

Kinetic and influence factors on debromination of decabromodiphenyl ether by organo-montmorillonite supported nanoscale zero-valent iron

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Abstract. The organo-montmorillonite supported nanoscale zero-valent iron material (M-NZVI) was synthesized to degrade decabromodiphenyl ether (BDE-209). The kinetic and influence factors of apparent rate constant on debromination of BDE-209 by M-ZVI were studied, the experiment was conducted to investigate the influences of initial concentration, different materials dogs and pH value. The results show that all reaction processes followed pseudo first order kinetic equation, The apparent rate constant increased respectively with the increase of initial concentration, different materials dogs and the decrease of pH value.

Introduction

Polybrominated diphenyl ethers (PBDEs) widely used in electronic, chemical, electrical, textile, and other industries as a typical kind of brominated flame retardants[1], are ubiquitous in the environment, with high hydrophobicity, persistence, bioaccumulation and toxicity[2], among which BDE-209 is the only one that is still in production and large-scale use. It is a new way to degrade BDE-209 by M-ZVI, In this study, the kinetic and influence factors of apparent rate constant on debromination of BDE-209 by M-ZVI were studied, the experiment was conducted to investigate the influences of initial concentration, different materials dogs and pH value.

Materials and methods

Preparation and characterization of materials

Preparation and characterization of M-ZVI materials reference this method[3].

Process of batch experiment

First, 50 mL BDE-209 mixed solution ($2.0 \text{ mg}\cdot\text{L}^{-1}$) were added into 100 mL conical flask with plug as a reactor, and adding the synthetic material. The reactor was then sealed and stirred with rotating speed controlled at $150 \text{ rpm}\cdot\text{min}^{-1}$ at $25\pm 1^\circ\text{C}$. Timing sampling was conducted and then filtered, and the filtration was used for the analysis of the concentration of BDE-209. All samples were performed in four replications.

Influence factors of apparent rate constant include initial concentration, different materials dogs and pH value. Initial concentration of BDE-209 Solution is $1.0 \text{ mg}\cdot\text{L}^{-1}$, $2.0 \text{ mg}\cdot\text{L}^{-1}$ and $5.0 \text{ mg}\cdot\text{L}^{-1}$ respectively, the different materials dogs is 0.20g, 0.40g, 0.60g and 0.80g respectively, the different pH value is 3.0, 5.5, 7.0 and 9.0.

Analytical method

The concentration of BDE-209 was measured by HPLC (Shimadzu LC-20AT) equipped with a SupelcosilTMK C18 chromatographic column (250 mm \times 4.6 mm, 5 μm) and detected by UV spectrophotometry at a wavelength of 204 nm and 226 nm in a mobile phase (1.0 mL/min) composed of acetonitrile/water=98/2(V/V).

The concentration of bromide ion was determined by ion selective electrode method with instrument of Leici PHS-3C equipped with 301 bromide ion selective electrode and 801 double liquid junction saturated calomel electrode.

Results and discussion

The sorption kinetic on debromination of BDE-209 by M-ZVI

In the BDE-209 water solution, the surface which is contacted with the Nano iron particles and the BDE-209 water solution is called the Solid-liquid two phase interface, it is the place which Nano iron reduced BDE-209 to carry out the reaction of bromine. So the reaction steps of the debromination of BDE-209 by M-ZVI is similar to the steps of the debromination of halogen organic pollutants by M-ZVI, and the results of most scholars study show that all reaction processes of BDE-209 and the Nano iron (or other metals) followed Pseudo first order kinetic equation [4,5,6]. So pseudo first order kinetic equation is fitted for reaction process of it. The Equation is allowed.

$$\ln \frac{C_{BDE-209}}{C_{0BDE-209}} = -k_{obs}t \quad (1)$$

In the formula, t is the reaction time, the unit is min; the k_{obs} is pseudo first order kinetic reaction rate constant, the unit is min^{-1} ; $C_{BDE-209}$ is concentration of BDE-209 in the reaction time t , the unit is $\text{mg}\cdot\text{L}^{-1}$, $C_{0BDE-209}$ is the initial concentration of BDE-209, the unit is $\text{mg}\cdot\text{L}^{-1}$. In this study, M-NZVI and NZVI were chose to fit the degradation kinetics of BDE-209, the curve fitting graph is shown in Fig.1.

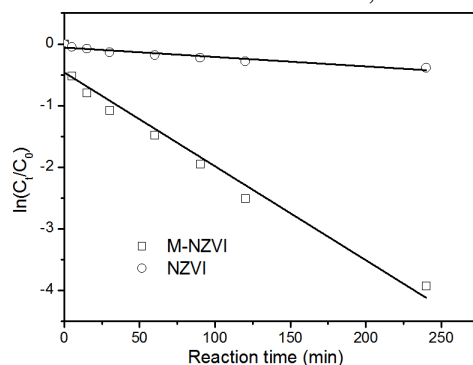


Fig.1 The kinetic fitting on BDE-209 removal of M-NZVI and NZVI

The results of Fig.1 show that the reaction processes of BDE-209 by M-NZVI and NZVI all follow pseudo first order kinetic equation, and it Has a good linear relationship, R^2 is 0.9622 and 0.9083 respectively. The apparent rate constant of the degradation of BDE-209 by M-NZVI and NZVI were 1.525×10^{-2} and 0.153×10^{-2} respectively, the apparent rate constant of NZVI materials for 9.96 times that of NZVI, and it shows that M-NZVI material has higher reactivity.

The influence of different factors on the apparent rate constant

(1) The influence of initial concentration of BDE-209 on the apparent rate constant

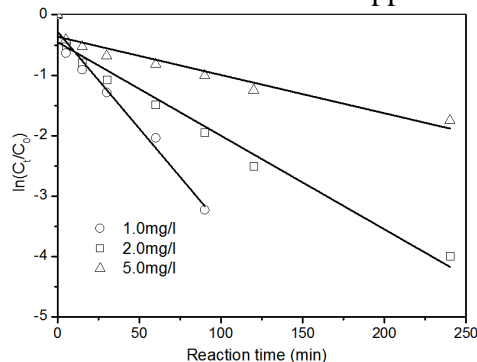


Fig.2 The kinetic fitting on BDE-209 removal of M-NZVI with different initial concentration

The results of Fig.2 show that the reaction processes of initial concentration of BDE-209 by M-NZVI follow pseudo first order kinetic equation. When the initial concentration of BDE-209 were $1.0 \text{ mg}\cdot\text{L}^{-1}$, $2.0 \text{ mg}\cdot\text{L}^{-1}$ and $5.0 \text{ mg}\cdot\text{L}^{-1}$, its k_{obs} were 2.821×10^{-2} , 1.550×10^{-2} and 0.633×10^{-2} , the results show that with the increase of initial concentration of BDE-209, the apparent reaction rate constant gradually reduce, so the degradation reaction rate of BDE-209 by M-NZVI gradually reduced, the result is consistent with the research results of many scholars[4,5,6]. For a certain amount of M-NZVI material, the total effective reactive sites in its material number is certain, with the increase of pollutants concentration, the reactive sites by all gradually occupy, and BDE-209 between molecules due to the increase in the number and there is more competition, leading to removal rate is reduced, so the rate constant k_{obs} gradually reduced.

(2) The influence of different materials dogs of M-ZVI on the apparent rate constant

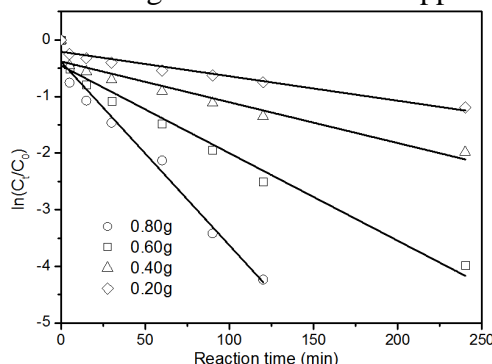


Fig.3 The kinetic fitting on BDE-209 removal of M-NZVI with different materials dogs

The results of Fig.3 show that the reaction processes of different materials dogs of M-ZVI follow pseudo first order kinetic equation too. When the M-NZVI dogs were 0.20 g, 0.40 g and 0.60 g and 0.80 g, the apparent reaction rate constant gradually increases, its k_{obs} were 0.433×10^{-2} , 0.721×10^{-2} , 1.548×10^{-2} and 2.245×10^{-2} respectively, the results show that with the increase of M-NZVI dogs, the degradation reaction rate of BDE-209 by M-NZVI increased, the result is consistent with the research results of many scholars[7,8]. M-NZVI material cast will increase with the increase of the amount is the total specific surface area, is also increase the material in the total number of reactive sites effectively, increased the number of reactive sites to BDE-209 adsorption and reduction of pollutants, leading to removal rate increases, so the rate constant gradually rise.

(3) The influence of the initial reaction solution pH value on the apparent rate constant

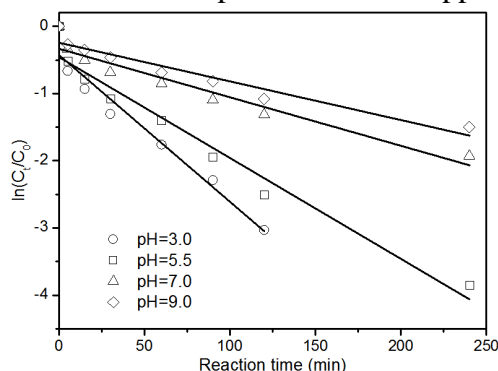


Fig. 4 The kinetic fitting on BDE-209 removal of M-NZVI with different pH

The results of Fig.4 show that the reaction processes of the initial reaction solution pH value of M-ZVI follow pseudo first order kinetic equation too, the initial reaction solution pH value have bigger influence on the apparent reaction rate constant, k_{obs} value decrease with increasing initial pH value of reaction solution. When the initial reaction solution pH value were 3.0, 5.5, 7.0 and 9.0, its k_{obs} were 2.184×10^{-2} , 1.502×10^{-2} , 0.722×10^{-2} and 0.576×10^{-2} respectively, of the apparent reaction rate constant when pH value is 3.0 is three times of which pH value is 9.0. The results show that the acid

environment conducive to the degradation of BDE-209 by M-NZVI material, in the acidic conditions of BDE-209 rapid reaction rate, the result is similar with many scholars research results[9,10]. It also shows that acid environment can prevent the formation of iron oxide and hydroxide precipitation, promote zero-valent iron surface and BDE-209 electron transfer between the pollutants, which was beneficial to the improvement of the degradation effect of BDE-209, so the apparent reaction rate constant reduce with the increase of pH value.

Summary

(1) The results on the debromination of decabromodiphenyl ether by organo-montmorillonite supported nanoscale zero-valent iron show that all reaction processes followed pseudo first order kinetic equation.

(2) The apparent rate constant increased respectively with the increase of initial concentration, different materials and the decrease of pH value.

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