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Catalytic dechlorination and detoxification of 1-(2-chlorophenyl) ethanol by Pd/Fe*

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Abstract: 1-(2-chlorophenyl) ethanol (CPE) is of health and environmental concern due to its toxicity and its use as an intermediate in pharmaceutical manufacturing. The current work deals with the catalytic reductive dechlorination and detoxification of CPE by Pd/Fe bimetal. CPE was effectively dechlorinated to 1-phenyl ethanol (PE) accompanied by the equivalent release of chloride. The extent of CPE dechlorination increased with temperature, Fe dosage and Pd loading. A decrease in solution pH increased CPE dechlorination, resulting presumably from an increase in hydrogen production. Under the specific conditions of 20 g/L Pd/Fe, 0.10% Pd (w/w) and initial pH 5–6, the CPE dechlorination was completed within 145 min. The dechlorination followed a pseudo-first-order kinetics with an activation energy of 56.7 kJ/mol. The results of toxicity testing showed that CPE was very toxic to *Chlorella*, whereas PE showed little toxicity. The toxicity of the reaction solution declined gradually and the promoting effects on *Chlorella* intensified consequently with the dechlorination process. Thus, the reductive dechlorination of CPE to PE by Pd/Fe was a detoxification process. It may be used to effectively reduce the toxicological effects of CPE-contaminated wastewater, thereby enhancing the performance of subsequent biological processes in wastewater treatment.

Keywords: 1-(2-chlorophenyl) ethanol (CPE), Pd/Fe, Catalytic reductive dechlorination, Detoxification, 1-phenyl ethanol (PE)
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1 Introduction

Aromatic alcohols with halogens on the ring are key intermediates in the syntheses of pharmaceuticals and many other compounds. They are of health and environmental concern due to their toxicity and recalcitrance. There is an urgent need to understand their transfer and environmental fate and to develop effective technologies for their removal from water. Dechlorination of chlorinated contaminants is an effective detoxification process and has recently been a key research subject. It has been found that chlorinated aromatic hydrocarbons are much more resistant to dechlorination than chlorinated aliphatic hydrocarbons, due to the much higher bond strength of the C-Cl bond on the aromatic ring (Aikawa *et al*., 2003). This is especially true for aromatic molecules with fewer chlorines, such as 1-(2-chlorophenyl) ethanol (CPE).

For halogenated aromatic compounds, biological processes are efficient only under anaerobic conditions and concurrently slow. Cost-effective zero-valent iron (ZVI) provides an alternative approach to reductive dechlorination of these organic compounds (Choi *et al*., 2007; Kouznetsova *et al*., 2007; Shin *et al*., 2007). Previous studies showed that ZVI effectively degrades many chlorinated organic compounds (including some herbicides and pesticides) at room temperature and normal atmospheric pressure (Arnold and Roberts, 2000; Dombek *et al*., 2001; Farrell *et al*., 2003; Kim *et al*., 2008). Both iron and chlorinated organics are transformed into benign, or much less toxic, compounds such as hydrocarbons, chloride and iron oxides. The overall reaction rate may become progressively slower due to the precipitation of ferrous hydroxides on the surface of ZVI during reaction that blocks the reactive sites on ZVI and hin-

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ders the direct contact between the chlorinated organic compounds and Fe (Doong and Lai, 2005). Further research with ZVI has led to the discovery that a bimetallic preparation with iron and palladium (Pd/Fe) is a superior reductant for chlorinated organics (Xu *et al*., 2003). ZVI with a negative reduction potential serves as the electron donor that produces molecular hydrogen when in contact with water by anodic corrosion, and palladium with a relatively high (positive) reduction potential as the reducing catalyst. The presence of a catalyst reduces the activation energy, which can substantially accelerate the reductive dechlorination (Kim and Carraway, 2003; He and Zhao, 2005). This type of rapid decontamination process has obvious commercial implications suitable for in-situ wastewater treatment and remediation. It is therefore essential to evaluate the factors which may influence the rate of dechlorination and to determine the kinetics of the dechlorination reaction.

With a relatively high reduction potential, halogenated organics do not readily oxidize. Comparatively, they are readily reduced via dechlorination. As the toxicity of chlorinated organics originates primarily from the chlorines in the molecular structures, the bimetal Pd/Fe reduction technique may be employed to effectively reduce or eliminate the toxicity of chlorinated organics through rapid dechlorination. Dechlorinated organics with less or no chlorines are more biodegradable and can be treated or removed later by more cost-effective conventional biological processes. In this study, CPE was selected as a model chlorinated organic compound to identify the factors that may affect the reductive dechlorination by Pd/Fe and to determine its reaction kinetics. A chiral alcohol with a chlorine on the aromatic ring, CPE is usually used as an intermediate for pharmaceutical synthesis and hence of great health and environmental concern. The toxicity tests of solution in reaction system to *Chlorella* were also conducted to analyze the detoxification of chlorinated organics CPE. The chemical structures of CPE and its dechlorination product (PE) are shown in Fig. 1.

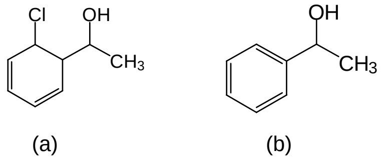

Fig. 1 Chemical structures of (a) CPE and (b) PE

2 Materials and methods

2.1 Materials

Potassium hexachloropalladate (purity of >99%) was purchased from Sigma-Aldrich (St. Louis, MO). CPE (96%) and PE (96%) were obtained from Alfa Aesar Tianjin (Tianjin, China). Iron power reduced (>200 mesh, >98.0%), methanol (>99.9%), acetone and sulfuric acid were of analytical grade.

The Pd/Fe catalyst powder was prepared by wet impregnation of Fe powder with an aqueous solution of potassium hexachloropalladate. The Fe powder was washed with 0.1 mol/L H_2SO_4 and acetone and then rinsed with distilled water to remove surface oxide layers and undesired organic compounds prior to palladization. An aqueous solution of potassium hexachloropalladate was prepared and added to a bottle containing the cleaned Fe powder. The mixture in the bottle was continuously stirred until its color turned from dark orange to pale yellow. The deposition of palladium on the surface of iron particles resulted in a bimetallic surface (Pd/Fe). Then, the palladized iron was rinsed twice with deionized water and used without drying. More details of preparation are referred to He and Zhao (2005).

2.2 Methods

2.2.1 Batch experimental procedures

Batch experiments were conducted using CPE as the substrate. CPE stock solution was prepared in methanol. A CPE solution of 0.32 mmol/L (50 mg/L) was prepared by pipetting appropriate amount of the stock solution to water with its pH previously adjusted to 6.88. A flask was fixed on a hob, and placed in a water bath operating at (298±1) K. The reductive dechlorination was performed by placing the CPE solution in the flask containing 10 g of Pd/Fe in 500 ml solution. The Pd loading (i.e., the ratio of Pd/Fe by weight) was 0.10%. The content in the flask was continuously stirred at 150 r/min with an electronic stirrer during reaction. At given times, samples were withdrawn from the supernatant using a syringe and filtered through a 0.22-μm filter membrane for analysis. To evaluate the effects of experimental conditions on CPE dechlorination, the reaction was also conducted at various Pd loadings, Fe dosages, temperatures, solution pH values, stirring speeds and initial CPE concentrations.

2.2.2 Toxicity tests for reaction solution

All glassware used in the tests was rinsed with 1 mol/L HCl and then deionized water for at least 1 h before use, then autoclaved at 394 K for 20 min. Five milliliters *Chlorella* culture at the logarithmic growth phase was inoculated into a 45 ml sterile culture medium and thoroughly mixed, which was used as blank sample for comparison. Similarly, a 100 mg/L CPE sample—25 ml CPE (200 mg/L), with 5 ml *Chlorella* culture added to the flask containing culture medium, was prepared to analyze its toxicological effects. After various dechlorination times, 25 ml supernatant was sampled and filtered, then treated as described in the CPE sample to test the toxicity of the reaction solution. Dechlorination conditions included a CPE initial concentration 1.28 mmol/L (200 mg/L), Fe 20 g/L, 0.20% Pd (w/w, on Fe), a reaction temperature of 298 K, and a stirring rate of 150 r/min. For comparison, the reaction solutions without CPE under the same conditions were also prepared and tested in a similar way. Each sample, including the blank, had three replicates. The flasks were then covered with four layers of gauze and continuously incubated for 96 h. The incubation conditions were the same as those for *Chlorella* culturing: temperature, (298±0.2) K; humidity, 50%; illumination, 16 h; light intensity, 2000 Lux. The beakers were gently shaken 4–5 times daily to prevent cell settling. Nutrients were not supplemented during incubation. After 24 h, the absorbance (ABS) values of the solutions were measured at 690 nm by a UV-754N spectrophotometer (China), which were proportional to the amounts of the *Chlorella*, and the increase of the ABS values indicated the growth promotion of the *Chlorella*.

2.3 Analytical methods

Analysis of chloride was performed by ion chromatography (792 Basic IC, Metrohm) equipped with a column (Metrosep asupp5, 4 mm×250 mm) and suppressed conductivity detection. The chromatographic conditions were: mobile phase, $NaHCO_3$ (1.7 mmol/L)+Na_2CO_3 (1.8 mmol/L)+acetone (5%, for chemical suppression); acidified solution, H_2SO_4 (0.1 mol/L); flow rate, 1.0 ml/min; injection volume, 20 μl; column temperature, 298 K. Prior to injection, samples were filtered through a 0.22-μm filter membrane.

CPE and PE were analyzed by high performance liquid chromatography (HPLC) (Jasco, Japan). The analytical conditions were: column, RP-C_{18}, 4.6 mm ×250 mm; detection, UV at 210 nm; mobile phase, methanol/H_2O (v:v=70:30); flow rate, 0.8 ml/min; injection volume, 20 μl.

The extent of CPE dechlorination was expressed as the ratio of free chloride determined in solution at the time of sampling to that calculated from the complete dechlorination of CPE, and the denominator was equal to the initial CPE concentration (mmol/L) in value. So, dechlorination efficiency $\eta = C_{\mathrm{Cl}^-} / C_{\mathrm{CPE}_0}$. Similarly, the extent of CPE removal was defined as the concentration of CPE reduced, i.e., the difference between the initial CPE concentration and that of CPE at the sampling time, divided by the initial CPE concentration. Likewise, the extent of PE production was calculated as the ratio of PE determined in solution at the time of sampling to that from the potentially complete dechlorination of CPE.

3 Results and discussion

3.1 Dechlorination of CPE

The curve of Cl^- control illustrated that the background chloride in the reaction system could be neglected (Fig. 2). The experimental results showed that CPE was effectively dechlorinated under test conditions. These conditions included the initial CPE concentration of 0.32 mmol/L, iron powder 20 g/L solution, the Pd/Fe loading ratio of 0.10% (w/w), the reaction temperature of 298 K, a stirring rate of 100 r/min, and a pH of 6.88. The concentration of CPE decreased with reaction time. Concurrently, concentrations of both chloride and PE increased. At

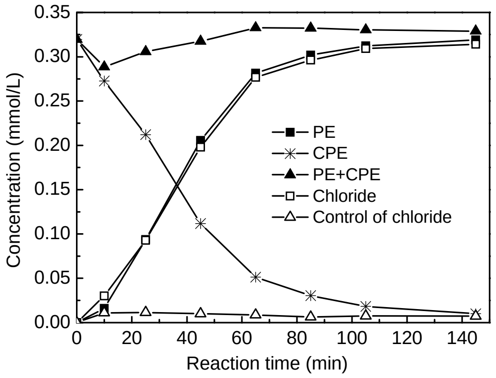

Fig. 2 Time-dependent reduction in CPE, production of PE and release of Cl^-

65 min, the extents of CPE dechlorination, CPE removal and PE production were 87.5%, 87.9% and 87.8%, respectively. The complete CPE dechlorination was achieved within 145 min. A mass balance existed during the reaction. That is, the sum of CPE and PE remained essentially constant. This indicates a stoichiometric dechlorination of CPE to PE, demonstrating that the catalytic dechlorination of CPE by Pd/Fe to PE was the mechanism and that PE was the end product of the reaction.

3.2 Factors that affected CPE dechlorination

The variation in the extent of CPE dechlorination (η%) during reaction with various Pd loading rates in the bimetal was presented in Fig. 3a. Less than 10% of dechlorination efficiency was obtained for iron particles without Pd. The extent of CPE dechlorination increased with the Pd loading. With 0.10% Pd in the bimetal, the extent of CPE dechlorination reached 88.9% at 65 min; the reaction was completed within 105 min. By comparison, only 44.4% CPE was dechlorinated at the same time (65 min) when the Pd loading in the bimetal was 0.05%. With 0.15% Pd in the bimetal, the CPE dechlorination was further enhanced such that the reaction was almost completed within 65 min. As Pd is a precious metal, and also based on the determined time-dependent extent of CPE dechlorination (Fig. 3a), a Pd loading of 0.10% was chosen for further study.

It has been reported that the corrosion of Fe produces hydrogen, which is subsequently adsorbed on Pd and dissociates to atomic hydrogen. The thus-formed atomic hydrogen is expected to attack CPE to displace the chlorine on the phenyl ring, leading to the formation of PE and the release of chloride. This suggests that an increase in Pd loading enhances the formation of atomic hydrogen and hence

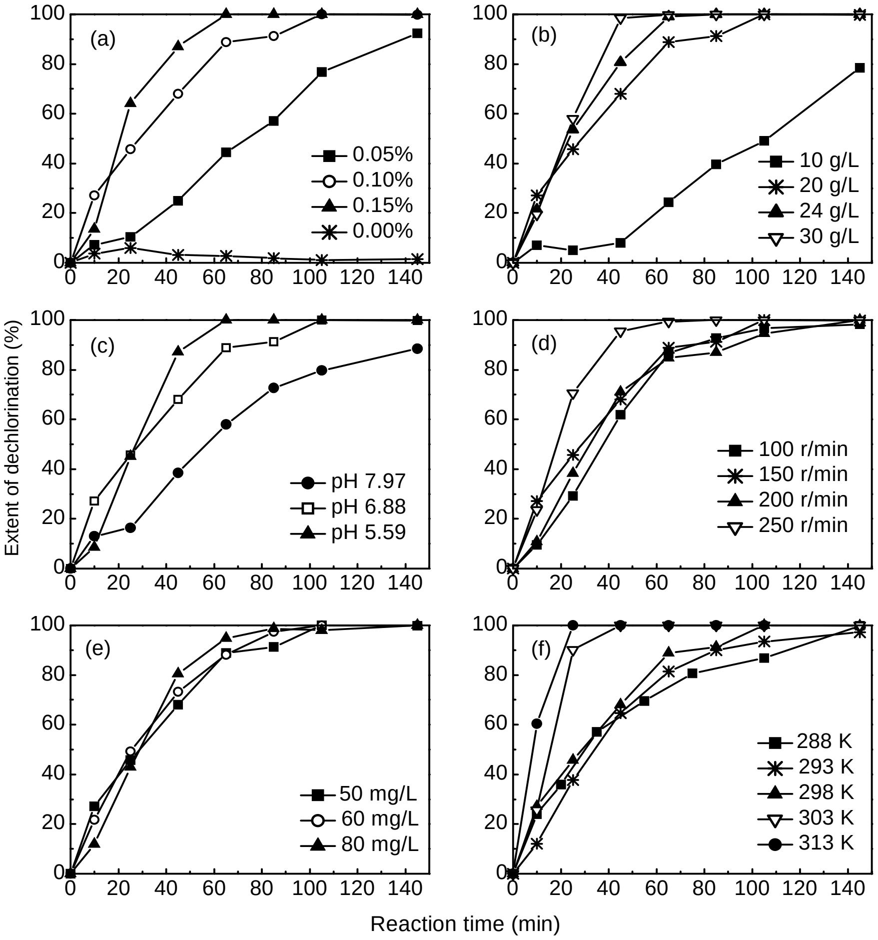

Fig. 3 Effects of experimental conditions on CPE dechlorination. (a) Pd loading; (b) Fe dosage; (c) Solution pH; (d) Stirring speed; (e) Initial concentration of CPE; (f) Reaction temperature

CPE dechlorination, a conclusion our results support. A higher Pd loading may also increase the surface area of the bimetal, an additional contribution to CPE dechlorination.

The CPE dechlorination also increased with increasing Pd/Fe dosage (Fig. 3b). With a Fe dosage of 5 g in 500 ml of solution, only 5.0% CPE was dechlorinated within 25 min. When the Fe dosage was increased to 20 g/L, the extent of CPE dechlorination within the same time period was increased to 45.8%, a >9-fold increase. At this Fe dosage, CPE was completely dechlorinated within 105 min. It is believed that the dechlorination reaction occurred on the surface of Pd/Fe. As the Fe dosage increased with a fixed Pd loading (i.e., 0.10%), the amounts of both the reactive Fe sites and the adsorptive Pd sites increased, enhancing the rate of CPE dechlorination. With a further increase in Fe dosage to 24 and 30 g/L, the extent of CPE dechlorination leveled-off with only a slight increase (Fig. 3b). It was thus recommended that Fe concentration of 20 g/L be used for further study.

Fig. 3c shows the effect of solution pH on CPE dechlorination. After 65 min reaction, 58.0% and 88.9% CPE was dechlorinated at initial pH 7.97 and 6.88, respectively, while the dechlorination was nearly completed at pH 5.59. It is expected that lower pH results in more severe corrosion of Fe and thus higher production of hydrogen. Our results showing that the CPE dechlorination increased with decreasing solution pH were consistent with this prediction. Low pH may also effectively prevent the precipitation of metal hydroxides and carbonates on the surface of Pd/Fe, diminishing the potential of the formation of surface passivating layers.

The influence of stirring speed on CPE dechlorination is shown in Fig. 3d. There were no obvious differences in CPE dechlorination with stirring speeds of 100, 150 and 200 r/min, although in all these cases the dechlorination was completed within 145 min. At the stirring speed of 250 r/min, however, the CPE dechlorination was clearly more rapid. It was presumed that the iron particles were not stirred completely due to the high specific gravity of Fe with stirring speeds of 100–200 r/min. Some iron particles settled to the bottom of the flask, and reacted with CPE very little. At the stirring speed of 250 r/min, the particles were almost fully mixed with CPE solution; the reaction surface of Pd/Fe was higher, resulting in more rapid dechlorination. Considering that the loss of Pd/Fe particles resulting from full mixing and a high power required for a high speed of stirring, the speed of 150 r/min was chosen in this study.

Fig. 3e shows the CPE dechlorination at the initial concentrations of 50, 60, and 80 mg/L. The initial CPE concentration had little influence on the dechlorination. This, along with the curve shape that the dechlorination initially occurred more rapidly and then leveled off with time, suggests that the CPE dechlorination followed a pseudo-first-order kinetics.

The CPE dechlorination was influenced by reaction temperature (Fig. 3f). Degree of dechlorination increased with increasing temperature within the tested range from 288 to 313 K. At 313 K, CPE was completely dechlorinated within 45 min, in comparison to 62.0% at 288 K.

3.3 Rate constants and activation energy of CPE dechlorination

From the effect of reaction temperature on CPE dechlorination (Fig. 3f), $\ln(C/C_0)$ is plotted versus reaction time; linear lines are obtained (Fig. 4, correlation coefficients range from 0.96 to 0.99), indicating again a pseudo-first-order kinetics for CPE dechlorination. The reaction rate constants (k), i.e., the slopes of the lines, are determined to be 0.021, 0.026, 0.030, 0.092 and 0.110 min^{-1} at the temperatures of 288, 293, 298, 303 and 313 K, respectively.

These rate constants are further used to plot $\ln k$ versus $1/T$; a linear line is obtained (Fig. 5, correlation coefficient R is 0.94). It is observed that an increase in the reaction temperature could significantly raise the reaction rates. The k values of various temperatures are correlated by $k = A\times e^{-E_a/(RT)}$, linear regression gives: $-\ln k=6821.7/T-19.7$, which gives rise to an estimated activation energy E_a of 56.7 kJ/mol.

3.4 Detoxification of CPE

As shown in Fig. 6, in the absence of CPE the ABS value of *Chlorella* suspension increased steadily with incubation time (Fig. 6, blank sample). In contrast, a decrease in ABS of *Chlorella* suspension was observed when the CPE concentration was increased to 100 mg/L in the suspension (Fig. 6, 100 mg/L CPE sample). The growth of *Chlorella* was completely inhibited, which indicated that CPE was toxic to

Chlorella. Moreover, previous experimental results showed that the growth inhibition of *Chlorella* was enhanced with CPE concentration (0–100 mg/L). Conversely, the growth of *Chlorella* with PE of various concentrations present (0–100 mg/L) was little affected, even promoted slightly (figure not shown). This suggested that PE, the dechlorination product of CPE, was non-toxic to *Chlorella*. Compared with the blank sample, the ABS value of *Chlorella* suspension increased in the presence of the supernatant of Pd/Fe bimetallic system without CPE after 30- and 120-min reaction (Fig. 6, control of reaction solution), and it is speculated that the iron ion produced by Fe-H_2O reaction served as nutrient and facilitated the growth of *Chlorella* (Xing *et al.*, 2007, Liu *et al.*, 2008). The curve of a 30-min reaction solution sample shown in Fig. 6 demonstrated that the *Chlorella* thrived on the reaction solution after 30 min dechlorination (at this time, both CPE and PE present), and the ABS value of the suspension was much higher than that of the blank sample and control of 30-, 120-min reaction solution. Furthermore, the promoting effects intensified with reaction time (Fig. 6, 120 min-reaction solution), when CPE was almost completely dechlorinated to PE and hardly detected in the solution. The toxicity of the reaction solution declined gradually with the dechlorination process, which was expected to be later beneficial to biodegradation.

Previous studies reported that some kinds of organic pollutants were always supplied as nutrition sources and stimulated the growth of the algae in low concentrations (Shen and Zhou, 2002; Yan *et al.*, 2002). It was observed that lower concentrations of N, N-dimethyl formamide (DMF) enhanced *Chlorella pyrenoidosa* growth. Similar results were obtained; that low concentration of methyl *tert*-butyl ether (MTBE) induced increase in the growth rate of *selenastrum capricornutum* (Rousch and Sommerfeld, 1998). In this case, the non-toxic PE may be utilized as an additional carbon source and accelerate the growth of *Chlorella* together with iron ion. In addition, lower concentrations of Cl^- from CPE dechlorination possibly contributed to the growth promotion of *Chlorella* (Abdel-Rahman *et al.*, 2004). The probable causes of the above-mentioned need further study.

Thus, the reductive dechlorination of CPE to PE catalyzed by Pd/Fe is a detoxification process. It may therefore be suggested that the catalytic dechlorination by Pd/Fe be utilized as a pretreatment of CPE-contaminated wastewater to enhance the performance of subsequent biological processes.

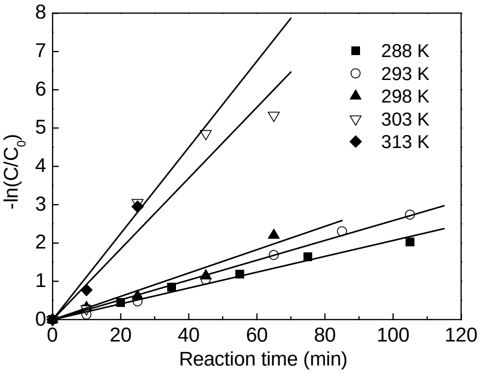

Fig. 4 Linear decrease of dechlorination efficiency with the reaction time under different temperatures

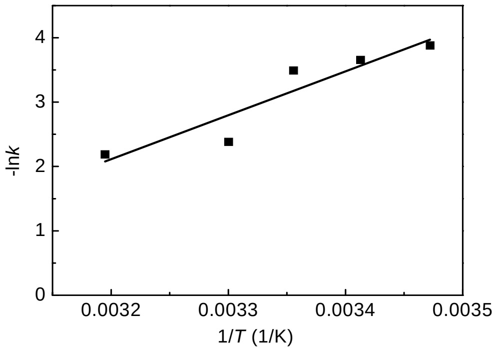

Fig. 5 Correlation for reaction rate constant −ln*k* with 1/*T*

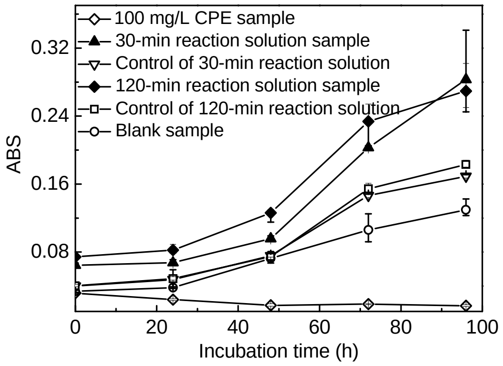

Fig. 6 Effects of test samples on the ABS of *Chlorella* suspension

4 Conclusion

Reductive dechlorination of CPE was effectively catalyzed by Pd/Fe bimetal. The factors that affected the reaction included temperature, pH, Pd loading, and the amount of Pd/Fe, which should be carefully evaluated to enhance the performance of the catalyst. The dechlorination followed a pseudo-first-order kinetics with an activation energy of 56.7 kJ/mol within the temperature range of 288–313 K. While CPE was rather toxic to *Chlorella*, PE showed little, if any, toxicity. The toxicity of the reaction solution declined gradually and the promoting effects on *Chlorella* intensified consequently with the dechlorination process. Thus, the reductive dechlorination of CPE to PE by Pd/Fe is a detoxification process. It may be utilized as a pretreatment technique to effectively reduce the toxicological effects of CPE-contaminated wastewater and thus enhance the performance of subsequent biological processes in wastewater treatment.

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