

Dechlorination of *p*-Chlorophenol by Fe-Pd Nanoparticles Promoted by Poly (γ -glutamic acid)–Dopamine Composite

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Palladium-doped nanoscale zerovalent iron nanoparticles (Fe-Pd NPs) was fabricated and stabilized by poly (γ -glutamic acid)–Dopamine composite (PGA-DA). The fabricated nanoparticles had high dechlorination activity towards *p*-Chlorophenol (*p*-CP). PGA-DA modified Fe-Pd NPs significantly outperformed PGA modified ones in catalytic activities even in weak alkaline condition. Fe-Pd NPs@PGA-DA (10 mg PGA-DA and 0.4 wt% Pd loading) could achieve 100 % *p*-CP removal within 60 min. It is worth mentioning that the presence of DA alone could overwhelm dechlorination capacity of Fe-Pd NPs toward *p*-CP. The coordination bonding between catechol and Fe ions was also investigated in detail. This study demonstrated that PGA-DA is a promising modifier and stabilizer for Fe-Pd NPs, which was expected to be applied in real environmental remediation technology.

1. Introduction

Chlorophenols (CPs) are important chemicals and intermediates those are highly toxic to human health and the environment. Generally, CPs are introduced into aquatic systems through discharges from the excessive consumption of dyes, pesticides, and pharmaceuticals. Although the uses of chlorophenols were ceased or highly restricted, the past extensive production and applications have left an environmental legacy that chlorophenols are widely detected in a wide range of environmental circumstances (Zhou et al., 2016). Therefore, efficient technologies for CPs removal are really required.

Nanoscale zero-valent iron (nZVI) has been intensively studied for reductive removal of CPs from water in the past decade, especially the bimetallic nanoparticles (such as Fe-Pd). Many studies have demonstrated that the iron-based bimetallic nanoparticles can degrade kinds of chlorophenols in water much faster than monometallic nZVI nanoparticles (Liu et al., 2014). However, because of the very high surface energy and magnetic attraction, nZVI nanoparticles tend to agglomerate rapidly to form micron-scale or even larger aggregates, thereby losing their mobility and reactivity. In addition, iron-based nanoparticles are easily oxidized in air, and the generated iron oxides can accumulate on the nZVI surface, which will block the reactive sites and thus affect the reactivity (Gisi et al., 2017). Therefore, several strategies have been documented to limit passivation and aggregation for enhanced CPs degradation by nZVI or iron-based bimetallic nanoparticles. Considering the simplicity and low cost of the nZVI synthesis method, modifying the surface of nZVI particles with agents (such as surfactants, biopolymers and polyelectrolytes) becomes an attractive and feasible option. Liu et al. (2016) synthesized nZVI stabilized by carboxymethyl cellulose (CMC) and observed that CMC modification made nZVI disperse well and have higher contaminant removal efficiency than that of bare nZVI. Petersen et al. (2012) prepared nZVI in the presence of poly (acrylic acid) (PAA), achieving a high degradation rate for chlorinated contaminants. In essence, modifiers could prevent the passivation and aggregation by electrostatic repulsion with surface charges, steric repulsion with steric hindrance, or both.

Poly (γ -glutamic acid) (PGA), a natural anionic polypeptide produced by *Bacillus subtilis* with abundant anion groups of carboxyl. As a nontoxic and biodegradable biomaterial, this water-soluble poly (amino acid) is

particularly advantageous for chemical and biomedical applications. In addition, PGA is a potential biosorbent for the removal and recovery of some contaminants from waste water in some previous studies reporting very promising results (Clarke et al., 2017). Dopamine and its derivatives are from the mussel foot proteins, which can bind metal ions using the catechol functional group. Moreover, because of the catechol functionality, one can prepare nanoparticles based on dopamine modifications with desirable physicochemical properties (Xu et al., 2017).

Taking into consideration that anionic PGA has abundant carboxyl groups, which can provide electrostatic and steric repulsion to prevent particle aggregation, and dopamine has high binding ability towards the metal ions via chelation, PGA-DA composites could be synthesized and used as a stabilizer for Fe-Pd NPs and improve the dechlorination performance of Fe-Pd NPs.

In this study, the PGA-DA-modified Fe-Pd nanoparticles (denoted as Fe-Pd NPs@PGA-DA) were synthesized. *p*-Chlorophenol (*p*-CP) (one of the most toxic phenolic derivatives) was selected as a model pollutant to evaluate the dechlorination activity of the nanoparticles. The effects of PGA modification on Fe-Pd NPs reactivity to *p*-CP were also investigated for comparison. It is worth mentioning that all the experiments were conducted in weakly alkaline conditions without pH control. The results further clarified the important role of PGA-DA modification in the reactions of *p*-CP with Fe-Pd NPs and also demonstrated the potential of Fe-Pd NPs@PGA-DA for efficient remove of *p*-CP from wastewater even in weakly alkaline conditions.

2. Materials and methods

Poly (γ -glutamic acid) (PGA, M_w 50-100 kDa) were purchased from Yuanye Bio-Technology (Shanghai, China). Dopamine hydrochloride (DA), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl), N-hydroxysuccinimide (NHS), Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, > 99.0 %), potassium borohydride (KBH_4 , 97 %), potassium chloropalladite (K_2PdCl_4 , 98 %) and *p*-chlorophenol (*p*-CP, 99 %) were supplied by Aladdin Reagent Company (Shanghai, China). Methanol (CH_3OH , HPLC grade, 99.9 %) was purchased from Concord Technology (Tianjin, China). All chemicals were used without further purification. All water was purified by a Sartorius arium pro VF water purification system (18.2 M Ω resistivity).

2.1 Synthesis of PGA-DA

PGA (200 mg) was stirred in 30 mL of PBS (0.02M, pH=6.0) buffer for 15 min until a clear solution was obtained. 5 mL EDC·HCl solution (150.02 mg) and 5 mL NHS solution (69.054 mg) were introduced into the PGA solution in sequence. The mixture was then sparged with N_2 and stirred for 5 min followed by addition of 5 mL DA solution (113.784 mg). The reaction was carried out for 9 h under N_2 atmosphere. The resultant was dialyzed against weakly acidic deionized water for purification using dialysis tubes (MWCO 14,000 Da) for one week. The resulting solution was lyophilized to yield the dry copolymer of PGA-DA.

2.2 Preparation of Fe-Pd NPs@PGA-DA

The Fe-Pd NPs were synthesized using chemical reduction method where the potassium borohydride served as a reduction reagent. 250 mg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added into 50 ml PGA-DA solution ($m_{\text{PGA-DA}}/m_{\text{Fe}^{2+}} = 10\%$, 20 %). The mixture was then sparged with argon for about 20 min to assure formation of Fe^{2+} -PGA-DA complex and to remove dissolved oxygen (DO). Then 3 mL KBH_4 (50 mg mL^{-1}) was injected into the mixture at a BH_4^- -to- Fe^{2+} molar ratio of 3.0 to form the Fe NPs. To ensure efficient use of reductant, the suspension was purged with Argon for 15 minutes until gas (hydrogen) evolution ceased. Then Fe nanoparticles were loaded with trace amounts (0.1 wt%, 0.4 wt%) of Pd to yield the stabilized bimetallic nanoparticles by adding known quantities of potassium chloropalladite aqueous solution into the nanoparticles suspension. In addition, Fe-Pd NPs@PGA (PGA-modified Fe-Pd nanoparticles, mass ratio of PGA/ Fe^{2+} was 20 %) of different Pd loading were also prepared for comparison. Argon was constantly purged during the synthesis and dechlorination reaction. The temperature of the solution was kept at 25 °C by a thermostatic water bath.

2.3 Batch dechlorination experiments

The 550 mg L^{-1} stock solution of *p*-CP was prepared by dissolving *p*-CP in water at 25°C. 2 mL *p*-CP stock solution was added into the prepared Fe-Pd suspension with the desired initial molar ratio of Fe to *p*-CP (105:1) and initial *p*-CP concentration of 20 mg L^{-1} . Then the degradation of *p*-CP was initiated. For the measurement of the concentration of *p*-CP, 0.8 mL of liquid sample was taken off from the solution at desired selected times, then a magnet was used to speed up the sedimentation, and then the liquid supernatant was filtered through syringe membrane filter (0.22 μm) and furtherly tested with high performance liquid chromatography (HPLC). All the experimental points were duplicated in two consecutive experiments, and the standard deviations were calculated.

2.4 Characterization

The Fourier transform infrared spectroscopy (FTIR, Nicolet Nexus 670) analysis was conducted to identify the structure of PGA-DA. Scanning electron microscopy (SEM, Hitachi S-4800) was used to investigate morphology, size of the bare and PGA-DA modified Fe-Pd NPs. X-ray photoelectron spectroscopy (XPS, ULVAC-PHI) measurement was performed to analyze the surface elemental composition. The samples mentioned before characterization must be washed by water and alcohol for three times, then dried in vacuum oven at room temperature and stored. The *p*-CP concentration in solution was measured by HPLC.

3. Results and discussion

3.1 Characterization of PGA-DA and Fe-Pd NPs@PGA-DA

FTIR spectra of PGA, DA and PGA-DA composite were measured in the range of 4,000-400 cm^{-1} to reveal the interaction between PGA and DA. As shown in the FTIR spectra of DA (Figure 1a), the absorption peak at 3,300 cm^{-1} is a characteristic of the O-H stretching vibration of phenolic hydroxyls. The absorption peak at 1,220 cm^{-1} arises from the in-plane deformation of phenolic hydroxyls (O-H bond) in DA. The shift of absorption peak of O-H of PGA-DA composite indicating the involvement of O-H groups in the synthesis of PGA-DA composite. As shown in the FTIR spectra of PGA (Figure 1b), absorption peak at 3,440 cm^{-1} is a characteristic of the O-H stretching vibration of the hydroxyls in the carboxyl groups. The absorption peak at 1,570 cm^{-1} and 1,392 cm^{-1} are characteristic of the C=O stretching vibration of carboxyl groups, which are apparently weakened in FTIR spectra of PGA-DA. The slight change of the absorption peak indicated the formation of amido bond and the interaction of PGA and DA (Li et al., 2017).

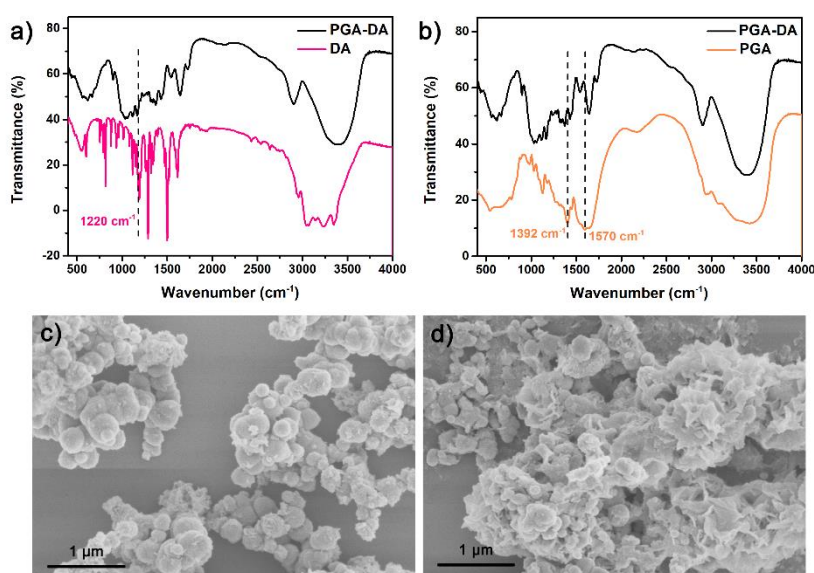


Figure 1: FTIR spectra of (a) PGA-DA composite and PGA and (b) PGA-DA composite and DA. SEM micrographs of (c) Fe-Pd@PGA-DA NPs and (d) pristine Fe-Pd NPs

The morphologies and size of pristine and PGA-DA modified Fe-Pd NPs were characterized by SEM. As shown in Figure 1c, the majority of Fe-Pd NPs@PGA-DA had relatively spherical shapes and smooth surfaces in the size range of 100–200 nm. In the absence of PGA-DA in synthesis process, the resulted Fe-Pd NPs formed irregular aggregations, which proved that pristine Fe-Pd NPs were easily oxidized and PGA-DA could inhibit the aggregation and restrain oxidation. In general, similar with most stabilizers in previous works, PGA-DA could enhance the stability of Fe-Pd NPs, and the Fe-Pd NPs@PGA-DA had similar morphologies and size.

XPS was employed to investigate the elemental surface chemistry of Fe-Pd NPs@PGA-DA, and their spectra are shown in Figure 2. As seen in Figure 2a, Fe-Pd NPs@PGA-DA is mainly composed of carbon (C 1s), iron (Fe 2p) and oxygen (O 1s), with small amounts of nitrogen (N 1s). The presence of carbon and nitrogen mainly comes from the PGA-DA composite and iron comes from the reduction of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The high resolution XPS spectra of Fe 2p is displayed in Figure 2b, the peaks at binding energies of 711.1 eV and 724.9 eV were attributed to the $2p_{3/2}$ and $2p_{1/2}$ states of oxidized iron (Fe^{3+}), and the peaks at 706.8 eV and 719.9 eV were assigned to the $2p_{3/2}$ and $2p_{1/2}$ of Fe^0 (Lee et al., 2008). These results confirmed the existence of zero-valent

iron (Fe^0) on the surface of nanoparticle. And the coexistence of iron oxides and Fe^0 further suggested that the Fe^0 NPs consisted of a core-shell structure with a core of Fe^0 and a shell of iron (hydro) oxide. Moreover, Fe^0 nanoparticles were successfully prepared and incorporated into the PGA-DA framework.

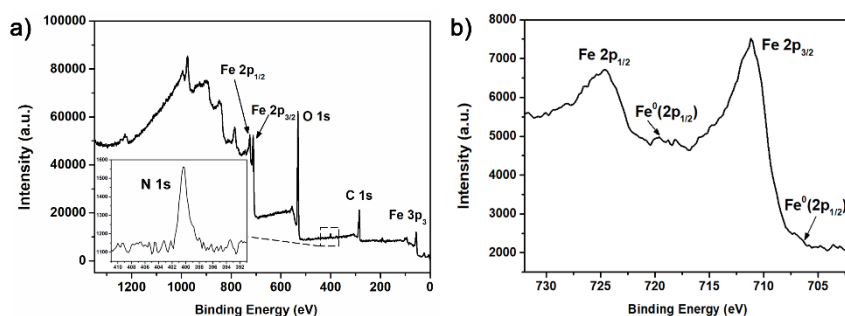


Figure 2: XPS spectra of Fe-Pd NPs@PGA-DA: (a) wide-scan and N 1s spectrum (b) Fe 2p spectrum

3.2 Dechlorination of *p*-CP by Fe-Pd NPs@PGA-DA

The dechlorination activity of *p*-CP by Fe-Pd@PGA-DA NPs was investigated through batch experiments. Figures 3a and Figures 3b show the dechlorination profiles of *p*-CP by Fe-Pd NPs@PGA and Fe-Pd NPs@PGA-DA (same amounts of modifier loadings) with different Pd loadings. The results indicated that Fe-Pd NPs@PGA-DA and Fe-Pd NPs@PGA both have relatively high degradation efficiency for *p*-CP, and Fe-Pd@PGA-DA NPs showed a largely enhanced dechlorination activity. Specifically, Fe-Pd NPs@PGA (10 mg PGA and 0.4 wt% Pd loading) could only remove approximately 70% *p*-CP in 150 min, while Fe-Pd NPs@PGA-DA (10 mg PGA-DA and 0.4 wt% Pd loading) could achieve 100% *p*-CP removal within 60 min. These results demonstrated that PGA-DA is more suitable as a modifier of Fe-Pd NPs for the dechlorination of *p*-CP.

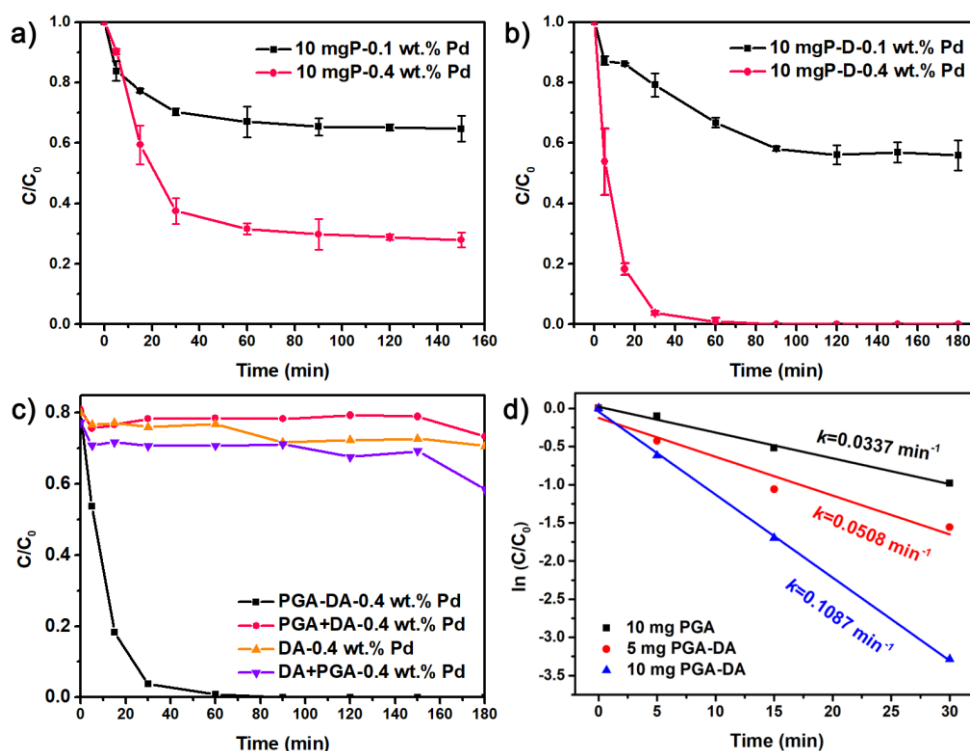


Figure 3: Time courses of dechlorination using (a) Fe-Pd NPs@PGA and (b) Fe-Pd NPs@PGA-DA with same amounts of modifier (10 mg) and different Pd loadings (0.1 wt% and 0.4 wt%). (c) Time courses of dechlorination using Fe-Pd NPs@PGA-DA, Fe-Pd NPs@DA and Fe-Pd NPs@PGA in different DA systems. (d) The rate constant (k) for the dechlorination of *p*-CP with different modifier (Pd loading = 0.4 wt%)

During the dechlorination reaction of *p*-CP by Fe-Pd NPs, the factor of Pd content may have an important effect on the dechlorination activity. As shown in Figures 3a and Figures 3b, The Fe-Pd NPs with high Pd content displayed remarkable dechlorination activity regardless of modifier. Fe and Pd can form galvanic cells, Fe passed electrons to the catalytic Pd, which played catalytic roles not only accelerating Fe corrosion but also improving dechlorination activity

To investigate the role/function of DA on PGA-DA modified Fe-Pd NPs, batch experiments were conducted in different kinds of DA systems (Figure 3c). With DA modification, Fe-Pd NPs didn't show dechlorination reactivity even with high Pd loading. Moreover, addition of DA into Fe-Pd NPs suspension or reaction systems showed little degradation efficiency for *p*-CP in 180 min. The results suggested that the presence of DA alone can overwhelm dechlorination capacity of Fe-Pd NPs toward *p*-CP. Further study is required to understand the mechanism for the inhibition of DA.

Generally, dechlorination of *p*-CP by Fe-Pd NPs follows a pseudo-first order rate law (Xu et al., 2012), which can be modeled using the following equation: $\ln(C/C_0) = kt$, where C and C_0 are chemical concentrations of *p*-CP at times t (min) and 0 respectively, k (min^{-1}) is the rate constant and t is the reaction time. Therefore, the k value of the dechlorination systems is the slope of $\ln(C/C_0)$ versus t over time. Calculations of the rate constant for the dechlorination of *p*-CP with different modifiers (10 mg PGA, 10 mg PGA-DA and 5 mg PGA-DA) are shown in Figure 3d. The rate constants of Fe-Pd NPs@PGA-DA with 10 mg PGA-DA loading ($k = 0.1087 \text{ min}^{-1}$) were approximately three orders of magnitude higher than that of Fe-Pd NPs@PGA with 10 mg PGA loading ($k = 0.0337 \text{ min}^{-1}$), and Fe-Pd NPs@PGA-DA with only 5 mg PGA-DA loading also show high degradation efficiency for *p*-CP, which demonstrated that PGA-DA is a promising stabilizer of nZVI for the dechlorination of *p*-CP.

3.3 Mechanism of the enhanced dechlorination of *p*-CP by Fe-Pd NPs@PGA-DA

It was demonstrated that acidic conditions favor avoiding the surface passivation of nZVI and keeping its surface activation in previous works (Liu et al., 2006). Therefore, pH value is a crucial parameter that affects the degradation rate of *p*-CP. With this in mind, the pH values during the synthesis and dechlorination reaction of Fe-Pd NPs@PGA and Fe-Pd NPs@PGA-DA were recorded as shown in Figure 4a. It was divided into three periods (a, b and c) to elucidate the overall pH changes: period a was the process of adding Fe^{2+} to modifier solution, period b was reductive preparation process of Fe-Pd NPs and period c was dechlorination reaction process. The result showed that the different dechlorination system of two kinds of nanoparticles have similar pH change tendency. A decrease in pH values was observed with adding Fe^{2+} to modifier solution, then there is an obvious increase in pH values during the reductive preparation, and finally, relatively stable values of pH = 9.0 were observed in dechlorination reaction process. The results indicated that Fe-Pd NPs@PGA-DA have remarkable degradation efficiency for *p*-CP at weakly alkaline conditions, which indicated the feasibility of field application.

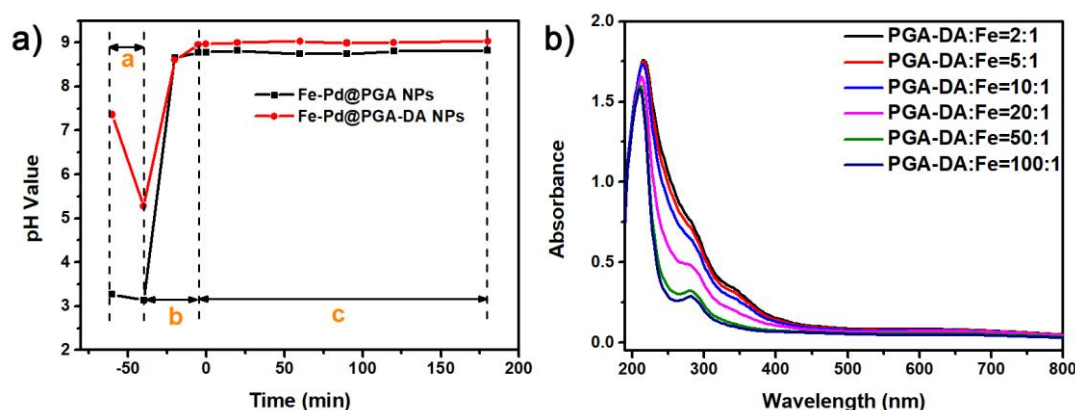


Figure 4: (a) The changes in pH value during the synthesis and dechlorination reaction of Fe-Pd NPs@PGA-DA and Fe-Pd NPs@PGA. (b) UV-vis spectra of complexes of PGA-DA and Fe^{2+} ions with different Fe^{2+} concentration (pH = 9.0).

DA could chelate $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions generated from the corrosion of Fe-Pd NPs due to the coordination bonding between catechol and Fe ions. In order to confirm the complexation of DA and Fe ions, the UV-vis spectroscopy measurements were performed on the complexation. UV-vis spectra of solutions containing Fe ions and DA at pH = 9.0 with various Fe ratios (Figure 4b) indicated the formation of DA-iron complexes because of the obvious

formation of adsorption band (Ejima et al., 2013). The intensity of adsorption increased with the increasing of the concentration of Fe ions, indicating the increasing concentration of DA-iron complexes.

Anionic PGA has abundant carboxyl groups, which can provide electrostatic and steric repulsion to prevent particle aggregation, DA has high binding ability towards the metal ions via chelation and can be used as coordination agent to chelate Fe²⁺/Fe³⁺ ions generated from the corrosion of Fe-Pd NPs. Therefore, PGA-DA can largely improve the stability and dechlorination performance of Fe-Pd NPs even under alkaline conditions.

4. Conclusions

In summary, a high-efficiency Fe-Pd bimetal dechlorination system was designed in which PGA-DA functions as the stabilizer and coordination agent scavenger of Fe ions. The Fe-Pd NPs@PGA-DA had high catalytic dechlorination activity for *p*-CP under alkaline conditions. It was observed that Fe-Pd NPs@PGA-DA showed a largely enhanced dechlorination activity over that of Fe-Pd NPs@PGA, achieving a high *k* value of 0.1087 min⁻¹, and the presence of DA alone can overwhelm dechlorination capacity of Fe-Pd NPs toward *p*-CP. Furthermore, the complexation of DA and Fe ions were studied by the UV-vis spectroscopy, and the results indicated the formation of DA-iron complexes. It was proposed that the high dechlorination activity of Fe-Pd NPs@PGA-DA is mainly attributed to the electrostatic-steric repulsion interaction and the prevention of Fe hydroxide formation because of the binding ability of DA to Fe²⁺/Fe³⁺ ions. Therefore, due to its uncomplicated synthesis and excellent performance in *p*-CP removal, the Fe-Pd NPs@PGA-DA are expected to be suitable for applications in the treatment of *p*-CP contaminated water under alkaline conditions.

Acknowledgments

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