Diphenylarsinic acid contaminated soil remediation by titanium dioxide (P25) photocatalysis: Degradation pathway, optimization of operating parameters and effects of soil properties

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HIGHLIGHTS

• DPAA was degraded into arsenate through TiO2 (P25) photocatalytic oxidation.
• Soil/water ratio was more influential on the removal of DPAA in soil by TiO2 (P25).
• Soil properties affected the adsorption of DPAA and the generation of OH• by TiO2.

GRAPHICAL ABSTRACT

Abstract

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ABSTRACT

Diphenylarsinic acid (DPAA) is formed during the leakage of arsenic chemical weapons in sites and poses a high risk to biota. However, remediation methods for DPAA contaminated soils are rare. Here, the photocatalytic oxidation (PCO) process by nano-sized titanium dioxide (TiO2) was applied to degrade DPAA in soil. The degradation pathway was firstly studied, and arsenate was identified as the final product. Then, an orthogonal array experimental design of L9(3)4, only 9 experiments were needed, instead of 81 experiments in a conventional one-factor-at-a-time, was used to optimize the operational parameters soil:water ratio, TiO2 dosage, irradiation time and light intensity to increase DPAA removal efficiency. Soil:water ratio was found to have a more significant effect on DPAA removal efficiency than other properties. The optimum conditions to treat 4 g soil with a DPAA concentration of 20 mg kg⁻¹ were found to be a 1:10 soil:water ratio, 40 mW cm⁻² light intensity, 5% TiO2 in soil, and a 3-hour irradiation time, with a removal efficiency of up to 82.7%. Furthermore, this method (except for a change in irradiation time from 3 to 1.5 h) was validated in nine different soils and the removal efficiencies ranged from 57.0 to 78.6%. Removal efficiencies were found to be negatively correlated with soil...
electrical conductivity, organic matter content, pH and total phosphorus content. Finally, coupled with electron spin resonance (ESR) measurement, these soil properties affected the generation of OH• by TiO₂ in soil slurry. This study suggests that TiO₂ photocatalytic oxidation is a promising treatment for removing DPAA from soil.

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1. Introduction

Diphenylarsinic acid (DPAA) is the hydrolytic or oxidative derivative of diphenylchloroarsine and diphenylycyanarsine, both of which were once used for the manufacture of arsenical chemical weapons (Daus et al., 2010). After World War II most of these chemicals were discarded and subsequently, due to leakage, have led to serious arsenic pollution in several parts of China (Wada et al., 2006), Japan (Hanaoka et al., 2005) and Europe (Daus et al., 2008; Hempel et al., 2009). DPAA has been detected as one of the main arsenic species in these contaminated sites (Ishizaki et al., 2005). DPAA has high neural and genetic toxicity (Ishii et al., 2004) and is difficult to be degraded under natural conditions (Hempel et al., 2009). Along with its high mobility (Maejima et al., 2011; Wang et al., 2013) DPAA poses a high risk to humans. In 2002 DPAA was reported to be the culprit in a serious arsenic poisoning accident in Kamisu, Japan, when local people drank underground water from a well near a deposit of arsenic chemical weapons (Hanaoka et al., 2006).

Hence, it is important to find an effective decontamination method for the rapid removal of DPAA from contaminated soils. A possible remediation method for DPAA contamination is to degrade the DPAA completely into inorganic arsenics and then to phytoextract the inorganic arsenic (Chong et al., 2010), allowing degradation to arsenate in TiO₂ solution and OH• plays a primary role in the PCO. Moreover, nanocrystalline TiO₂ can also work as an absorbent for the removal of inorganic/organic arsenics (Guan et al., 2012b). However, there is no related report on DPAA.

Recently TiO₂ PCO has also gained scientific interest for treating pollutants adsorbed onto soil surfaces. Two main methods are utilized. One method is to wash the soils contaminated by PAHs or PCBs with nonpolar solvents and then treat the solvent washings with TiO₂ PCO to eliminate the contaminants (Davezza et al., 2013). The other method is to add TiO₂ directly to the soil to degrade organic pollutants under UV irradiation (Zhang et al., 2008). The first method needs multiple treatments to remove contaminants completely. The second one is usually limited by the poor depth of light penetration into soils (Balmer et al., 2000).

The efficiency of photodegradation of organic pollutants by TiO₂ depends mainly on the adsorption capacity for the pollutant and the ROS quantum yield of the catalyst (Fujishima et al., 2000). The effects of common environmental conditions on the adsorption of arsénics onto TiO₂ surface have been studied a lot (Jiang et al., 2005; Xu et al., 2008) but studies on the influence of soil properties on the generation of ROS by TiO₂ are very rare. Ng et al. (2013) once reported the production of OH by TiO₂ was influenced by its stability in solution, and the stability of TiO₂ in soil slurries appeared to be correlated with soil properties (Fang et al., 2009). Thus, it can be inferred that the generation of ROS by TiO₂ in soil can also be affected by soil properties.

In the present study TiO₂ (P25) was used to directly degrade the DPAA adsorbed onto soil. Soil was transformed into slurry and stirred under high-pressure mercury lamp irradiation to break through the limitation of light penetration into the soil surface (Huang and Hong, 2000). The aims of the study were to understand the PCO pathway of DPAA by TiO₂, to optimize and validate an efficient remediation method for DPAA-contaminated soils which would be affected by irradiation time, TiO₂ dosage, irradiation intensity and soil:water ratio, and to elucidate the possible mechanism of DPAA degradation efficiency as affected by soil properties (soil electrical conductivity, soil pH, organic matters content, and phosphate content) and especially their effects on the generation of ROS by TiO₂.

2. Materials and methods

2.1. Reagents

DPAA (purity 97%) was purchased from Wako Company, Osaka, Japan. PAA (purity 99%) was provided by Aldrich Company, Shanghai, China. Nanocrystalline titanium dioxide (TiO₂, Degussa P25, a mixture of 80% anatase and 20% rutile with an average surface area of 50 m² g⁻¹, size 20–30 nm) was purchased from Degussa Company, Essen, Germany. Huminic acids (HA, Fluka no. 53680) was purchased from Sigma Aldrich, Inc. Milwaukee, WI, and its stock solution (−200 mg L⁻¹) was prepared according to Qu et al. (2012) procedure. High-performance liquid chromatography (HPLC) grade acetonitrile was acquired from Tedla Inc., Fairfield, OH. Ultrapure water (18.2 MΩ) was obtained using a Millipore-Milli Q system (Millipore Corporation, Billerica, MA) and was used to prepare all necessary solutions. Other chemical reagents were of analytical grade and used as received.

2.2. Preparation of soil and clay samples

The Ca-saturated smectite and hematite were purchased from Zhejiang Geology. Goethite and Al₂O₃·3H₂O were artificially synthesized (detailed in SI). All soil samples were obtained from the surface layer (0–10 cm depth) of soils collected from different Chinese provinces. They were air-dried and passed through a 0.25 mm sieve prior to use. Each soil was then artificially contaminated with DPAA at a level of 20 mg kg⁻¹. The detailed procedure was as follows. soil (10 g) was placed in a petri-dish, added with 5 mL DPAA stock solution (400 mg L⁻¹), and then the soil slurry was equilibrated for 2 d to allow the sorption of DPAA onto the soil particles. The soil slurry was vacuum freeze dried, grinded and passed through a 0.25 mm sieve, and mixed thoroughly with another 90 g soil.

2.3. Photocatalytic degradation of DPAA in TiO₂ slurry

All photocatalytic reactions were conducted in a merry-go-round photochemical reactor equipped with a 500 W high pressure mercury lamp at the room temperature (25°C). The light intensity was changed by adjusting the electrical current. Fifty-mL Pyrex glass tubes which can filter light with a wavelength < 300 nm were employed to contain the reaction solutions or soil slurries.
Thirty-mL dispersion containing 1000 mg L\(^{-1}\) TiO\(_2\) and 20 mg L\(^{-1}\) DPAA was prepared and magnetically stirred in the dark for 30 min prior to irradiation (30 min of stirring was sufficient to reach adsorption equilibrium). The dispersion was then transferred to the photochemical reactor and was stirred constantly during irradiation. The light intensity was 40 mW cm\(^{-2}\). Samples were withdrawn at different time intervals and filtered through a 0.22-μm membrane filter (Nylon, Anpel Scientific Instrument Co., Ltd., Shanghai, China) for subsequent analysis.

### 2.4. Optimization of the degradation method of DPAA by TiO\(_2\)

The degradation method was optimized using a multifactorial orthogonal experiment. Four parameters, namely soil/water ratio, TiO\(_2\) dosage, light intensity and irradiation time, were studied at three levels using an L\(_9\) (3\(^4\)) orthogonal array as shown in Table 1. In conventional one-factor-at-a-time design, the number of experiments required is 3\(^4\) = 81. However, using the orthogonal design the number of experiments can be reduced to 9 with a considerable saving of time and cost.

Three statistical coefficients (K, R and F-ratio) were used to evaluate the orthogonal data. In this study, K was the sum of the degradation efficiencies for each impact factor at each level, and was the average of K and used to determine the optimum combination of experimental conditions. The higher the k value the higher was the removal efficiency of the factor considered. The extreme difference R represented degree of the influence of various parameters on the removal efficiency. The larger the R value the more substantial influence was the corresponding factor on the removal efficiency. F-ratio was used to compare the critical F value, a statistic that can be found in most books on statistics and experimental design (Montgomery, 2001), so as to evaluate whether or not the impact factors were statistically significant. The F-ratio was calculated using the method previously described by Gonder et al. (2010).

An accurately weighed soil sample of 4.0 g (M\(_0\)) was placed in a Pyrex glass tube and mixed with a certain amount of TiO\(_2\) powder and pure water at a given volume (V\(_s\)). The whole mixture was then irradiated for a given period with a different light intensity. Multifactor orthogonal experiments were applied to optimize the degradation conditions and the soil tested was BA-1. The orthogonal arrays are detailed in Table 1. After irradiation the soil slurry was carefully transferred to a centrifuge tube and was centrifuged at 2000 rev min\(^{-1}\) for 15 min. The supernatant was collected to determine the concentration of DPAA (C\(_s\)). The residual soil was then extracted with 0.1 M Na\(_2\)HPO\(_4\) to determine the residual DPAA in soil (C\(_r\)). The degradation efficiency (Y) of DPAA was expressed according to the following equation:

\[
Y = \left(\frac{C_0 - (C_{Vs} + C_{rM_0})}{C_0M_0}\right) \times 100\%
\]

where \(C_0\) was the initial concentration of DPAA in prepared contaminated soil.

The optimal degradation method condition was also applied to nine different soils to study the effects of soil properties on the removal efficiency of DPAA.

### 2.5. ESR studies

The ESR study was conducted using mixed slurry of 0.2% (w/v) soil clays, 0.1% (g:mL) TiO\(_2\) powders and 0.1 M spin trapping agent 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, 97%, Sigma Aldrich) in various electrolytes as needed. One mL of the resulting slurry was then injected into a borosilicate glass capillary and irradiated with a 200 W mercury lamp for 1 min in the cavity of an ESR spectrometer (Bruker EMX 10/12, Germany) at room temperature. The changes in peak intensities of DMPO-adducts in ESR spectra were used to indicate changes in concentration of hydroxyl radicals according to Fang et al. (2013). The ESR settings were: modulation frequency 100 kHz, modulation amplitude 2.00 125 G, microwave frequency 9.40 GHz and power 5.10 mW.

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Fig. 1. Photocatalytic reaction kinetics of DPAA, PAA and inorganic As in P25-TiO\(_2\) slurry (IS = 1 mM NaNO\(_3\), pH = 4.5).
2.6. Analytical method

The concentration of DPAA was determined by HPLC (Shimadzu, Japan) equipped with a Shimadzu VP-ODS C18 column (4.6 × 150 mm, 5 μm). The mobile phase was 19% acetonitrile and 81% 0.02 mol L \(^{-1}\) in KH\(_2\)PO\(_4\) solution (pH 2.7). The detector wavelength was 220 nm. The minimum detection limit of DPAA was 0.1 mg L \(^{-1}\) and the recovery was 95.9%. The concentration of PAA was determined using a Thermo Fisher TSQ Quantum Access MAX triple stage quadrupole mass spectrometer equipped with an Ion Max™ source with Negative HESI mode. Mass spectrometry detection was performed under the selective reaction monitoring (SRM) mode. A SunFire C18 column (4.6 × 250 mm, 5 μm, Waters Corp., Milford, MA) was used. The mobile phase was 19% acetonitrile and 81% acetic acid solution (0.1%, pH = 2.7) at a flow rate of 0.8 mL min \(^{-1}\). The minimum detection limit of PAA was 0.1 mg L \(^{-1}\) and the recovery was 104.1%. Main organic arsenical intermediates were identified with an LCQ Fleet ion-trap spectrometer (Thermo Fisher Scientific, Waltham, MA) operated in negative-ion mode. The chromatographic conditions were the same as those employed for PAA determination. The inorganic arsenics were analyzed by LC-ICP-MS (Williams et al., 2007; Wu et al., 2011).

3. Results and discussion

3.1. Photodegradation of DPAA in TiO\(_2\) slurry and possible degradation pathways

The P25-TiO\(_2\) photocatalytical oxidation of DPAA was studied to investigate the main end-products and possible reaction pathway. As shown in Fig. 1, DPAA was reduced from the initial concentration of 5.72 mg As L \(^{-1}\) to 0.41 mg As L \(^{-1}\) during 90 min irradiation. The arsenate concentration increased to 0.98 mg As L \(^{-1}\) and PAA was also formed in solution but its concentration at the end was only 0.14 mg As L \(^{-1}\). In control experiments there were no obvious losses of DPAA in the absence of TiO\(_2\). The 20% decrease of DPAA concentration in the TiO\(_2\) slurry without light irradiation was due to the adsorption of DPAA onto the TiO\(_2\) surfaces and the amount adsorbed was reported as (2896.1 ± 96.2) mg kg \(^{-1}\) (Wang et al., 2014), indicating that the TiO\(_2\) efficiently absorbed DPAA just as it did for other arsenics (Guan et al., 2012b).

Intermediates other than inorganic arsenics and PAA were also identified to elucidate the possible reaction pathways involved in the photocatalytic degradation of DPAA. The ion chromatography and mass
PAA, monohydroxylated and dihydroxylated DPAA, respectively. The possible degradation pathway is proposed in Fig. 2. During the photocatalytic degradation of DPAA, TiO₂ absorbed UV light to generate electron–hole pairs (Hong et al., 1998). Then OH⁻ could add on the aromatic group or break the As–C bond and inorganic arsenics, PAA and hydroquinone were ultimately evolved via different oxidation steps.

On the basis outlined above, TiO₂ (P25) cannot completely convert PAA into inorganic arsenics but can adsorb DPAA and its final arsenical products, all which suggests that TiO₂ can be used as a useful material for treating DPAA pollution.

3.2. Optimization of the photocatalytic degradation method for DPAA contaminated soil

As shown in Table 2, the results showed that the highest k value for each factor was at the second level for irradiation time (3 h) and the third level for the other three factors (soil:water ratio = 1:5, TiO₂ dosage = 5%, light intensity = 40 mW cm⁻²). The regression coefficient R ranged from large to small as follows: soil: water ratio > light intensity > irradiation time > dosage of TiO₂. Therefore the optimum combination might be A₃B₃C₂D₂. The F-ratio was used in the variance test to evaluate whether or not the impact factors were statistically significant. According to the variance test, all four impact factors significantly influenced the removal efficiency of DPAA in soil slurry at the 99% confidence level.

Increasing the volume of water promoted removal efficiency more effectively than the other factors, perhaps because adding more water diluted the whole reaction system, thus promoting the penetration of UV light so as to increase TiO₂ adsorption of UV light and thereby increase degradation efficiency. The photo-reaction depends mainly on the number of photons adsorbed (Konstantinou and Albanis, 2004) and the high light intensity can supply sufficient protons to make better use of the photocatalytic ability of TiO₂. However, due to the large amounts of organic matter (OM) in soils, many of the TiO₂ particles would be embedded by OM (Yang et al., 2009) or the generated OH⁻ can also be consumed by OM (Bachman and Patterson, 1999), resulting in an increase in the dosage of TiO₂ having little effect on the removal efficiency of DPAA. Basically, most of the photocatalytic reactions can be fitted by first-order reaction kinetics (Xu et al., 2007a), thus the initial

### Table 2

<table>
<thead>
<tr>
<th>A (Soil/water ratio)</th>
<th>B (TiO₂ dosage)</th>
<th>C (Light intensity)</th>
<th>D (Irradiation time)</th>
<th>Degradation efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(g/v (mL)) %</td>
<td>(%)</td>
<td>mW cm⁻²</td>
<td>hours</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1%</td>
<td>1.6</td>
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<td>24.5%</td>
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<tr>
<td>2</td>
<td>1%</td>
<td>3 h</td>
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<tr>
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<td>6 h</td>
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</tr>
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<td>1.5 h</td>
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</tr>
<tr>
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<td>3 h</td>
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</tr>
<tr>
<td>7</td>
<td>1%</td>
<td>40 h</td>
<td>53.6%</td>
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</tr>
<tr>
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<td>3 h</td>
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</tr>
<tr>
<td>9</td>
<td>5%</td>
<td>1.5 h</td>
<td>38.1%</td>
<td></td>
</tr>
</tbody>
</table>

K1: 82.9 99.3 87.4 85.0 1% 2% 40 h 1.5 h 38.1%
K2: 69.3 81.2 80.9 100.9 1% 2% 40 h 3 h 25.7%
K3: 128.9 100.6 112.8 95.2 1% 2% 40 h 3 h 25.7%
k1: 27.6 33.1 29.1 28.3 1% 2% 40 h 3 h 25.7%
k2: 23.1 27.1 27.0 33.6 1% 2% 40 h 3 h 25.7%
k3: 43.0 33.5 37.6 31.7 1% 2% 40 h 3 h 25.7%
R: 19.9 6.4 10.6 5.3 1% 2% 40 h 3 h 25.7%
Optimum level: A₃B₃C₂D₂

### Table 3

| Soil | Electrical conductivity | pH | SOM g kg⁻¹ | CEC cmol kg⁻¹ | Total P mg | Total Fe g | Total Al g | FeOx⁺ g kg⁻¹ | Fe₃⁺ g kg⁻¹ | AlOx⁺ g kg⁻¹ | Al₃⁺ g kg⁻¹ | Classification |
|------|------------------------|----|------------|----------------|------------|------------|------------|---------------|--------------|--------------|--------------|--------------|----------------|
| BA-1 | 85                     | 6.85 | 25.81 | 53.38 | 32.78 | 68.18 | 3.69 | 10.31 | 1.51 | 3.61 | Phaeozems |
| HBB-1 | 115                    | 6.87 | 35.32 | 26.18 | 806.7 | 26.93 | 66.51 | 0.78 | 7.75 | 1.26 | 3.55 | Phaeozems |
| QQ-3  | 133                    | 6.27 | 21.02 | 13.3 | 1335 | 28.65 | 52.23 | 1.24 | 9.94 | 0.7 | 2.09 | Luvisols |
| QQ-2  | 47                     | 5.19 | 11.55 | 18.98 | 477.8 | 35.6 | 62.97 | 0.57 | 16.68 | 0.88 | 3.68 | Luvisols |
| QQ-1  | 106                    | 6.63 | 25.35 | 14.41 | 443.9 | 23 | 49.47 | 2.01 | 19.62 | 1.37 | 4.46 | Luvisols |
| QQ-0  | 71                     | 5.38 | 9.76 | 17.36 | 329 | 41.61 | 71.34 | 3.48 | 11.89 | 0.74 | 2.51 | Luvisols |
| Y-11  | 32                     | 5.01 | 5.47 | 8.76 | 226.5 | 14.09 | 28.63 | 0.87 | 8.67 | 0.73 | 3.66 | Acrisols |
| Y-17  | 52                     | 6.23 | 15.7 | 11.57 | 883.8 | 42.09 | 79.64 | 1.66 | 30.71 | 1.53 | 7.29 | Acrisols |

### Text Table

<table>
<thead>
<tr>
<th>Texture (v/v) %</th>
<th>Clay (-2 μm)</th>
<th>Silt (2–20 μm)</th>
<th>Sand (20–2000 μm)</th>
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<td>59.9</td>
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<td>72.92</td>
</tr>
</tbody>
</table>

*a* FeOx and AlOx mean amorphous Fe and Al extracted by acidified ammonium oxalate buffer.

*b* FeOx and AlOx mean Citrate-Dithionite (CD) extractable Fe and Al.
reaction rate was more rapid than at later stages of the reaction. Thus, the irradiation time also had little influence on removal efficiency.

The optimization degradation method A3B3C3D2 could lead to a removal efficiency of 64.8% of DPAA in BA-1. Considering the soil:water ratio had a more significant impact on removal efficiency, the soil:water ratio was changed to 1:10 and then the removal efficiency increased to 82.7%, degrading most part of the DPAA in BA-1 soil.

3.3. Effects of soil properties on the removal efficiency of DPAA by TiO2 PCO

3.3.1. Removal efficiencies of DPAA in various soils by TiO2 photocatalytical oxidation

The optimum remediation method A3B3C3D2 was also validated in different soils which were typical of the regions subject to DPAA contamination in China (Tu, 2011). The soil properties are summarized in Table 3. In the study, the irradiation time was reduced to 1.5 h for better elucidating the effects of various soils on the degradation efficiency because the DPAA in some Acrisols and Luvisols soils was undetected after 3 h of irradiation in preliminary study. As shown in Table 3 the photodegradation efficiency in 9 soils varied, ranging from 57.0 to 78.6%, with the lowest removal efficiency found in soil HRB-1, and when the irradiation time was increased to 3 h the removal efficiency in this soil also increased to 68.7%. This optimum remediation method could be used widely in other soil types.

Correlation analysis was performed to define the relationship between degradation efficiency and soil properties and the results show that degradation efficiency was significantly negatively related to soil electrical conductivity, organic matter content, pH value and total

| Table 4 | Correlation coefficients between soil properties and degradation efficiency. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Electrical conductivity | pH | SOM | CEC | Fe_{tot} | Total Fe | Al_{tot} | Al_{oct} | Total Al | Total P |
| Degradation efficiency | −0.931 ** | −0.705 * | −0.839 ** | −0.326 | 0.161 | 0.420 | 0.345 | 0.156 | 0.411 | 0.191 | −0.700 * |

* p < 0.05.
** p < 0.01.

![ESR spectra of samples a-o](image)

Fig. 3. ESR spectra of samples a–o. If needed the tested slurry contained TiO2 and hematite, pH 5.5, IS = 1 mM Na2SO4. Irradiation time was 1 min.
phosphorus (Table 4). This result can be attributed to the effects of these parameters on the adsorption of DPAA onto TiO₂ particles. Our previous research has shown the amounts of DPAA adsorbed by absorbent declined with increasing pH value or competing adsorbates (e.g. dissolved organic materials (DOM), phosphorus) (Wang et al., 2013). Thus, it can be inferred that increasing pH value and contents of DOM and phosphorus inhibited the adsorption of DPAA by TiO₂ particles. In addition, the ionic strength (I) of soils can be calculated from the simple linear equation of ionic strength and electrical conductivity (EC) (Fang et al., 2009): I = 0.0127 × EC. Thus, the higher EC indicates the higher ionic strength which can accelerate the agglomeration of TiO₂ particles, reduce their surface active sites for DPAA adsorption, and then decreased the absorption of DPAA by TiO₂ (von der Kammer et al., 2010). In summary, some selected soil properties (pH, EC or I, content of DOM and phosphorus) can affect the removal efficiency of DPAA by TiO₂ PCO by controlling the adsorption of DPAA onto TiO₂ particles.

3.3.2. Effect of soil properties on generation of OH· by TiO₂–ESR evidences

Here, the effects of soil properties on the generation of OH· by TiO₂ were also studied and the results show that these soil properties (listed above) can also influence the generation of OH· by TiO₂.

As shown in Fig. 3, firstly, in acid (pH 3.0, Fig. 3f) or alkaline (pH 9.0, Fig. 3g) conditions the OH· intensities in the soil clay (hematite) and TiO₂ mixture were lower than those at pH 5.5 (Fig. 3b). The pH values of the tested soils ranged from 4.5 to 6.8 and it could be inferred in this study soil pH could inhibit the generation efficiency of OH· by TiO₂ as it did on the adsorption of DPAA by TiO₂. Furthermore, the OH· intensity was amplified markedly by ionic strength (SO₄²⁻) increasing (Fig. 3j–l). However, as mentioned above, the removal efficiency of DPAA by TiO₂ in soil was inhibited by increasing ionic strength. This suggests that the removal efficiency of DPAA was affected more by the promotion of ionic strength on the adsorption of DPAA by TiO₂ than the promotion of ionic strength on OH· generation. In addition, under the same total ionic strength, PO₄³⁻ lowered the OH· intensity slightly, but did not enhance the inhibition by increasing phosphate concentration (Fig. 3h,i). This also indicates the negative effect of PO₄³⁻ contents on the degradation efficiency of DPAA depended more on the competition of PO₄³⁻ with DPAA for adsorption sites on TiO₂ particles than the effect of PO₄³⁻ on OH· generation. Lastly, DOM was found to enhance the OH· intensity at a lower concentration (4 mg L⁻¹) (Fig. 3m) but inhibited the generation of OH· gradually as its concentration increased (Fig. 3n,o). This result could be explained that DOM acted as both a photo-sensitizer of TiO₂ at low concentration (Styliani et al., 2004) and a scavenger of OH· at high concentration. This suggests that DOM can suppress the removal of DPAA by TiO₂ by prohibiting the adsorption of DPAA on TiO₂ particles and the generation of OH· by TiO₂.

The effects of selected soil properties on the generation of OH· by TiO₂ could be attributed to the charge transferring from the excited TiO₂ to soil clays, which was induced by the electrostatic interaction between the soil clays and TiO₂ particles in various solutes (Zhou et al., 2012) (the mechanism was detailed in SI).

In conclusion, soil pH, ionic strength (or electrical conductivity), and the contents of phosphorus and DOM can influence the removal efficiency of DPAA by affecting both the generation of OH· by TiO₂ and the adsorption of DPAA onto TiO₂ particles, and the former may be less important than the latter in deciding the degradation efficiency of DPAA in soils by TiO₂ PCO.

4. Conclusions

More than 90% of DPAA was degraded in TiO₂ slurry under UV irradiation and arsenate was found to be the main end-product. Photodegradation experiments in soil showed this remediation method by TiO₂ could also obtain satisfactory removal efficiency which was affected by both manipulating external factors and soil properties. Soil:water ratio was found to have the largest impact on the degradation efficiency perhaps due to dilution of the soil slurry and enhancement of light penetration. Removal efficiency showed negative relationships with soil pH, ionic strength, organic matter content, total phosphorus, all of which could affect the amounts of DPAA adsorbed onto TiO₂ particles and the generation of OH· by TiO₂. The ecological toxicity and the recycling of the soil after photocatalytic treatment must be monitored in future studies. It is also worth being mentioned, soils amended with nanocrystalline TiO₂ can be regarded as Technosols (Yao et al., 2009) with high surface areas, and could be used as adsorbents for heavy metal immobilization in contaminated fields or wastewater treatment. This hypothesis is worth of study for recycling these treated soils.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.09.023.

References


