%), Aladdin Reagent Co. Ltd., China; N₂ (high purity N₂), Hangzhou Jingong Special Gas Compa, China; MWCNTs (AR, 99%), Shenzhen Nanoharbor Co. Ltd., China; FeSO₄·7H₂O (99.0-101.0% AR), Sinopharm Chemical Reagent Co. Ltd., China; n-Hexane (HPLC, 99.5%), Tiandi Reagent Company, USA.

Millipore Milli-Q ultrapure water (conductivity 18.2 MΩ·cm⁻¹) and anhydrous methanol were used to prepare 2,3-DCB, 2-chlorobiphenyl and 3-chlorobiphenyl solutions (methanol/water= 40/60 (V/V).

2.2. Experimental apparatus

The experimental apparatus is shown in Fig.1. The reaction takes place in a 500 mL three-necked flask placed in a KQ3200DB ultrasonic cleaner. The ultrasonic power is 150W and the frequency is 40kHz. The reaction temperature is controlled by a constant temperature water bath, and the protective gas is high purity nitrogen.

2.3. Experimental methods

Under ultrasonic irradiation, FeCl₃·6H₂O and FeSO₄·7H₂O (molar ratio 2:3) with a certain dosage of multi-walled carbon nanotubes were added into the 500 mL three-necked flask under N₂ protection, then dissolved in deionized water without oxygen, then ammonia solution was dripped slowly to the solution until pH=10. After stirring reaction of 40 min at 30 °C in water bath, the MWCNTs-Fe₃O₄ nanoparticles were washed to neutral by anaerobic deionized water. Then a certain amount of FeSO₄·7H₂O was added and dissolved in a certain volume of deionized water without oxygen, then the constant pressure funnel was used to slowly drop the same volume of NaBH₄ solution with the mole ratio of FeSO₄·7H₂O solution to NaBH₄ solution at 1:2, and the reaction time was 20 min at 15 °C in water bath. Pd/Fe-MWCNTs-Fe₃O₄ nanoparticles were prepared by adding a certain amount of K₂PdCl₆ solution and reacted for 1h. Pd/Fe-MWCNTs-Fe₃O₄ composites were first washed with a certain volume of ultrapure water and then washed by using anhydrous acetone and stored in anhydrous acetone. 2,3-DCB solution of a certain concentration was added to the 500 mL flask containing a certain amount of Pd/Fe-MWCNTs-Fe₃O₄ nanoparticles, and the whole degradation process was carried out at 25 °C under N₂ protection. The taking samples were carried out at regular intervals. The sample was filtered by 0.45µm polyethersulfone (PES) microporous membrane.

2.4. Methods of analysis

ASAR2020M+ surface analyzer was used in the measurement of BET specific surface area of Pd/Fe-MWCNTs-Fe₃O₄ nanocomposites. HITACHI S-4800 microscope was used in the characterization of...
SEM images. XPert Pro advanced X-ray diffractometer ($\lambda=1.5418$ Å) was used in XRD analysis. Organic compounds such as 2,3-DCB, 2-CB and 3-CB were analyzed by Thermo Scientific Trace 1310GC. ECD detector, chromatographic column: (30m×0.32mm,1.0µm), no split injection, injection port temperature 300°C, Column flow: 1.5mL/min (constant), injection volume: 1µL, ECD detector temperature: 250°C, detection temperature programmed: first 100°C in 0.5min, then 25°C/min to 300°C in 2min, carrier gas: N₂ (≥99.99%).

3. Results and discussion

3.1. Pd/Fe-MWCNTs-Fe₃O₄ nanocomposites characterization

![Figure 2](image)

**Figure. 2.** (a)SEM image of new Pd/Fe-MWCNTs-Fe₃O₄ nanocomposites synthesized under ultrasound irradiation, (b) SEM image of Pd/Fe-MWCNTs-Fe₃O₄ nanocomposites synthesized under ultrasonic irradiation after reaction, (c) XRD spectrum of new Pd/Fe-MWCNTs-Fe₃O₄ nanocomposites synthesized under ultrasonic irradiation and (d) XRD spectrum of Pd/Fe-MWCNTs-Fe₃O₄ nanocomposites synthesized under ultrasonic irradiation after reaction.

BET specific surface area of Pd/Fe-MWCNTs-Fe₃O₄ nanocomposites (Pd loading percentage 0.5%, wt%) synthesized in the presence and absence of 40kHz ultrasonic irradiation were 260.5 m²·g⁻¹ and 45.1 m²·g⁻¹, individually.

Fig. 2 (a) shows SEM image of the new Pd/Fe-MWCNTs-Fe₃O₄ nanocomposites synthesized under ultrasonic irradiation. Newly synthesized Pd/Fe-MWCNTs-Fe₃O₄ nanocomposites under ultrasonic irradiation, were ball-shaped with particle diameter between 20 and 80nm, and smaller sizes and better disparity. Fig. 2 (b) shows SEM image of Pd/Fe-MWCNTs-Fe₃O₄ nanocomposites synthesized under ultrasonic irradiation after reaction. It is found that the surface of the nanoparticles becomes rough after the dechlorination, the spherical structure is basically destroyed, and part of the particles agglomerate obviously, which is due to the fact that the magnetic and van der Waals force cause the inevitable reunion as the reaction goes on. Some of the particles and the surface of MWCNTs adhere to a layer of floc, which may be due to the formation of iron oxide, hydroxide and the passivation...
layer formed by Fe$_3$O$_4$ on the surface of the particles, but a relatively complete dendrimer can still be seen. Fig. 2(c, d) shows XRD spectrums of the new and the 300 min aged Pd/Fe-MWCNTs-Fe$_3$O$_4$ nanocomposites synthesized under ultrasound irradiation. XRD spectrum for the new nanocomposites presents a strong diffraction peaks of Fe$^0$ (2$\theta$=44.66$^{\circ}$) and some diffraction peaks of Fe$_2$O$_3$ and Fe$_3$O$_4$ (2$\theta$=29.9$^{\circ}$, 35.5$^{\circ}$, 57.1$^{\circ}$, 62.7$^{\circ}$) can be detected before and after the reaction. The increase of diffraction peak intensity of Fe$_2$O$_3$ and Fe$_3$O$_4$ is due to the formation of magnetic oxides, which can explain the reductive dechlorination of PCBs by nZVI. At the same time, the characteristic peak of MWCNTs (2$\theta$=26$^{\circ}$) can also be observed, the intensity of diffraction peak is not strong, which may be due to the small dosage of MWCNTs (0.25 g·L$^{-1}$), and the surface is covered by Fe$_3$O$_4$-Pd/Fe, so the absorbed X-ray is reduced and the intensity is weakened. The characteristic peak of Pd was not detected in the XRD spectra, mainly because the mass fraction of Pd was too low. This is consistent with the previous work[5,6,9,10].

3.2. Reductive dechlorination of 2,3-DCB by catalysts prepared with different methods

Figure 3 shows the concentrations of 2,3-DCB, CB (2-CB and 3-CB) and biphenyl (B), which are effects of Pd/Fe-MWCNTs-Fe$_3$O$_4$ nanoparticles prepared with different methods on the removal rate of 2,3-DCB. It can be seen that the Pd/Fe-MWCNTs-Fe$_3$O$_4$ nanoparticles prepared by ultrasonic enhanced liquid-phase reduction method has the best removal effect on 2,3-DCB, and the removal rate of 2,3-DCB can reach 95.8% after the reaction of 300 min. The 2,3-DCB removal rate in 300 min is only 54.6%, which was treated with Pd/Fe-MWCNTs-Fe$_3$O$_4$ synthesized by common liquid phase reduction, and the concentration of intermediate product such as chlorobiphenyl (CB) is obviously higher, that is to say, it exists in the form of intermediate products and was not completely degraded into the final product biphenyl (B). Consequently, Pd/Fe-MWCNTs-Fe$_3$O$_4$ nanocomposites were synthesized through ultrasonic enhanced reduction method in the following experiments.

3.3. Kinetics of 2,3-DCB dechlorination by Pd/Fe-MWCNTs-Fe$_3$O$_4$ nanoparticles

As can be seen from Fig. 3 and the previous studies[5,6,9-14], the dechlorination of 2, 3-DCB by Pd/Fe-MWCNTs-Fe$_3$O$_4$ nanocomposites includes the following five steps: (1) the diffusion of 2,3-DCB to Pd/Fe-MWCNTs-Fe$_3$O$_4$ nanocomposites surface; (2) 2,3-DCB was adsorbed on Pd/Fe-
MWCNTs-Fe³O₄ nanocomposites surface, (3) the adsorbed 2,3-DCB reacted with Pd/Fe-MWCNTs-
Fe₃O₄ nanocomposites for reductive dichlorination, (4) dechlorination products of 2,3-DCB were
desorbed from Pd/Fe-MWCNTs-Fe₃O₄ nanocomposites surface, (5) the dechlorination products of
2,3-DCB diffused to the host solution. Although the Pd/Fe-MWCNTs-Fe₃O₄ nanoparticles have a
certain adsorption effect on 2,3-DCB, the amount of adsorption is less than the amount of degradation,
and the adsorption occurs mainly in the first 10 minutes before the reaction begins. The amount of
intermediate and final product formed during this period is not right, so the reductive dechlorination
process plays a leading role in the whole dechlorination process. The control step in the reductive
dechlorination process is the surface chemical reaction. The dechlorination pathway of 2,3-DCB is
further simplified as following:

\[ 2,3-DCB \xrightarrow{h_{21}} CB + Cl^{-} \xrightarrow{h_{22}} B + 2Cl^{-} \] (1)

Most of 2, 3-DCB removed a chloride ion to form 2-CB and 3-CB, CB is the sum of 2-CB and 3-
CB, B is the final product of 2,3-DCB degradation, and the corresponding reaction rate equations are
shown as follows:

\[ \frac{-dC_{2,3-DCB}}{dt} = k_1 C_{2,3-DCB} \] (2)

\[ \frac{dC_{CB}}{dt} = k_1 C_{2,3-DCB} - k_2 C_{CB} \] (3)

\[ \frac{dC_{B}}{dt} = k_2 C_{CB} \] (4)

After integration, the above equations are shown as following:

\[ \alpha_{2,3-DCB} = e^{-k_1 t} \] (5)

\[ \alpha_{CB} = \frac{k_1}{k_2 - k_1} (e^{k_2 t} - e^{k_1 t}) \] (6)

\[ \alpha_B = 1 - \alpha_{2,3-DCB} - \alpha_{CB} \] (7)

Where \( \alpha_B \) is the molar ratio of biphenyl in the reaction solution to its initial theoretical
concentration in the reaction system. Pd/Fe-MWCNTs-Fe₃O₄ nanocomposites can adsorb part of 2,3-
DCB because of its large specific surface area, so the concentration of 2,3-DCB in the reaction
system needs to be modified. During the whole process of dechlorination, the adsorption of
chlorinated biphenyls on Pd/Fe-MWCNTs-Fe₃O₄ nanocomposites surface reached equilibrium in an
instant, so the total concentration of chlorinated biphenyls in the reaction system was considered to be
constant. The formula can be summarized as follows:

\[ \alpha'_B = \alpha_B \times (1 - a) = [1 - e^{-k_1 t}] \times (1 - \frac{k_1}{k_2 - k_1} (e^{k_2 t} - e^{k_1 t})) \times (1 - a) \] (8)

Where \( a \) represents is the ratio of the final product biphenyl adsorbed on Pd/Fe-MWCNTs-Fe₃O₄
nanocomposites surface to the total amount of the organic chemical compounds. Then the reaction rate
constants \( k_1 \) and \( k_2 \) were calculated through modelling the experimental data into Eq. (8). Experimental affecting factors including the synthesized method of Pd/Fe-MWCNTs-Fe₃O₄
nanocomposites, initial pH value, Pd percentage, the amount of Pd /Fe nanoparticles, Fe₃O₄
nanoparticles dosage, the amount of MWCNTs and reaction temperature on the 2,3-DCB
dehlorination rate were explored in the following sequences. \( k_1 \) and \( k_2 \) under varying experimental
conditions were obtained in Table 1.

From Table 1, it can be observed that the influential factors such as Pd mass fraction, Fe₃O₄
dosage, Pd/Fe dosage, MWCNTs dosage, reaction temperature, initial pH value and catalysts prepared
method, have obvious effects on the apparent rate constants. The apparent rate constants \( k_1 \) and \( k_2 \)
increase with the increasing of Pd mass fraction, Fe₃O₄ dosage and MWCNTs dosage, Pd/Fe dosage, and
with the decreasing of pH value. \( k_1 \) and \( k_2 \) increased at first and then decreased with the increasing
of temperature in a certain range.
Table 1  Kinetics of 2,3-DCB dechlorination by Pd/Fe-MWCNTs-Fe₃O₄ nanoparticles

| Experimental conditions | 1-α |  \( k_1(\text{min}^{-1}) \) |  \( k_2(\text{min}^{-1}) \) | \( R^2 \) |
|-------------------------|-----|-----------------|-----------------|------|
| 1. synthesized method   |     |                 |                 |      |
| no ultrasonic irradiation | 0.92 | 0.037 | 0.108 | 0.98 |
| ultrasonic irradiation  | 0.98 | 0.010 | 0.059 | 0.99 |
| 2. Pd% (wt%)            |     |                 |                 |      |
| 0.20                    | 0.96 | 0.015 | 0.059 | 0.99 |
| 0.30                    | 0.95 | 0.017 | 0.064 | 0.97 |
| 0.35                    | 0.92 | 0.037 | 0.108 | 0.98 |
| 0.40                    | 0.93 | 0.038 | 0.110 | 0.99 |
| 3. Pd/Fe (g·L⁻¹)        |     |                 |                 |      |
| 3.0                     | 0.97 | 0.011 | 0.089 | 0.96 |
| 3.5                     | 0.95 | 0.013 | 0.102 | 0.96 |
| 4.0                     | 0.94 | 0.025 | 0.105 | 0.98 |
| 5.0                     | 0.92 | 0.037 | 0.108 | 0.98 |
| 6.0                     | 0.91 | 0.043 | 0.132 | 0.96 |
| 4. Fe₃O₄ (g·L⁻¹)        |     |                 |                 |      |
| 1.0                     | 0.96 | 0.018 | 0.099 | 0.98 |
| 1.5                     | 0.95 | 0.022 | 0.104 | 0.98 |
| 2.0                     | 0.94 | 0.025 | 0.105 | 0.98 |
| 2.5                     | 0.90 | 0.057 | 0.020 | 0.92 |
| 3.0                     | 0.90 | 0.088 | 0.024 | 0.91 |
| 5. MWCNTs (g·L⁻¹)       |     |                 |                 |      |
| 0.15                    | 0.94 | 0.015 | 0.061 | 0.98 |
| 0.20                    | 0.95 | 0.022 | 0.098 | 0.96 |
| 0.25                    | 0.94 | 0.025 | 0.105 | 0.98 |
| 0.30                    | 0.91 | 0.028 | 0.110 | 0.94 |
| 0.35                    | 0.92 | 0.033 | 0.122 | 0.98 |
| 6. T (°C)               |     |                 |                 |      |
| 15                      | 0.98 | 0.009 | 0.073 | 0.98 |
| 20                      | 0.94 | 0.019 | 0.096 | 0.99 |
| 25                      | 0.94 | 0.025 | 0.105 | 0.98 |
| 30                      | 0.97 | 0.020 | 0.079 | 0.96 |
| 35                      | 0.98 | 0.010 | 0.048 | 0.97 |
| 7. initial pH value     |     |                 |                 |      |
| 3                       | 0.94 | 0.025 | 0.105 | 0.98 |
| 5                       | 0.94 | 0.018 | 0.082 | 0.98 |
| 7                       | 0.95 | 0.011 | 0.074 | 0.98 |
| 9                       | 0.94 | 0.009 | 0.052 | 0.94 |

Note: Exp.1. \( C_{2,3-DCB}=10 \text{ mg·L}^{-1}, \ C_{\text{PdFe}}=5 \text{ g·L}^{-1}, \ C_{\text{MWCNTs}}=0.25 \text{ g·L}^{-1}, \ C_{\text{Fe₃O₄}}=2 \text{ g·L}^{-1}, \) rotation speed 450 rpm, Pd mass fraction was 3.5 wt. %, \( T=25 \text{ °C}, \) pH in= 3.0; Exp.2. \( C_{2,3-DCB}=10 \text{ mg·L}^{-1}, \ C_{\text{PdFe}}=5 \text{ g·L}^{-1}, \ C_{\text{MWCNTs}}=0.25 \text{ g·L}^{-1}, \ C_{\text{Fe₃O₄}}=2 \text{ g·L}^{-1}, \) rotation speed 450 rpm, \( T=25 \text{ °C}, \) pH in= 3.0; Exp.3 \( C_{2,3-DCB}=10 \text{ mg·L}^{-1}, \ C_{\text{MWCNTs}}=0.25 \text{ g·L}^{-1}, \ C_{\text{Fe₃O₄}}=2 \text{ g·L}^{-1}, \) rotation speed 450 rpm, Pd mass fraction was 3.5 wt. %, \( T=25 \text{ °C}, \) pH in= 3.0; Exp.4. \( C_{2,3-DCB}=10 \text{ mg·L}^{-1}, \ C_{\text{PdFe}}=5 \text{ g·L}^{-1}, \ C_{\text{MWCNTs}}=0.25 \text{ g·L}^{-1}, \) rotation speed 450 rpm, Pd mass fraction was 3.5 wt. %, \( T=25 \text{ °C}, \) pH in= 3.0; Exp.5. \( C_{2,3-DCB}=10 \text{ mg·L}^{-1}, \ C_{\text{PdFe}}=5 \text{ g·L}^{-1}, \) rotation speed 450 rpm, Pd mass fraction was 3.5 wt. %, \( T=25 \text{ °C}, \) pH in= 3.0; Exp.6. \( C_{2,3-DCB}=10 \text{ mg·L}^{-1}, \ C_{\text{PdFe}}=5 \text{ g·L}^{-1}, \ C_{\text{MWCNTs}}=0.25 \text{ g·L}^{-1}, \ C_{\text{Fe₃O₄}}=2 \text{ g·L}^{-1}, \) rotation speed 450 rpm, Pd mass fraction was 3.5 wt. %, \( T=25 \text{ °C}, \) pH in= 3.0; Exp.7. \( C_{2,3-DCB}=10 \text{ mg·L}^{-1}, \ C_{\text{PdFe}}=5 \text{ g·L}^{-1}, \ C_{\text{MWCNTs}}=0.25 \text{ g·L}^{-1}, \ C_{\text{Fe₃O₄}}=2 \text{ g·L}^{-1}, \) rotation speed 450 rpm, Pd mass fraction was 3.5 wt. %, \( T=25 \text{ °C}. \)

4. Conclusion

Pd/Fe-MWCNTs-Fe₃O₄ nanocomposites synthesized under ultrasonic irradiation was a better method to improve the surface characteristics. The affecting factors including initial pH value, Pd mass fraction, Pd/Fe dosage, Fe₃O₄ dosage, the amount of MWCNTs, reaction temperature, significantly affect the degradation of 2,3-DCB. The degradation of 2,3-DCB followed pseudo-first-order kinetics, and the kinetics constants \( k_1 \) and \( k_2 \) increased with the increasing Fe₃O₄ dosage, the amount of
MWCNTs, Pd mass fraction and Pd/Fe dosage, and with the decreasing of pH value. $k_1$ and $k_2$ increased at first and then decreased with the increasing of temperature in a certain range.

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