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Periodate activation by concurrent utilization of UV and US for the degradation of para-nitrophenol in water: A synergistic approach

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Abstract−Para-nitrophenol (PNP) is a toxic compound widely used in various industries. The release of PNP into the environment not only threatens human health but the ecosystem. Hence, the treatment of contaminated water is necessary. Periodate (PI) is a new oxidant which is used for the generation of free radicals. In the current work, PI was concurrently activated by ultraviolet (UV) and ultrasound (US) to eliminate PNP from aqueous solution. The effects of operating parameters were studied and complete degradation of PNP was obtained in 30 min. The presence of ferrous ions increased the PNP degradation rate. Scavenging experiments confirmed that $HO^{\bullet}$ and $IO_3^{\bullet}$ were corresponding agents of the PNP degradation, which the latter had a bold role. The performance of PI/UV/US was examined on real wastewater and the results showed that 70% of total phenol was removed during 60 min. The PNP degradation intermediate was recognized and a pathway of PNP degradation was proposed. Although PI/UV/US process is high energy consuming, its excellent performance can be a rational reason for the scaling up the process.

Keywords: Periodate, 4-Nitrophenol, Advanced Oxidation Processes, Wastewater, Mineralization

INTRODUCTION

Water pollution is a major challenge for all countries. Water pollutants include various organic and inorganic contaminants originating from industrial and agricultural activity. Among organic pollutants, nitrophenols (NPs) have been widely used for production of products such as dyes, drug, herbicides, and fungicides [1]. NPs are stable and very soluble in water and the existence of the nitro group (-NO_2) on phenolic ring makes it more resistant to decomposition. Para-nitrophenol (PNP) has been extensively applied to synthesize drugs and explosive compounds [2]. PNP is an intermediate in the synthesis of acetaminophen which has been broadly produced in the world. The release of their wastewaters results in water pollution and consequently adverse human health effects. PNP as a hazardous substance, is a mutagenic and carcinogenic compound, which has been known as a priority pollutant [3]. PNP is a toxic compound with LD50 of 202 mg/kg and 21.9 mg/kg for rat and fish, respectively [4]. PNP has high solubility in the water (16,000 mg/L at 25 °C) and also is known as an inhibitor of nitrifying bacteria [5].

To remediate organic pollutants such as PNP, several biological and chemical processes have been utilized in recent years, but they have some limitations, such as high cost, pH dependency, low removal efficiencies, long treatment times, production of secondary pollutants, sensitivity to temperature and low mineralization [6]. In the past three decades, advanced oxidation processes (AOPs) have gained attention as effective methods for the degradation of organic pollutants through the production of reactive species such as hydroxyl radicals (E^0=2.8 V) [7,8]. H_2O_2, persulfate (peroxymonosulfate (PMS) and peroxydisulfate (PDS)) and O_3 are classical oxidants which have been extensively used for the production of hydroxyl radicals. Fenton oxidation ($H_2O_2+Fe^{2+}$) [9], UV/H_2O_2 [10], O_3, UV/O_3 [11], catalytic ozonation [11,12], PMS/PDS/Fe^{2+} [13,14] and peroxone processes [15,16] are examples of classical AOPs. The use of other reactive species has been developing for few years. Chlorine radicals ($Cl^{\bullet}$, $Cl_2^{\bullet-}$, $ClO^{\bullet}$), singlet oxygen ($^1O_2$), carbonate radicals ($CO_3^{\bullet-}$) and organic radicals ($R^{\bullet}$) are applied for the treatment of contaminated water [13]. These radicals are produced by the activation of peroxides or halides such as chlorine, peracetic acid and percarbonate. Periodate (IO_4^-, PI), with moderate redox potential (E^0=1.6 V), is another peroxide used to produce reactive species such as $HO^{\bullet}$,

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periodyl radicals ($IO_3^{\bullet}$), superoxide anions ($O_2^{\bullet -}$), singlet oxygen ($^1O_2$) and triplet oxygen ($O(^3P)$) [17]. PI is a soluble oxidant with molecular weight of 213.89 g/mol. The average I-O bond distance of PI is 1.775 Å. Although some studies have indicated that H_2O_2 and ozone may be generated during PI activation, very low amount of them ignores their contribution to the degradation of organic pollutants [18].

To activate PI, different methods have been proposed, including transition metals [19,20], ultraviolet (UV) [17], heat, ultrasound (US) [21] and carbon catalyst [22]. In recent years, UV have been widely used for PI activation. UV irradiation can break down I-O bond of PI and generate atomic oxygen and periodate radicals. UV is probably the most popular method for PI activation in which the degradation of various pollutants has been examined by UV/PI process [23,24].

$$IO_4^- + UV \rightarrow IO_3^{\bullet} + O^{\bullet -} \qquad k=(0.5-4.16)\times 10^{-3}\ s^{-1} \tag{1}$$

$$IO_4^- + UV \rightarrow IO_3^- + O(3P) \qquad k=(1-2)\times 10^{-4}\ s^{-1} \tag{2}$$

$$O^{\bullet -} + H^+ \rightarrow HO^{\bullet} \tag{3}$$

$$O^{\bullet -} + H_2O \rightarrow HO^{\bullet} + OH^- \qquad k=1\times 10^8\ M^{-1}\ s^{-1} \quad pKa=11.9 \tag{4}$$

$$O(3P) + O_2 \rightarrow O_3 \qquad k=4\times 10^9\ M^{-1}\ s^{-1} \tag{5}$$

Some researchers investigated the degradation of dye using UV/PI and determined the reactive species produced during the process [18,25]. Another method activation is US waves which has been rarely used for PI activation. US as well as UV irradiation is an effective method for the decomposition of PI into free radicals. Previous works have shown that simultaneous use of UV and US enhances the activation process for peroxymonosulfate and percarbonate oxidants [26]. The presence of UV and US probably enhances the activation rate of PI. According to what we know, the simultaneous use of UV and US has not been used for PI activation so far. This work is the first study about co-activation of PI via UV and US irradiation for the degradation of PNP. In this work, the effect of influential parameters (pH and PI dosage) was investigated. The contribution of reactive species was studied by specific probes. The impact of conventional anions and humic acids was studied on PNP degradation. The performance of PI was compared with PDS and hydrogen peroxide, and the mineralization degree was evaluated by total organic carbon (TOC). PI/UV/US process was assessed on a real wastewater and the by-products of the PNP degradation was also determined.

MATERIALS AND METHODS

1. Chemical and Reagents

Sodium periodate ($NaIO_4^-$, 99.8%) was purchased from Samchun Company. PNP ($C_6H_5NO_3$, 99%) was supplied from Merck. Sodium chloride (NaCl, >99%), sodium bicarbonate ($NaHCO_3$, >99%), potassium nitrate (KNO_3, >99%), sodium sulfate (Na_2SO_4, 99%) and ferrous sulfate ($FeSO_4$) were supplied from Chem-Lab company. Hydrogen peroxide (30%), sodium persulfate ($Na_2S_2O_8$, 99.9%), sodium hydroxide (NaOH, 99%) and sulfuric acid (98%) were obtained from Merck. Methylene Blue (MB), Bisphenol A (BPA) and Ciprofloxacin (CIP) were purchased from Sazehmorakab, Alfa Aesar and Sigma Aldrich, respectively. 1,4-Benzoquinone (98%), 2-Propanol. anhydrous (99.5%), furfuryl alcohol (FFA) were purchased from Acros-organic Company. Ethanol (EtOH, C_2H_5OH) and *tert*-butyl alcohol (TBA, $C_4H_{10}O$) were provided from Razi Company. A real petrochemical wastewater was collected from a manufacturer in the Mahshahr city (Iran). All samples were filtered to remove suspended solids. The characteristics of the sample are presented in Table S1.

2. PI/UV/US Set Up

The photo-reactor was a quartz cylinder (6.5 cm diameter×15.7 cm height). A certain volume (300 mL) of PNP solution (0.3 mM, constant in all the experiments) was introduced into the reactor. The solution pH was regulated by H_2SO_4 and NaOH (0.1 M). Ultrasound was applied by a Q125 ultrasonic generator (100 W, 20 kHz) equipped with a probe transducer. The probe was submerged in the solution (25 mm under the water surface). Two UVC lamps (4 W, 253.7 nm) were utilized as source of UVC. UVC lamps were vertically located out of the reactor. The distance of UVC lamp and a quartz cylinder was 20 mm. The temperature of solution was 26±2 °C. A specified amount of periodate was spilled to the solution and the PNP solution was commingled by a magnetic stirrer. When UV lamps and ultrasound generators were turned on, the sono-photo-degradation of PNP process was started. The sampling was done at preselected reaction intervals and the samples were quenched by concentrated nitrite ions. The intensity of UVC in the reactor (center) was measured as 1.24 mW/cm^2. To assess the presence of iron species, Fe(II) and Fe(III) were added to the reactor as PI/UV/US/Fe process. To evaluate reactive species, several quenching agents were added to the solution to determine the contribution of each oxidative agent.

3. Analytical Methods

The PNP concentration was measured by a Waters high pressure liquid chromatograph (HPLC) equipped with UV detector. A C-18 column was applied for separation and 20 µL was used as the injection volume with the flow rate of 1.0 mL/min. The wavelength of 320 nm was used and mobile phase was acetonitrile and water (50 : 50). Total organic carbon (TOC) was measured by TOC analyzer (Shimadzu). Chemical oxygen demand (COD) and total phenol (TP) were measured based on standard methods. COD was determined based on colorimetric method (5220), while 4-aminoantipyrine method (5530 D.) was utilized for TP. To determine the possible degradation intermediates, the sample was analyzed using a Waters Alliance 2695 HPLC-Micromass Quattro micro API mass spectrometer. An Atlantis T3-C18 column (3 µm particle size, 2.1× 150 mm) was used to separate the sample at 27 °C. The injection volume of the sample was 15 µL. The mobile phase was acetonitrile (0.1% formic acid) and water (0.1% formic acid) with a ratio of 60 : 40. 0.2 mL/min was set for the flow rate of mobile phase. The temperature of 35 °C was selected for the column.

RESULTS AND DISCUSSION

1. PI/UV/US Evaluation and Synergistic Effect

Fig. 1(a) demonstrates PNP degradation via different methods. UV, PI and US as individual processes were ineffectual for PNP degradation with less than 5% removal efficiency. Several studies

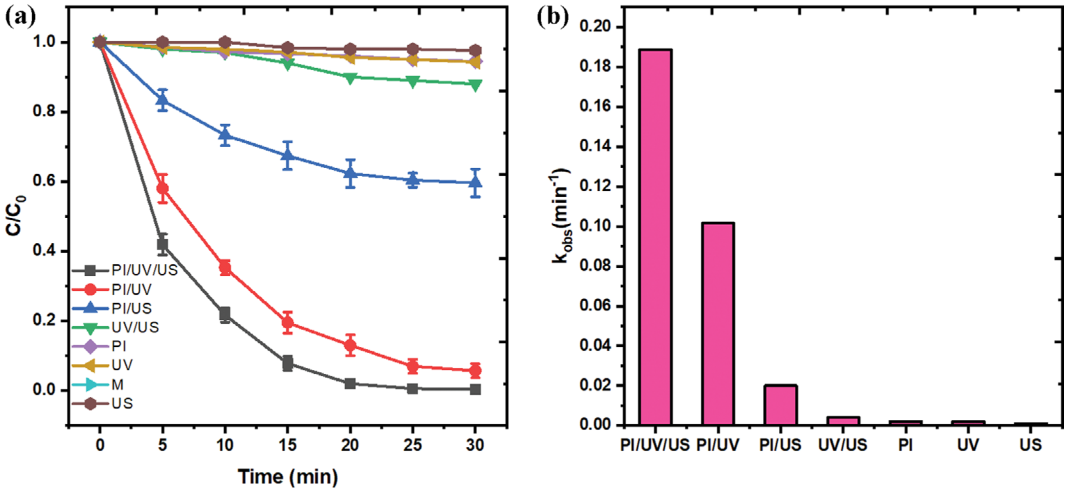

Fig. 1. (a) The PNP degradation using various methods, (b) the rate constants of PNP degradation by various methods (PI=2 mM and pH=3).

have shown that the sole utilization of US, UV and PI cannot produce the reactive species such as hydroxyl radicals for the degradation of organic compounds. Binary system of UV/US was also ineffective for the PNP degradation with 12% removal efficiency. The absence of an oxidant is the main reason for weak degradation of PNP. PI/US could degrade around 40% of PNP during 30 min reaction time. US as high energy input is able to decompose the PI to $IO_3^{\bullet -}$ and $O^{\bullet -}$ directly. Moreover, US can produce hydrogen radical as a strong reductant. Hydrogen radical can decompose the periodate ions to hydroxyl radicals and periodate radicals according to the following equations.

$$H_2O+)))\rightarrow H^{\bullet}+OH^{\bullet} \tag{6}$$

$$IO_4^-+H^{\bullet}\rightarrow IO_3^{\bullet}+HO^- \tag{7}$$

$$IO_4^-+H^{\bullet}\rightarrow IO_3^-+OH^{\bullet} \tag{8}$$

PI/UV process indicates high efficiency for the PNP degradation (95%) during 30 min reaction time. Compared to US as activator, UV had high performance for PI activation. This is due to the high energy of photons for the destruction of O-I bond. PI can be rapidly decomposed by UV irradiation; Bendjama et al. reported that 80% of PI was decomposed in only 7 min [18]. Simultaneous application of UV and US enhanced the PNP degradation rate significantly. Around 100% of PNP was degraded during 30 min reaction time. UV and US could increasingly affect the PNP degradation through enhanced activation of PI. In fact, the enhanced activation of PI via UV and US generates additional free radicals to remove PNP. To demonstrate the degradation rate of PNP using different methods, the pseudo-first order ($\ln(C_0/C)=k_{obs}t$) was applied for the determination of the rate constants (k_{obs}). Fig. 1(b) shows the rate constants of the PNP degradation by various methods. As mentioned, PI/UV/US process showed the highest rate constant (0.189 min^{-1}) while PI/UV and PI/US had the rate constant of 0.101 and 0.02 min^{-1}, respectively. Sole applications of PI, UV and US were ineffective and their rate constants were negligible. To determine the synergistic index (SI) of PI/UV/US, the ratio of rate constant of the ternary process to sum of each component was calculated (Eq. (9)). This value to be more than 1 demonstrates that there is a synergy during PI activation and PNP degradation consequently. The SI obtained from Eq. (9) was 1.58, indicating that there was a synergistic effect on the PNP degradation in PI/UV/US process.

$$SI=\frac{\mathrm{kPI/UV/US}}{\begin{array}{l}(\mathrm{kPI+kUV+kUS})+[(\mathrm{kPI/UV-kPI-KUV})\\ +(\mathrm{kPI/US-kPI-kUS})+(\mathrm{kUV/US-kUV-kUS})]\end{array}} \tag{9}$$

2. The Effect of Solution pH and PI Dosage

The solution pH is a critical variable in advanced oxidation affecting the reactive species and oxidant. Fig. 2(a) shows PNP degradation by PI/UV/US process in different pH values. As can be seen, the PNP degradation was at an acceptable level at all conditions. The highest efficiency took place at pH=3 with 96% PNP removal efficiency. With increase in the solution pH a slight decrement was seen at the PNP degradation. Long et al. reported a significant reduction in the removal efficiency at neutral and alkaline conditions [27]. Note that IO_4^- is the dominant species at pH<8, which is easily decomposed into free radicals [28]. Fig. 2(b) shows the rate constants of the PNP degradation at various pHs. A linear reduction in the rate constant at pH 3-7 was seen in this figure while the rate constant of pH=9 was similar to pH=7.

The effect of PI dosage was studied on the PNP degradation in the range of 0.25-4.0 mM (Fig. 3(a)). As can be seen, the PNP was dramatically degraded with increase of PI dosage from 0.25 to 2 mM. In this manner, the PNP degradation was 73.5, 80.5, 94.3, 99.6 and 91.4% at PI dosage of 0.25, 0.5, 1.0, 2.0 and 4.0 mM, respectively. Commonly, the increase of PI dosage improves the amount of free radicals and enhances the degradation of organic pollutants. However, in the PI dosage of more than optimum condition (2 mM), a decrease in the removal efficiency of PNP was clearly observed at PI of 4 mM. Excessive PI concentration may have a negative effect on the degradation process in which a recombination of reactive species may take place in the solution (Eqs. (10)-(13)) [23,29]. In fact, the reactive species react with themselves and produce some weaker oxidative agents. Moreover, when US is used, there is a pos-

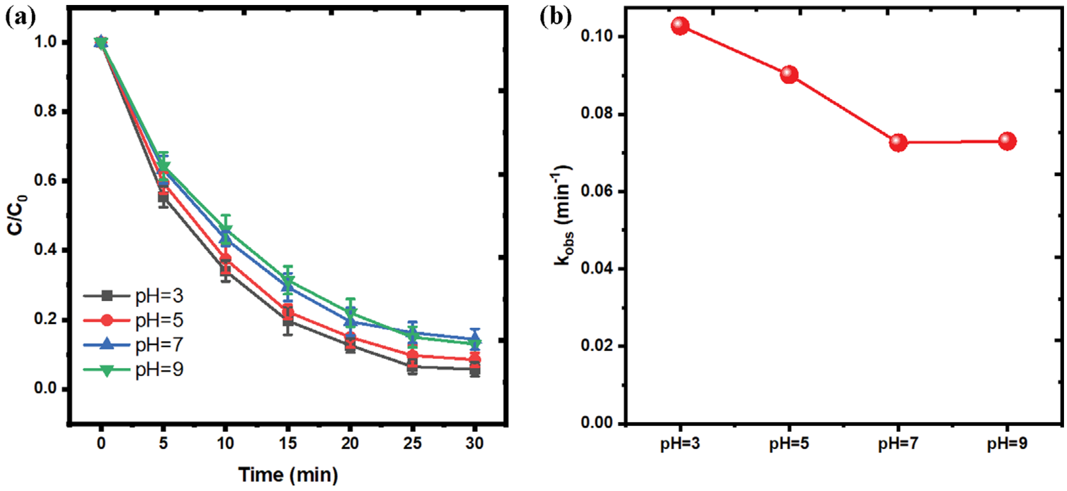

Fig. 2. **(a) The PNP degradation by PI/UV/US process at different pH values, (b) the rate constants of the PNP degradation by PI/UV/US process at different pH values (PI=1 mM and PNP=0.3 mM).**

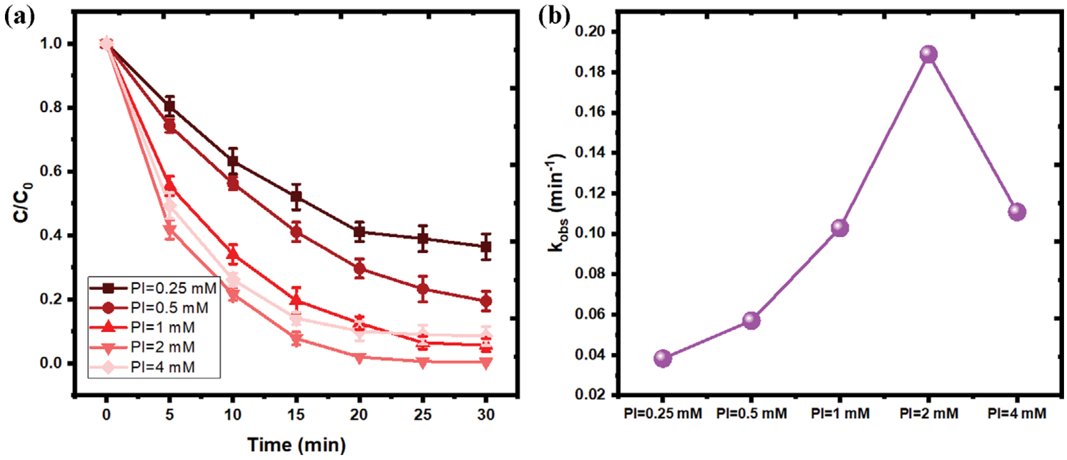

Fig. 3. **(a) The PNP degradation by PI/UV/US process at different PI concentrations, (b) the rate constants of the PNP degradation by PI/UV/US process at different PI concentrations (pH=3 and PNP=0.3 mM).**

sible reaction at high concentration of periodyl radicals in which $IO_3^{\bullet-}$ and $H^{\bullet}$ quench each other to produce IO_3^{-} and hydrogen ions (Eq. (14)) [19].

$$OH^{\bullet}+OH^{\bullet}\rightarrow H_2O_2 \qquad k=5\times10^{9}\ M^{-1}\ s^{-1} \tag{10}$$

$$IO_3^{\bullet}+IO_3^{\bullet}\rightarrow I_2O_6 \qquad k=(4.5-7)\times10^{8}\ M^{-1}\ s^{-1} \tag{11}$$

$$IO_4^{\bullet}+IO_4^{\bullet}\rightarrow I_2O_8 \qquad k=4.68\times10^{8}\ M^{-1}\ s^{-1} \tag{12}$$

$$O(3P)+O(3P)\rightarrow O_2 \tag{13}$$

$$IO_3^{\bullet}+H^{\bullet}\rightarrow IO_3^{-}+H^{+} \tag{14}$$

Fig. 3(b) displays the rate constants of PNP degradation via sonophoto-activation of PI. A negative effect of excess dosage of PI is obviously shown in this figure in which the rate constant was reduced from 0.189 min^{-1} to 0.11 min^{-1}. These results are in agreement with other studies [24,25].

3. The Determination of Reactive Species

To determine the reactive species in PI-based process, quenching experiments were conducted by different chemical probes. Several oxidative agents may contribute to the degradation of organic pollutants. Fig. 4(a) shows the PNP degradation in the presence of various chemical probes. FFA (k(FFA/$^1O_2$)=1.2×10^8 M^{-1} s^{-1}) [30] and BQ (k(BQ/$O_2^{\bullet-}$)=10^9 M^{-1} s^{-1}) are specific scavengers for singlet oxygen and superoxide anions, respectively. As can be seen, FFA and BQ did not affect the PNP degradation, indicating that singlet oxygen and superoxide anion are inoperative species in the degradation of PNP. TBA and 2-propanol are able to scavenge $HO^{\bullet}$ (k=1.2×10^8 M^{-1} s^{-1}) and $HO^{\bullet}$/O(3P) (k=1.9×10^9 M^{-1} s^{-1} for $HO^{\bullet}$ and k=0.96×10^8 M^{-1} s^{-1} for O(3P)) respectively [18,24,28]. As shown in this figure, no inhibitory effect was observed in the presence of 2-propanol, while TBA had a slight inhibitory effect, indicating that hydroxyl radicals have a minor role in the degradation of PNP. Phenol exhibited a high reactivity by $IO_3^{\bullet-}$ and hydroxyl radicals [18,31]. As can be seen, there is a strong inhibitory in the presence of phenol at various concentration, indicating that $IO_3^{\bullet-}$ has the major role in the degradation of PNP. To confirm this, IO_3^{-} was monitored during 30 min reaction time (Fig. 4(b)). IO_3^{-} concentration was increased during 30 min reaction time and it

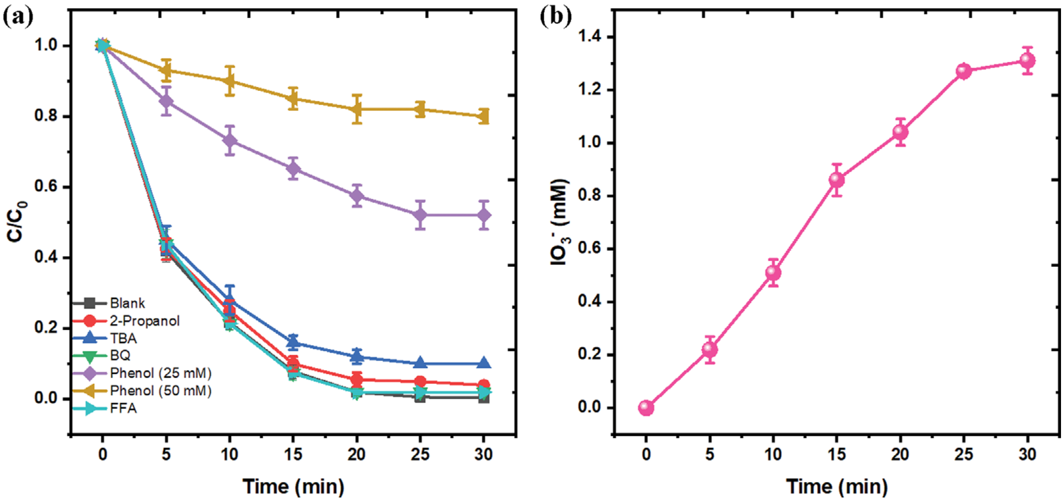

Fig. 4. (a) the PNP degradation by PI/UV/US in the presence of different chemical probes, (b) IO_3^- generation in PI/UV/US process (PI=2 mM, pH=3, PNP=0.3 mM, FFA and BQ=20 mM, TBA=50 mM).

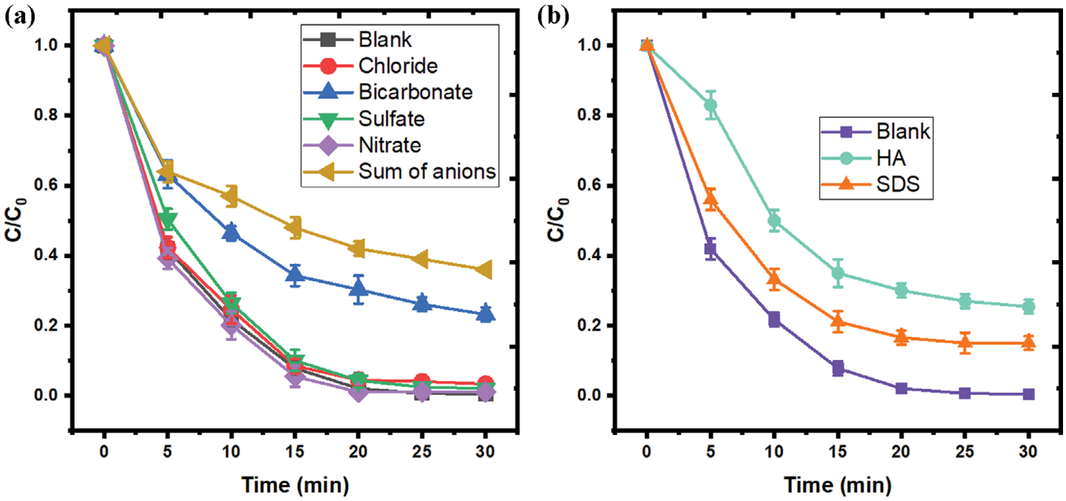

Fig. 5. (a) PNP degradation by PI/UV/US in the presence of different anions, (b) the PNP degradation by PI/UV/US in the presence of HA and SDS (PI=2 mM, pH=3, PNP=0.3 mM, anions=5 mM and HA=SDS=10 mg/L).

reached 1.31 mM, indicating that PI was decomposed into $IO_3^{\bullet}$ and $HO^{\bullet}$ as the main responsible oxidant of PNP degradation (Eq. (15)).

$$IO_3^{\bullet}\cdot HO^{\bullet}+PNP\rightarrow \text{by-products}+IO_3^{-} \qquad (15)$$

4. The Effect of Water Matrix

In a real condition, the presence of various organic and inorganic compounds usually influences the performance of AOPs. Fig. 5(a) depicts the PNP degradation using PI/UV/US process in the presence of anions. Chloride ions have demonstrated various impact on the performance of AOPs including inhibitory, promoting and neutral effect. In the current work, the neutral effect of chloride ions was observed, which may be due to the resultant of negative and positive impacts of chloride ions. Chloride ions have high reactivity for the reaction with hydroxyl radicals and periodyl radicals. Moreover, chlorine radical (E^0=2.47 V) and dichlorine radical (E^0=2.0 V) produced are strong oxidants which can degrade organic compounds [10].

$$HO^{\bullet}+Cl^{-}\rightarrow ClOH^{\bullet-} \qquad 4.3\times10^{9}\ M^{-1}\ s^{-1} \qquad (16)$$

$$ClOH^{\bullet-}+H^{+}\rightarrow Cl^{\bullet}+H_2O \qquad 2\times10^{10}\ M^{-1}\ s^{-1} \qquad (17)$$

$$IO_3^{\bullet}+Cl^{-}\rightarrow Cl^{\bullet}+IO_3^{-} \qquad (18)$$

$$Cl^{\bullet}+Cl^{-}\rightarrow Cl_2^{\bullet-} \qquad 6.5\times10^{9}\ M^{-1}\ s^{-1}\text{-}2.1\times10^{10}\ M^{-1}\ s^{-1} \qquad (19)$$

Sulfate ions did not influence the performance of PI/UV/US process. The degradation rate was similar to blank condition (no adding anions). Although sulfate ions have demonstrated a negative effect on sulfate radical-based AOPs [32], the current work showed that sulfate ions did not affect the PNP degradation in PI-based AOPs.

In the presence of nitrate ions, the PNP degradation rate was slightly increased. A positive effect of nitrate has been reported in literature. Nitrate ions generate free radicals in the presence of UVC irradiation according to the following equations. In this way, some

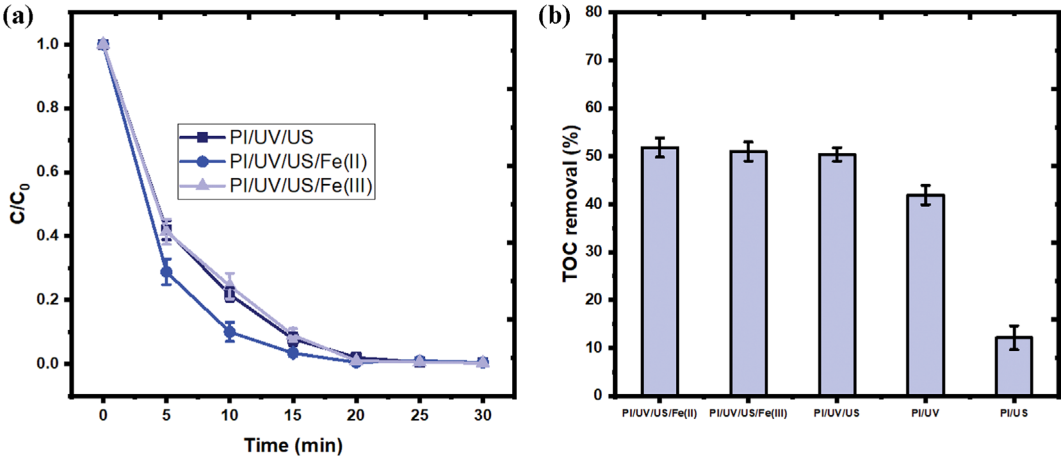

Fig. 6. (a) the PNP degradation by PI/UV/US process in the presence of iron, (b) TOC removal from PNP using PI-based processes (PI=2 mM, pH=3 and Fe=0.5 mM).

studies also focused on NO_3^-/UVC process as a new AOP for the degradation of organic compounds [26,33]. To confirm the promotional effect of nitrate ions, nitrate/UV/US process was tested and the results are presented in Fig. S1. As can be seen, nitrate/UV/US can degrade around 29% of PNP during 20 min reaction.

$$NO_3^-+H^++h\upsilon \rightarrow NO_2^\bullet+HO^\bullet \qquad k=8.5\times10^{-7}\,M^{-1}\,s^{-1} \qquad (20)$$

$$NO_3^-+h\upsilon \rightarrow NO_2^\bullet+O^{\bullet-} \qquad \Phi=0.01 \qquad (21)$$

$$2NO_2^\bullet+H_2O \rightarrow NO_3^-+NO_2^-+2H^+ \qquad k=4\times10^7\,M^{-1}\,s^{-1} \qquad (22)$$

The PNP degradation was remarkably decreased in the presence of bicarbonate ions. Bicarbonate ion is well known as a strong scavenger for free radicals, especially hydroxyl radicals (Eq. (23)) [34]. Periodyl radicals also may be scavenged by bicarbonate ions based on Eq. (24). The recombination of carbonate radicals may occur in high concentration of $CO_3^{\bullet-}$ (Eq. (25)) [35,36]. Moreover, adding the bicarbonate ions increased the solution pH (7.8), which is influential in the performance of the PI/UV/US process.

$$HO^\bullet+HCO_3^- \rightarrow CO_3^{\bullet-}+H_2O \qquad k=3.2-4.2\times10^8\,M^{-1}\,s^{-1} \qquad (23)$$

$$IO_3^\bullet+HCO_3^- \rightarrow CO_3^{\bullet-}+IO_3^-+H^+ \qquad (24)$$

$$CO_3^{\bullet-}+CO_3^{\bullet-} \rightarrow CO_4^{2-}+CO_2 \qquad k=1.5\times10^7\,M^{-1}\,s^{-1} \qquad (25)$$

The sum of anions exhibited a high inhibitory effect on the PNP degradation. Although nitrate, chloride and sulfate ions had neutral or promotional effect, the sum of them suppressed the performance of PI/UV/US, indicating that carbonate ions affected the reactive species. Moreover, the presence of several anions and cations enhanced ion strength leading to a slow activation of PI.

The effect of organic compounds on the PNP degradation was studied by humic acid (HA, a source of natural organic matter) and SDS. Fig. 5(b) shows the effect of organic compounds on the PNP degradation via PI/UV/US. The investigation on HA effect had different results. A negative or positive effect has been reported in literature. Positive effect of HA is related to an interaction of HA with PNP (benzene ring) leading to the formation of π-π interactions between one aromatic ring of the HA and benzene ring of PNP. This interaction enhances the density of electron cloud of PNP, resulting in enhanced PNP oxidation. However, this mechanism did not occur in our study since there was a decrease in efficiency in the presence of HA. Several studies have reported that HA acts as a sink for free radicals. Regarding the high reactivity of HA with free radicals (~$10^8\,M^{-1}\,s^{-1}$), HA probably scavenged $IO_3^\bullet$ and $HO^\bullet$ and decreased the PNP degradation rate [37].

SDS is an anionic surfactant present in municipal wastewater in the range of 3-20 mg/L [38]. SDS is used as a source of organic compounds to compete with PNP. As shown in Fig. 5(b), the PNP degradation rate declines in the presence of SDS. Free radicals generated are non-selective especially hydroxyl radicals; hence, SDS competes with PNP as target pollutant for the reaction with $IO_3^\bullet$ and $HO^\bullet$ as the major oxidative agents.

5. The presence of Iron and Mineralization Study

In UV-based AOPs, adding iron species accelerates the degradation rate based on Fenton and photo-Fenton reactions. Fig. 6(a) shows the PNP degradation by PI/UV/US process in the presence of Fe(II) and Fe(III) process. In our study, Fe(II) could enhance the PNP degradation rate, while the presence of Fe(III) was almost ineffective compared to PI/UV/US process. Fe(II) can directly activate PI according to the Fenton reaction (Eq. (26)) [35]. To confirm this, PI/Fe(II) and PI/Fe(III) processes were conducted for the degradation of PNP and the results are presented in Fig. S2. As can be seen, PI/Fe(II) process degraded around 35% of PNP during 30 min reaction time, while the PI/Fe(III) indicated a weak performance in the degradation of PNP (11%).

$$IO_4^-+Fe^{2+}+H^+ \rightarrow IO_3^\bullet+Fe^{3+}+HO^- \qquad (26)$$

Fe(II) depicted a catalytic activity for periodate activation in the PNP degradation. Moreover, there is another promotional phenomenon, ferrous ions in the presence of UV and US irradiation generates $HO^\bullet$ (Eq. (27)). In UV/Fe(II), the conversion of Fe(III) to Fe(II) is sped up via UV and US irradiation of Fe(III)-complex [26,39].

$$Fe(OH)^{2+}+UV/US \rightarrow Fe^{2+}+HO^\bullet \qquad (27)$$

The performance of PI-based process was also evaluated by TOC removal to determine mineralization degree. Fig. 6(b) shows the mineralization degree of PNP under the conditions of PI=2 mM,

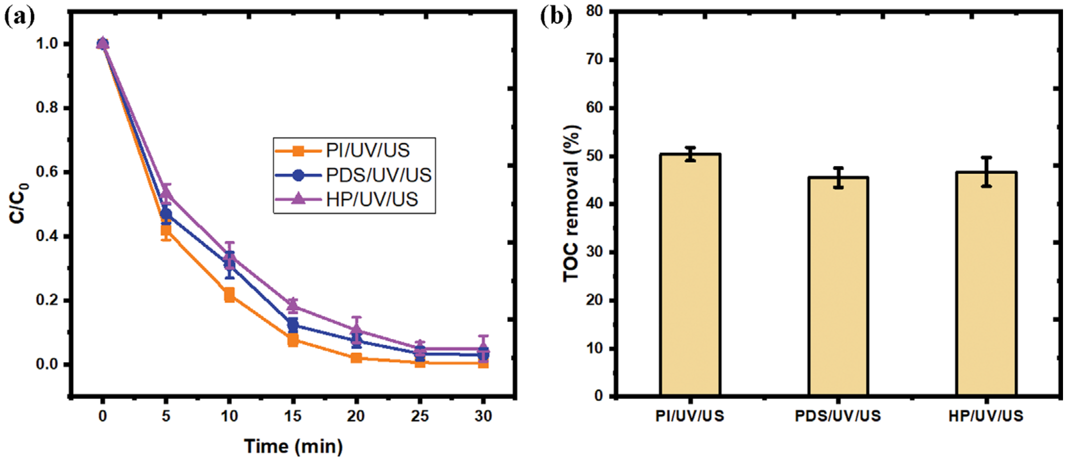

Fig. 7. (a) PNP degradation by PI/UV/US, PDS/UV/US and HP/UV/US processes, (b) TOC removal from PNP different processes (PI=HP=PDS=2 mM, pH=3 and Fe=0.5 mM).

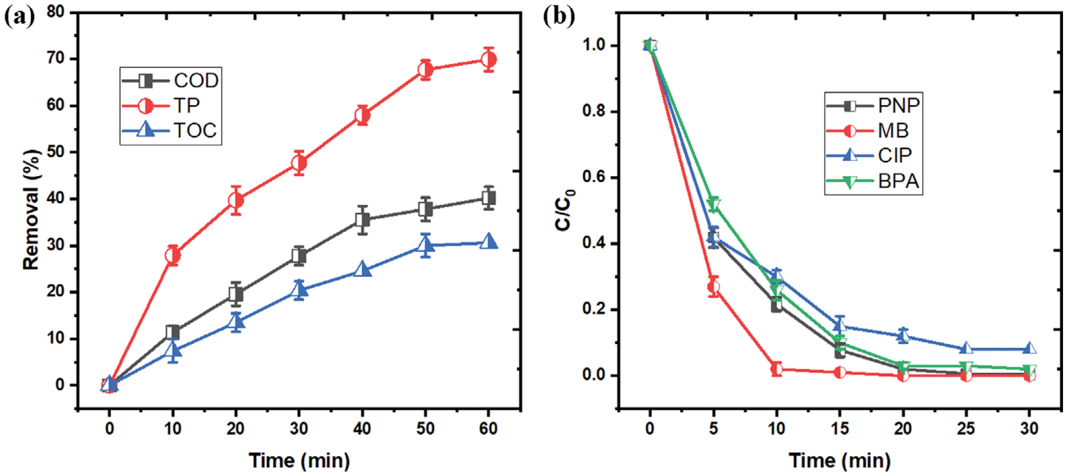

Fig. 8. (a) TOC, COD and TP removals by PI/UV/US process, (b) the degradation of various pollutants by PI/UV/US.

pH=3, Fe=0.5 mM, and 60 min reaction time. As can be seen, approximately half of PNP was mineralized by PI/UV/US, PI/UV/US/Fe(II) and PI/UV/US/Fe(III) processes. It can be stated that the presence of iron species did not affect the mineralization degree. On the other hand, PI/UV and PI/US could remove 41 and 12% of TOC, respectively. It is clear that US irradiation did not have the power for the PI activation and the generation of free radicals compared to UV irradiation. Compared to PNP degradation, the mineralization was relatively slight, which was attributed to resistance of intermediates formed to the oxidation. Indeed, the intermediates remained in the solutions while PNP was totally oxidized.

6. Comparison with Persulfate and Hydrogen Peroxide

PI oxidant was compared to PDS and hydrogen peroxide (HP) in photo-sonolysis systems. PDS and HP are activated by UV and US to generate sulfate radicals and hydroxyl radicals, respectively.

$$S_2O_8^{2-}+UV/US \rightarrow SO_4^{\bullet -}+SO_4^{\bullet -} \tag{28}$$

$$H_2O_2+UV/US \rightarrow HO^{\bullet}+HO^{\bullet} \tag{29}$$

Fig. 7(a) shows the PNP degradation in three systems under the same conditions [40]. In comparison with PDS and HP, PI exhibited a higher performance in terms of the PNP degradation. The simultaneous contribution of $IO_3^{\bullet}$ and $HO^{\bullet}$ gives an advantage to PI process for enhanced degradation of organic pollutants. However, this preference is insignificant for PNP degradation. Fig. 7(b) shows TOC removal by three processes. As mentioned, there is no significant difference between these oxidants. TOC removal obtained was 50.4%, 45.5% and 46.7% for PI/UV/US, PDS/UV/US and HP/UV/US, respectively. Although PI demonstrated high efficiency compared to others, some points should be considered before PI application such as iodate residual and the cost of oxidant (the cost of 1 kg sodium periodate is 4 USD *vs.* 0.74 USD for PDS and 1.5 USD for HP).

7. PI/UV/US Application for a Real Wastewater and other Pollutants

PI/UV/US process was employed for the treatment of a real wastewater. COD, TOC and Total Phenol (TP) were considered to evaluate treatment degree. TP is defined as hydroxy derivatives of benzene and its condensed nuclei. Petrochemical wastewater is well known as a source phenolic compounds especially nitrophenols [1]. Fig.

8(a) shows COD, TOC and TP removals using PI/UV/US process during 60 min reaction time. COD, TOC and TP removals obtained were 40.2, 30.6% and 69.9%, respectively. The presence of various organic and inorganic compounds in the real wastewater decreased the function of PI/UV/US process. Moreover, the presence of persistent organic pollutants may be the main reason of low COD and TOC removal efficiency in which organic compounds were oxidized to smaller organic compounds and maintained the organic content. However, around 70% of phenolic compounds were degraded by PI/UV/US process, indicating that the current system was successful in the degradation of TP for a real condition. To evaluate the implementation of PI/UV/US process, the electrical energy consumption was calculated based on the previous study [26]. PI/UV/US process showed a high energy consumption (220 kWh/m^3) due to UV and US irradiation. The obtained results were similar to other studies [26,41,42].

Fig. 8(b) shows the degradation of various pollutants by PI/UV/US process under the same conditions. PI/UV/US process was sufficiently effective for the degradation of different pollutants. MB is a conventional dye which has been extensively selected as a sample of colored effluent. As can be seen, a rapid degradation was obtained for MB pollutant in which MB was completely removed in only 10 min. BPA as an endocrine disruptor has been used as sample for the evaluation of AOPs. The BPA degradation rate was similar to PNP degradation approximately. 97% of BPA was eliminated during 15 min reaction time. CIP is a fluoroquinolone antibiotic utilized for the treatment of bacterial infection. 92% of CIP was degraded within 30 min reaction time. Among these pollutants, CIP was persistent to degradation while MB was easily degraded by PI/UV/US process. PI/UV/US system showed a high performance for a variety of organic pollutants, indicating that PI-based process can be an alternative for other chemical oxidants used in AOPs.

8. Degradation Pathway of PNP by PI/UV/US

The PNP degradation intermediates were determined by LC/MS analysis. The LC spectra of PNP degradation by PI/UV/US process are presented in Fig. S3. Six main intermediates were determined and the degradation pathway is presented in Fig. 9. Regarding the high degradation rate of PNP by PI/UV/US process, the intermediates of PNP degradation were evaluated in 20 min reaction time. As can be seen, PNP (**A**, m/z=139) was degraded into phenol (**B**, m/z=94) at the first step, indeed, NO_2 functional group was removed from PNP by attacking $IO_3^{\bullet}$ and $HO^{\bullet}$ and nitrate ions that were probably released into the solution. Hydroxyl radicals attacked into para position of aromatic ring and hydroquinone (**C**, m/z=110) were formed through radical-addition mechanism. Further oxidation process resulted in the formation of p-benzoquinone (**D**, m/z=108) in which -CH= group was converted to C=O group (carbonyl) [43]. Benzene ring is opened by free radicals and a large aliphatic molecule was formed as maleic acid (**E**, m/z=116) as the first aliphatic acid. Moreover, maleic acid was converted into some small carboxylic acids such as acetic acid (m/z=45) by further oxidation initiated by $IO_3^{\bullet}$ and $HO^{\bullet}$ [44]. Finally, carboxylic acids were mineralized into carbon dioxide and water.

9. Comparison with other AOPs

The function of various AOPs for the degradation of PNP was compared to our work and the results are presented in Table 1. Briefly, we expressed pros and cons of several studies to gain a new insight into different AOPs. Catalytic ozonation [45] with excellent performance (100% PNP removal) may produce aldehydes as by-product, which is a toxic compound. Photocatalysis process (B-TiO_2/UV) [46] needs a long reaction time for the PNP degradation while it works without any external chemical oxidant. Classic Fenton oxidation must be operated in acidic conditions (pH=3) [47]. In addition, the sludge produced in Fenton oxidation (as a disadvantage) should be remediated. However, simple operation and high degradation rate are rational reasons for its application on large scale. Persulfate-based AOPs such as PDS/heat [48] have demonstrated high efficiency for PNP degradation. However, the high energy consumption and residual sulfate ions are limiting factors for the application on industrial scale. Heterogeneous PMS activation by transition metals (Fe/Co_3O_4) [49] showed a good performance for the PNP removal, while the cost of nanocomposite synthesis, leaching of metals and residual sulfate ions are the main drawbacks of the heterogeneous AOPs. Electrooxidation process [50] has been used for PNP degradation. Electrochemical processes are environmental compatibility and green technology since the

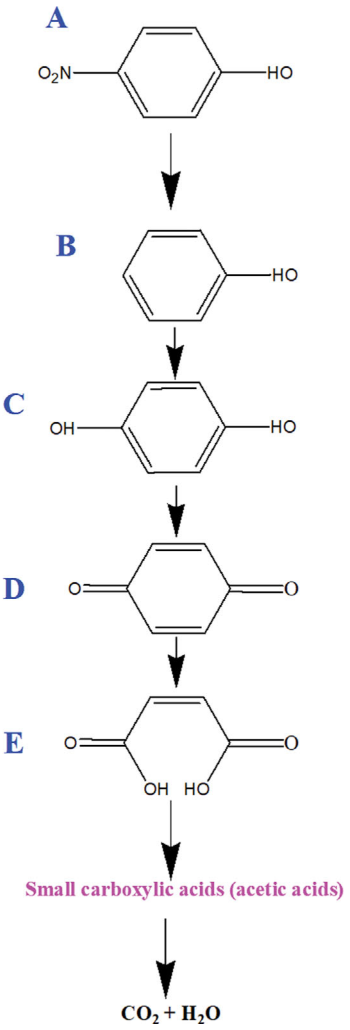

Fig. 9. The pathway of PNP degradation using PI/UV/US.

Table 1. PNP degradation by various AOPs

Process	Conditions	PNP removal (%)	TOC removal (%)	Ref.
O_3/MnO_2	pH=7, Catalyst=0.1 g/L, O_3=2 mg/min, PNP=25 mg/L and Time=30 min	100	~35	[45]
B-TiO_2/UV	Catalyst=1 g/L, PNP=1 mg/L and Time=180 min	90	-	[46]
Fenton oxidation	pH=3, H_2O_2=2.4 g/L, Fe^{2+}=140 mg/L and Time=60	100	43.8	[47]
PDS/heat	pH=5, PDS=6.4 g/L, Temperature=70 °C, PNP=500 mg/L and Time=180 min	80.1	45.6	[48]
Fe/Co_3O_4/PMS	pH=5.5, Catalyst=0.2 g/L, PMS=0.5 mM, PNP=10 mg/L and Time=60 min	100	-	[49]
Electrooxidation/H_2O_2	pH=11, NaCl=0.5 g/L, H_2O_2=10 mM, PNP=10 mg/L and Time=160 min	95		[50]
PI/UV/US	pH=3, PI=2 mM, US=100 W and Time=30 min	~100	50.4	Our work

main reactions are conducted by electron transfer. The use of electricity for the chemical reactions increases the cost of the process. PI/UV/US, as above-mentioned, showed excellent performance for PNP degradation. However, the residuals of iodate ions and high energy consumption are the limiting factors for the PI/UV/US process.

CONCLUSION

PI/UV/US process as a new AOP was used to degrade PNP. The simultaneous application of UV and US exhibited a synergistic effect on PI activation. Complete degradation of PNP was obtained at pH=3 and 2 mM PI within 30 min. $HO^{\bullet}$ and $IO_3^{\bullet}$ were recognized as corresponding oxidation agents of PNP. The presence of iron increased the PNP removal rate through enhanced activation of PI. The PI/UV/US process showed high efficiency in the presence of various anions except for bicarbonate ions. HA and SDS suppressed the degradation rate of PNP through competition with target pollutant for the reaction with $HO^{\bullet}$ and $IO_3^{\bullet}$. The mineralization degree of PNP degradation was at an acceptable level in which ~50% of PNP was mineralized in terms of carbon element. The performance of PI/UV/US process was evaluated on real wastewater and around 70% of TP was removed during 60 min reaction time. PI-based process indicated a higher performance compared to PDS and HP. However, the residual of iodate is truly a disadvantage for a PI-based process. Note that iodate ions can be easily removed by activated carbon, ion exchange and membrane processes. PI-based processes can be extended in the near future for the degradation of various organic pollutants and treatment of contaminated water.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Periodate activation by concurrent utilization of UV and US for the degradation of para-nitrophenol in water: A synergistic approach

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Table S1. Charactristics of petrochemical wastewater

Parameter	Unit	Value
COD	mg/L	610
BOD5	mg/L	150
TDS	mg/L	890
Cl-	mg/L	163
pH	-	7.5
TP	mg/L	48.9
SO_4^{2-}	mg/L	41
Fe	mg/L	<0.1 mg/L

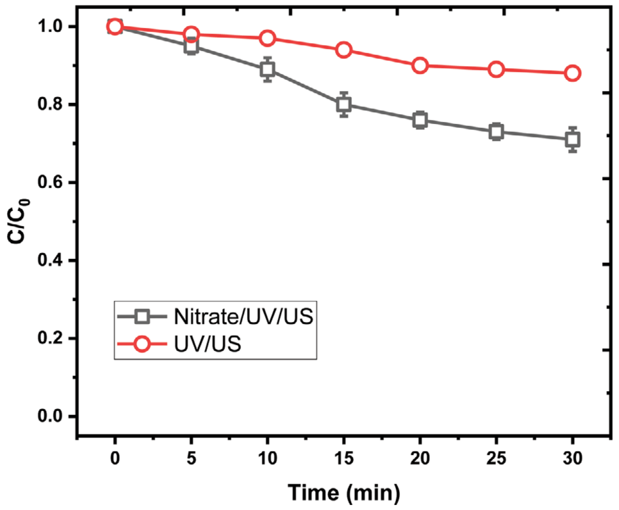

Fig. S1. PNP degradation by UV/US and Nitrate/UV/US processes.

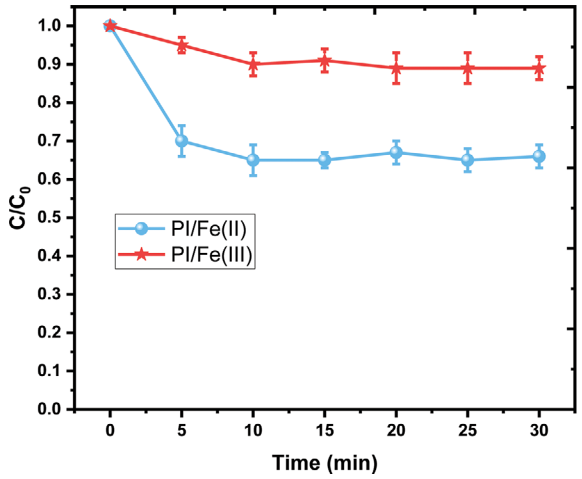

Fig. S2. The PNP degradation by PI/Fe(II) and PI/Fe(III) processes (PI=2 mM, pH=3 and Fe=0.5 mM).

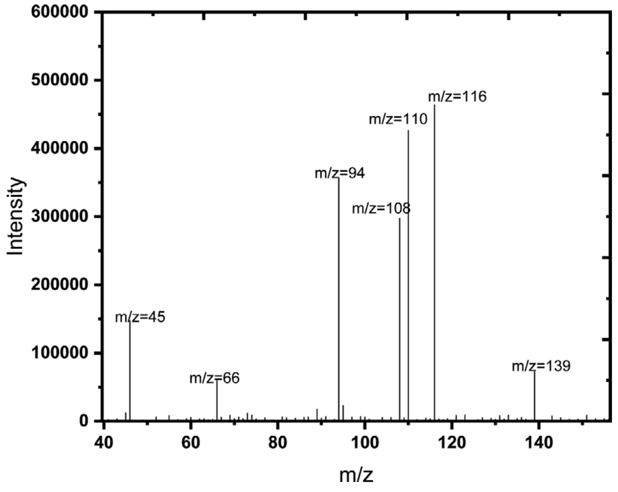

Fig. S3. LC/MS spectra of PNP degradation by PI/UV/US process.