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Fabrication of resin supporting Au-Pd bimetallic nanoparticles composite to efficiently remove Chloramphenicol from water

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Abstract

The evolution of antibiotic resistance and the potential impact on human health of Chloramphenicol (CAP) made it an urgent pollutant in environment. In this study, Au-Pd bimetallic nanoparticles (BNPs) were firstly synthesized and then successfully loaded on the amberlite 717 to form an amberlite 717 supporting Au-Pd BNPs catalytic system (717@Au-Pd) with the mass fraction of Au-Pd at about 4.5%. The as-synthesized catalytic system was used to degrade CAP in water at H_2 atmosphere at room temperature. When 0.5 g of 717@Au-Pd was added into the CAP solution (50 mg L^{-1}, 50 mL, pH = 7), about 60% of CAP was absorbed on the 717@Au-Pd in the first 10 h and then all of CAP can be completely removed in the following 3 h at H_2 atmosphere. The degradation process of the reaction can be fit with first order kinetics equation with the kinetics constants of 4.3 h^{-1} ± 0.009. The degradation products and mechanism were studied by using LC/MSD Trap-XCT. The results showed that CAP was removed by the 717@Au-Pd via cleaving the carbon-halogen bond of CAP while keeping the nitro-group silent and this made the degradation products less environmental toxicity. The recycled experiments showed that the removal rate of CAP can still maintain at 99% even after 5 cycles. The study indicated that 717@Au-Pd is a promising catalyst for removing environmental pollutants containing carbon halogen bond like CAP.

Introduction

Chloramphenicol (CAP) is a broad spectrum antibiotic exhibiting strong activity against most of micro-organisms, including gram-positive and gram-negative bacteria. It had been widely used for the treatment of wound healing and ocular infections in clinical practice. While, in the last decades, CAP has been prohibited to treat food-producing animals in many countries, such as E.U., U.S. and Canada, because residual CAP in food may cause human bone marrow aplasia and therefore aplastic anemia [1]. However, due to broad spectrum of action, high efficiency and relatively low cost, CAP is still in use illegally or legally in some other countries. The persistent use of CAP in the world caused the universal existence of CAP in environment due to its stability. For example, up to 26.6 μg L^{-1} of CAP was found in effluents of sewage treatment plants in China [2]. The persistent existence of CAP in environment can result in evolution of multidrug-resistant bacteria and novel antibiotic-resistant genes, which have attracted increasing attentions as their harm to human health [3, 4]. It is therefore urgent to search for effective method to remove CAP in environment.

The molecule of CAP contains a benzene ring, two carbon-chlorine bonds and a nitro-group. The CAP including carbon-chlorine bonds ensures it one of toxic chlorinated organic compounds in the environment [5]. Meanwhile, the nitro-group in the molecule of CAP is easily reduced to nitroso-group or amine group, which is strongly carcinogenic [6]. In this context, it is admirable to break carbon-chlorine bonds and prevent the formation of nitroso-group and amine group during the degradation of CAP. In recent years, various methods have been used to degrade CAP. Among them, advanced oxidation processes (AOP) was considered an effective way to degrade CAP. Although lots of studies already proved that the antimicrobial activity of CAP was negative after treated with AOP methods, the degree of mineralization was still not high and carbon-chlorine bonds may not be broken in these studies [2, 7-10]. Bioelectrochemical systems were also used for the degradation of CAP [11, 12]. In this method, the carbon-chlorine bonds could be broken, and the nitro-group could also be reduced to nitroso-group and amine group, an unfavorable agent. Notably, promising nano-catalysts were also introduced to degrade CAP [13, 14]. For example, Singh et al. removed CAP by using zero-valent iron–silver bimetallic nanoparticles (ZVBMNPs) as catalysts [13], but the results showed that the by-products also contained amine group, which was a probable precursor of N nitroso compounds. Furthermore, some other studies suggested that CAP can be removed by reductive dechlorinating microorganisms or enzyme, but these studies showed that the process is very slow and still far beyond real application [15, 16]. Microwave radiation method was an effective method to remove CAP but the high radiation power made this method real application impossible [17]. Therefore, it is significant to find a promising way to cleave the carbon-chlorine bonds of CAP without reducing the nitro-group to amine or nitroso group.

Pd is a prominent catalyst that can cleave carbon-chlorine bond in H_2 atmosphere [18], but the usage of Pd catalyst was limited as the catalytic efficiency of Pd is very low at room temperature. The catalytic performance of Pd catalyst can be enhanced when combined with other metals in various kinds of reactions[19-25]. It has been shown that the catalytic performance of Pd in cleaving carbon-halogen bond can be greatly improved by Au-Pd bimetallic nanoparticles (BNPs) [26, 27]. In our recent research, Au-Pd BNPs with core-shell structure has also been proved to be an effective catalyst in the degradation of diclofenac by cleaving carbon-halogen bonds [28]. As the performance of Pd catalyst in H_2 atmosphere has strict selectivity, it is possible to use Au-Pd BNPs to cleave carbon-chlorine bonds of CAP while keeping the nitro-group silent. Inspired by this idea, in this work we used Au-Pd BNPs with core-shell structure as catalyst to degrade CAP.

As the particle size of Au-Pd BNPs was too small to be separated and recycled easily, we utilized the anion exchange resin to support the Au-Pd BNPs catalyst, with aim to develop a simple and reusable catalytic system. Firstly, Au-Pd BNPs with core-shell structure were synthetized and then supported on the surface of the strong-base anion exchange resin (amberlite 717) for the degradation of CAP. Amberlite 717 supporting Au-Pd BNPs composite was found to be an efficient catalyst for the dechloridation reaction of CAP, and the nitro-group remained silent during the reaction. This suggested composite could be used as a promising material for degradation of CAP in water without producing high toxic intermediated substances.

Experimental

Preparation of Au NPs

Au NPs were synthesized according to the reported method [29]. In a typical synthesis, a gold salt solution (125 mg L^{-1}, 80 mL) was heated to 60 °C with stirring. Then a reducing agent with 40 mg of sodium citrate, 50 mg of tannic acid, and 18 mg of potassium carbonate dissolved in 20 mL of ultrapure water was added to the gold salt solution. The solution was then heated to boiling. Two minutes later, the solution was removed from the heat source and Au NPs solution (58 mg L^{-1}, 100 mL) was obtained.

Preparation of Au-Pd BNPs

Au-Pd BNPs were also synthesized according to the reported method [29]. 2 mL of 600 mg L^{-1} H_2PdCl_4 solution, 10 mL of 58 mg L^{-1} Au NPs solution and 10 mL of ultrapure water were mixed and stirred for more than 20 min. Then, H_2 was bubbled the solution for at least 3 min, and the Au-Pd BNPs solution was obtained. By diluting the Au-Pd BNPs to certain volume of ultrapure water, a 50 mg L^{-1} Au-Pd BNPs solution with a mass ratio of Au and Pd about 1:1 was obtained.

Pretreatment of amberlite 717

Amberlite 717 (10 g) was firstly soaked in ethanol solution (50 mL) for 2 h, and then was soaked sequentially in aqueous NaOH solution (2 M, 50 mL), HCl solution (2 M, 50 mL) for several cycles, and finally in NaOH solution (4 M, 50mL) for 4 h to exchange anions from Cl^- to OH^-. The resultant resin was filtered and washed with water until the filtrate was neutral. After that, the resin was dried at 80 °C overnight. The amberlite 717 used in this study were all pretreated with this procedure unless otherwise noted.

Preparation of amberlite 717 supporting Au-Pd BNPs catalytic system (717@Au-Pd)

Amberlite 717 (10 g) was soaked in Au-Pd BNPs solution (50 mg L^{-1}, 50 mL) for 1 h and then was separated. The resultant resin was washed with water and then dried at 80 °C. The above procedure was repeated several times until the resin attained saturation, which indicated by the filtrate of washing water appeared obvious dark brown. Finally, the amberlite 717 supporting Au-Pd BNPs catalytic system (717@Au-Pd) was obtained and used in this study.

Characterizations

A Hitachi S-4800 SEM and a JEOL JEM-2010 HRTEM were used for illustrating the structure of samples. A NETZSCH Tarsus TG 209 F3 was used for thermogravimetric analysis to evaluate the amount of Au-Pd BNPs loaded on the amberlite 717. Sample masses of around 10 mg were heated from 40 to 1000 °C at a rate of 5 °C min^{-1} in a N_2 atmosphere. An Agilent Technologies 1260 Infinity HPLC with an autosampler and a ZORBAX SB-C18 column (4.6 × 250 mm, 5 μm) was used to analyze the concentration change of CAP and its degradation products. The mobile phase was composed of 45%/55% (v/v) methanol and water at a flow-rate of 1.0 mL·min^{-1}. The injection volume was 20 μL, and CAP and its degradation products were detected by an UV detector at the wavelength of 278 nm. CAP and its degradation products were monitored and identified by using an Agilent Technologies 1100 LC/MSD Trap-XCT. Chromatography was carried out on a Nano HPLC comprising of a quaternary pump and an autosampler, equipped with a ZORBAX Eclipse XDB -C18 column (4.6 × 150 mm, 5 μm). The mobile phase was composed of 45%/55% (v/v) methanol and water. Analytes were detected with negative ion mode. A PerkinElmer Optima 7000DV ICP-OES was used for analysing the Au and Pd element released to liquid phase.

Catalytic performance testing

In a typical catalytic degradation process, the reaction was carried out in a 50 mL of round-bottom flask equipped with a magnetic stirrer. As CAP could be partly adsorbed by amberlite 717, we set a pretreatment process before the catalytic degradation started. 717@Au-Pd (0.5 g) were firstly mixed with 50 mL of CAP (50 mg L^{-1}) and then stirred in the flask for 10 h to achieve adsorption equilibrium. Then the degradation reaction was carried out in H_2 atmosphere at pH = 7 and at room temperature if not noted additionally.

Results and discussion

Characterization

The morphology and composition of 717@Au-Pd were characterized by SEM, EDX and TEM. Figure 1a showed a full view of 717@Au-Pd. The size of amberlite was about 600 μm, which ensured it an excellent macroscopical supporter in the catalytic system. In our previous research, it was already shown that the Au-Pd BNPs was of core-shell structure with Au as core and Pd as shell and the particle size of the BNPs was 7.88 ± 1.59 nm [28]. After loaded, as shown in the Figure 1b and 1c, Au-Pd BNPs were successfully supported on the amberlite 717. The BNPs were well distributed on the surface of amberlite 717 and the sizes of BNPs were homogeneous with about 8 nm, which were similar to that in our previous study [28]. As shown in the Figure 1d, EDAX spectra also confirmed the existence of elements Au and Pd on the composite.

In the literatures, metallic/bimetallic nanoparticles were supported on the various carriers and used in the degradation of organic pollutants [30-32]. As far as Au-Pd BNPs was concerned, the nanomaterials have been successfully supported on the graphene oxide, metal oxides and many other macro supporters, and the catalytic activity of resulted composites was all highly enhanced compared with those of unsupported Au-Pd BNPs [33-40]. But for Au-Pd BNPs with core-shell structure, the literatures were rare. Edwards et al loaded Au-Pd BNPs with core-shell structure on the carbon, TiO_2 and Al_2O_3 by using incipient wetness method [41]. The catalyst was used for the direct synthesis of hydrogen peroxide with high efficiency and selectivity. This composite was far less to be applied in the treatment of water due to not easy separation. Sarkany et al. loaded Au-Pd BNPs with core-shell structure on SiO_2 for acetylene hydrogenation. The catalytic activity of the catalyst decreased with the increasing thickness of the Pd shell [25]. In this study, by stepwise synthesis, the Au-Pd BNPs with core-shell structure were successfully supported on the amberlite with a simple method, which might be used to treat polluted water because of easily separation, low-cost and high-throughput.

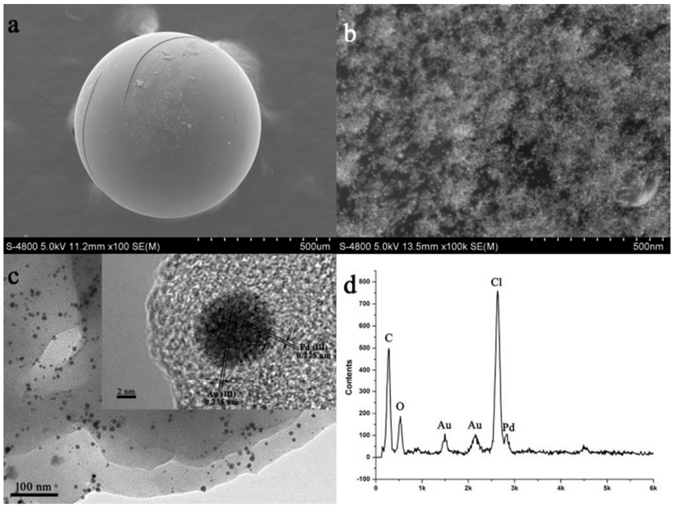

Figure 1. SEM images of 717@Au-Pd of low magnification (a), high magnification (b), HRTEM image of 717@Au-Pd (c) and EDAX spectra of 717@Au-Pd (d).

In order to figure out the amount of Au-Pd in the composite, Thermogravimetry (TG) - Derivative Thermogravimetry (DTG) was used to analyze the decomposition of composite. Figure 1a showed the thermogravimetric analysis process of amberlite 717 and 717@Au-Pd from 40 °C to 1000 °C. The residual mass percentage of amberlite 717 and 717@Au-Pd were $w_1\%$ = 12.91% and $w_2\%$ = 16.80 %, respectively.

The residual mass percentage of amberlite 717 can be described by Equation **1**:

$$w_1\% = {w'_{a1}}/{w_{a1}} \times 100\% \quad (\mathbf{1})$$

Where $w_1\%$ is the residual mass percentage of amberlite 717, w'_{a1} is the residual mass of amberlite 717 and w_{a1} is the initial mass of amberlite 717.

Same as Equation **1**, the residual mass percentage of 717@Au-Pd can be described by Equation **2**:

$$w_2\% = \frac{{w'_{a1}}/{w_{a1}} \times w_{a2} + w_{BNPs}}{w_{a2} + w_{BNPs}} \times 100\% \quad (\mathbf{2})$$

Where $w_2\%$ stands for the residual mass percentage of 717@Au-Pd, w_{a2} stands for the initial mass of amberlite 717 used for loading Au-Pd BNPs and w_{BNPs} stands for the mass of Au-Pd BNPs loaded on the amberlite 717.

Then, the mass percentage of Au-Pd BNPs loaded on the amberlite 717 ($w_{BNPs}\%$) can be described by Equation **3**.

$$w_{BNPs}\% = {w_{BNPs}}/{(w_{a2} + w_{BNPs})} \times 100\% \quad (\mathbf{3})$$

By combining these three equations, $w_{BNPs}\%$ can be calculated by the following equation:

$$w_{BNPs}\% = \frac{w_{a2}\% - w_{a1}\%}{100\% - w_{a1}\%} \times 100\% \quad (\mathbf{4})$$

The calculated mass percentage of Au-Pd BNPs successfully loaded on amberlite 717 was about 4.5%.

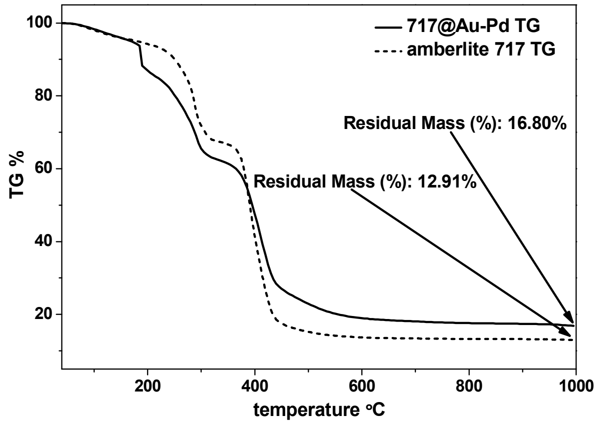

Figure 2. TG and DTG curves of amberlite 717 and 717@Au-Pd.

Catalytic performance of 717@Au-Pd

It is well known that the catalytic performance of Pd in breaking carbon-halogen bond can be greatly improved by forming Au-Pd BNPs with core-shell structure [26]. Meanwhile, it is necessary to support Au-Pd BNPs on macro substrate for development of a simple and reusable catalytic system as the particle size of Au-Pd BNPs was too small to be separated and recycled easily. In this study, a series of controlled experiments were set to evaluate the catalytic performance of 717@Au-Pd. As shown in the Figure 3, CAP can be partly adsorbed by amberlite 717 and 717@Au-Pd. After pretreatment of 717 and 717@Au-Pd to the adsorption equilibrium, about 60 % of CAP was absorbed before the catalytic degradation started. For the amberlite 717, the concentration of CAP kept nearly constant in the following experimental process with or without H_2 atmosphere. This result showed that the amberlite 717 has good adsorption property for CAP and it acquired equilibrium after pretreatment with CAP for 10 hours. For the 717@Au-Pd composite, similar amount, about 60 % of CAP was absorbed after the pretreatment process. In the following catalytic degradation, the concentration of CAP kept constant for 717@Au-Pd without H_2 atmosphere. In contrast, an obvious concentration drop of CAP was showed for 717@Au-Pd with H_2 atmosphere. After 3 h of reaction, no CAP can be detected by HPLC. The results showed that 717@Au-Pd has an excellent ability in removal of CAP in H_2 atmosphere and the removal was caused by synergistic effect from catalytic degradation reaction by Au-Pd BNPs and the adsorption property of amberlite 717.

The curve 4 in Figure 3 suggested that the catalytic degradation process of CAP may comply with apparent first order kinetics model. By kinetic analysis, the concentration data of CAP showed a well pertinence with apparent first order kinetics with the initial concentration of CAP at about 22 mg L^{-1}, yielding an apparent rate constant (k_1) of 4.3 h^{-1} ± 0.009 for 717@Au-Pd in H_2 atmosphere. Several groups also studied the first order reaction rate constant of CAP degradation reactions in various reaction systems [7-10, 14]. In most of these studies, the initial concentration of CAP was above 50 mg L^{-1} and they all degraded CAP with comparable first order reaction rates, which suggested these methods are promising ways to remove CAP. In this study, the removal of CAP was synergistic effects of adsorption and following degradation reaction. The first order reaction rate constant can be used to describe the catalytic degradation process in the removal process. The high first order reaction rate showed 717@Au-Pd composite was a promising catalyst in degrading CAP.

In the literatures, Wong et al. have been studying the hydrodechlorination property of Au-Pd BNPs with core-shell structure for a long time[19, 26, 42-45]. In their studies, the chloroform, trichloroethene, and perchloroethene were selected as the hydrodechlorination target objects and the hydrodechlorination efficiencies and catalytic kinetics of Au-Pd BNPs were investigated. The results showed that the hydrodechlorination efficiencies of Au-Pd BNPs with core-shell structure was improved obviously compared with that of Pd catalyst. De Corte et al. also studied the hydrodechlorination property of biosupported Au-Pd BNPs for the removal of environmental contaminations, such as trichloroethene and diclofenac [30, 46]. They confirmed that by combining Pd with Au, the catalytic activity of the catalyst can be greatly enhanced. Tnaka et al. prepared TiO_2 loaded Au-Pd BNPs as catalysts and studied the dechlorination property to remove chlorobenzene under irradiation of visible light [47]. The results showed that the conversion of chlorobenzene was improved by using Au(0.8)@Pd(0.2)/TiO_2 instead of Pd(0.2)-TiO_2. All these studies unambiguously proved that Au-Pd BNPs was a promising catalyst in hydrodechlorination application.

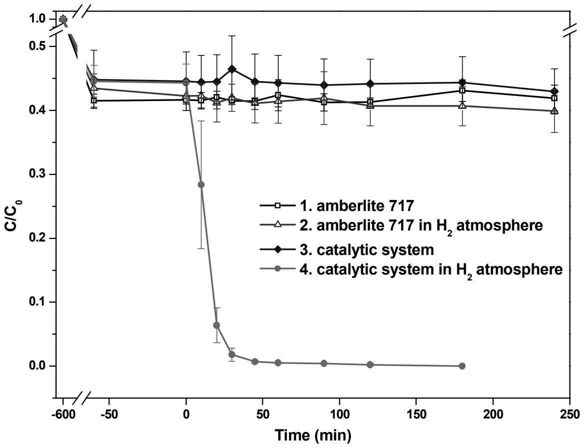

Figure 3. Concentration variation of CAP with different experimental conditions, C_0: 50 mg L^{-1}.

Mechanism of degradation

The degradation reaction was carried out with 717@Au-Pd in H_2 atmosphere at pH = 7, and when the reaction ended, the pH of the solution was found to be about 5.5. It is already known that when carbon-halogen was broken by Pd catalyst in H_2 atmosphere, the pH of the reaction system would be lowed as HCl was produced. Therefore, it can be inferred that the carbon-halogen bonds might be cleaved in this degradation reaction. Figure 4a showed the chromatograms of the degradation products of CAP at pH 7 by use of 717@Au-Pd with H_2 bubbles after 45 min of reaction time. As shown, up to 6 peaks were observed and peak **1** belongs to that of CAP. The HPLC spectra implied that there may be more than 5 by-products appeared in the degradation process. A further studied was carried on by an Agilent Technologies 1100 LC/MSD Trap-XCT. The LC-MS spectra showed that only CAP and two other by-products can be detected, as shown in the Figure 4b-d. In the Figure 4b, m/z of 322.5 （M^-, 100%）, 258.5 (41), 193.5 (39) and 151.5 (16) belonged to the three characteristic fragment ion peaks of CAP [48]. The molecular ion peak and fragment peak of Figure 4c and d conformed to 2-chloro-N-(1,3-dihydroxy-1-(4-nitrophenyl)propan-2-yl)acetamide and N-(1,3-dihydroxy-1-(4-nitrophenyl)propan-2-yl)acetamide, respectively. These two substances can be ascribed to the products of CAP losing one Cl and two Cl atoms, respectively. These degradation products proved that a standard catalytic hydrogenolytic cleavage occurred in the degradation of CAP by 717@Au-Pd, and it is worthwhile to mention that the nitro-group cannot be reduced to nitroso-group or amine group.

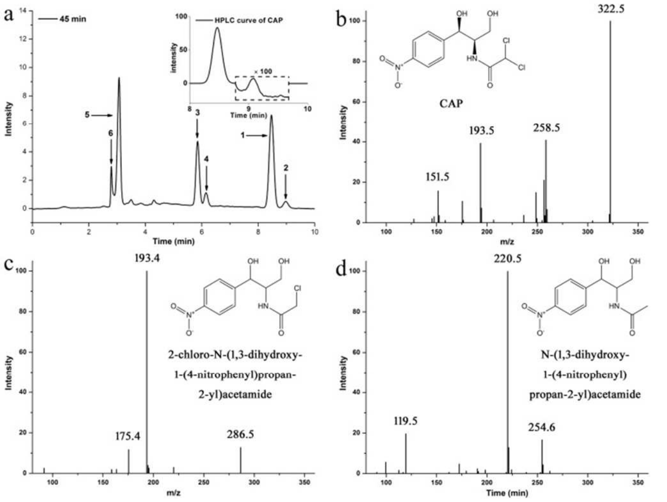

Figure 4. HPLC and LC-MS of CAP and its by-products (a) HPLC spectrum of CAP treated with 717@Au-Pd for 45min, (b) LC-MS of CAP, (c) LC-MS of 2-chloro-N-(1,3-dihydroxy-1-(4-nitrophenyl)propan-2-yl)acetamide, (d) LC-MS of N-(1,3-dihydroxy-1-(4-nitrophenyl)propan-2-yl)acetamide.

The possible mechanism of degradation reaction route of CAP was shown in the Figure 5. In one degradation route, Pd can break either of these two carbon-chlorine bonds of CAP, and in the following degradation, the remained carbon-chlorine bond can be further cleaved. In another route, both of these two carbon-chlorine bonds can be cleaved at the same time. This suggested degradation route of CAP by 717@Au-Pd was similar to that of the degradation of diclofenac by using Au-Pd BNPs with core-shell structure in our previous work [28]. The stepwise or one step of cleaving two carbon-chlorines of CAP was also found in the possible pathways of CAP reduction by ZVBMNPs [13]. In that study, Singh et al. found that both of carbon-halogen bonds and nitro group in the CAP molecule can be reduced completely by one step degradation route, or carbon-halogen bonds of CAP were cleaved by stepwise degradation route, forming the same intermediate substance of 2-chloro-N-(1,3-dihydroxy-1-(4-nitrophenyl)propan-2-yl)acetamide. The most interesting thing is that the different intermediate substance of CAP was found for the one-step degradation route. In another degradation of CAP by microwave radiation, the CAP was cleaved into 4-nitrobenzoic acid and CH_2Cl_2 or $CHCl_3$ [17]. Contrastively, 717@Au-Pd may be a more promising catalyst for degrading CAP due to cleaving the carbon-halogen bonds and preserving nitro group.

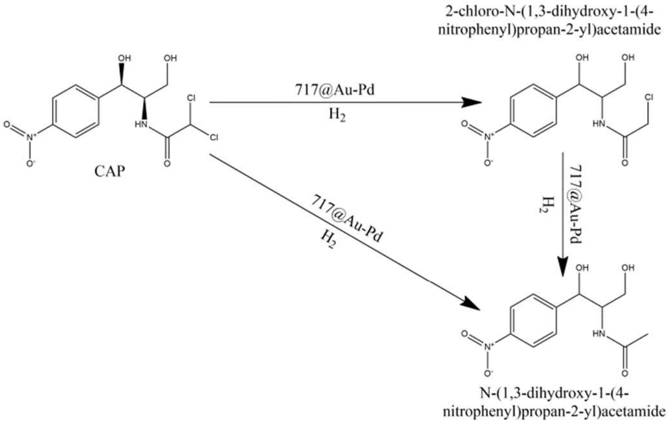

Figure 5. The reaction route of CAP in H_2 environment with 717@Au-Pd.

CAP is a chiral compound as its structural formula was shown as inset in the Figure 4b. The enantiomorphs of organic molecule have different polar property despite with same molecular weight. Bjorn et al. showed the HPLC peaks of two pairs of enantiomorphs of CAP molecule in different mobile phase situations [49]. Combined with the data provided by HPLC and LC-MS, tiny enantiomorphs of CAP were existed in the raw samples and its enantiomorphous by-products were also produced in the degradation process. By supposing this, peak 1 and 2 belonged to the enantiomorph of CAP, while peak 3, 4 and 5, 6 were stand for two enantiomorphes of by-products of CAP.

Recycled performance

In order to test the recycled performances of 717@Au-Pd, the recycled experiment on the degradation reaction of CAP was carried out by soaking 717@Au-Pd in the NaOH solution (2 M, 50 mL) for 1 h and washed with water until the filtrate was neutral before each circle. The recycled performance of 717@Au-Pd was displayed in the Figure 6. After 5 cycles, the removal rate of CAP can still maintain at 99%. It can be observed that the degradation performance was maintained without significant decline with the increase of cycle times. No Au or Pd element can be detected in the reaction liquid phase throughout the recycled experiment according to the analysed using ICP-OES. These results indicated that the loading of Au-Pd BNPs on amberlite 717 was very stable for the application of removing CAP in water.

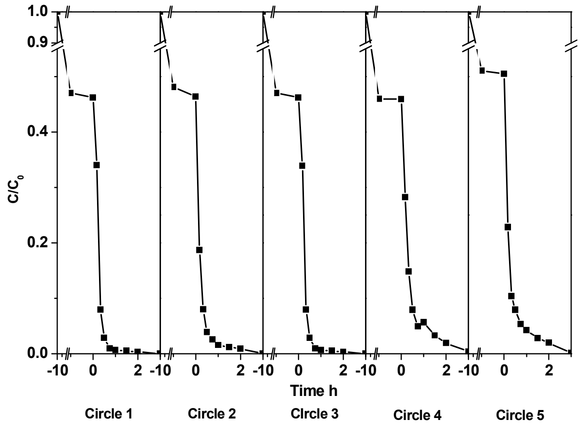

Figure 6. Cycling tests of degradation reaction of CAP by using 717@Au-Pd as catalysts, C_0: 50 mg L^{-1}.

Conclusions

In this study, Au-Pd BNPs with core-shell structure was synthesized and further loaded on amberlite 717 to form a macro catalyst system of 717@Au-Pd. The as-synthesized 717@Au-Pd was proved to be promising catalysts for the cleavage of carbon-chlorine bonds in the CAP molecule and preservation of nitro group. The catalytic process can be described by apparent first order kinetics and $k_1 = 4.3\ h^{-1} \pm 0.009$. The recycled experiments showed that the catalytic performance of 717@Au-Pd was stable in experiment condition. The relatively high reaction rate and its stable recycle performance made 717@Au-Pd a promising catalyst for removing environmental pollutants containing carbon halogen bonds like CAP.

Acknowledgements

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