Degradation of phenol using US/periodate/nZVI system from aqueous solutions

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Abstract

In the present work, the degradation of phenol from aqueous solutions was investigated using periodate/zero valent iron nanoparticle (nZVI) in the presence of ultrasound at a batch reactor. The Experimental tests were carried out using pre-designated concentrations of nZVI, periodate, and pH ranging from 1-7 mM, 0.5-5 mM, 3-11 respectively. During the all experimental tests the ultrasonic reactor was operated at a fix frequency (40 kHz), temperature (33±1) and power (350 W). The results of nZVI/periodate/ultrasound system on degradation of phenol showed that the removal efficiency was indeed affected by the amount of free radicals produced to initiate the oxidative decomposition of phenol. also, by increasing the nZVI loading to 3 mM and periodate concentration to 3 mM, the efficiency of phenol removal was increased. Besides, the acidic pH (pH = 3) was found to be more effective than neutral and alkaline pH in degradation of phenol.

Keywords: Periodate, nZVI, ultrasound, phenol, degradation.
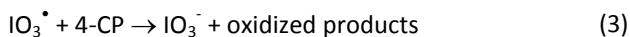
1. Introduction

Wastewater caused by industrial activities might be contained by various chemical compounds in the quantities that can change the quality of water resources. Many of these compounds are organic-based, toxic, and characterized by high stability in the environment (Rahmani *et al.*, 2016). The presence of recalcitrant organic compounds in the environment is undesirable and will create various unpleasant undesirable consequences for all creatures (Baziar *et al.*, 2018a). Phenol (C_6H_5OH), a well-known toxic and hazardous organic compound, has been widely utilized in several industries like pulp and paper, paint, petrochemical, herbicide and pesticide production (Azevedo *et al.*, 2006; Manshouri *et al.*, 2012; Ghasemi *et al.*, 2015). The wastewater generated from these industries might be introduced to the surface and groundwater. As a result, it can produce severe adverse effects on aquatic life as well as human health with exacerbating the water contamination issues (Zhong *et al.*, 2011). Phenol has been listed by USEPA as a priority pollutant due to high perniciousness on human and biota, high permanence in the aquatic environment, low biological decomposition property, high carcinogenic and mutagenic nature (Azevedo *et al.*, 2006). Consequently, the elimination of this compound and its derivatives from industrial effluent/wastewater is an environmental concern.

A number of treatment methods to eliminate the phenol from contaminated water and/or from industrial wastewater (e.g., treatment by biological, physico-chemical and advanced oxidation process approaches) have been extensively investigated. From above mentioned procedures, the application of biological treatment compared to the other two methods has recently fallen out of favor due to the toxicity of phenol to the bacteria (the organism that is responsible for decomposition) as well as its low efficacy and long time needed for adaptation of the bacteria water contaminated with phenol. Physico-chemical techniques are usually needed after treatment or disposal of produced sludge (Alavi *et al.*, 2018; Baziar *et al.*, 2018b). In the last few decades, applications of AOPs in the aqueous solution have been increasingly used because of their good performance to degrade a broad range of persistent organic pollutants (Seidmohammadi *et al.*, 2016; Seid-Mohamadi *et al.*, 2015; Seidmohammadi *et al.*, 2018; Naghan *et al.*, 2015). The performance of AOPs are underlying the production of strong reactive intermediates, e.g. sulfate ($SO_4^{-\bullet}$), hydroxyl ($OH^\bullet$) and iodyl ($IO_3^\bullet$) via different activation methods. Therefore, these

strong intermediates can entirely degrade the persistent organic pollutants to CO_2 and H_2O or convert them to a less toxic product (Lee *et al.*, 2014).

More recently, the application of periodate (IO_4^-) as an oxy-anion in water treatment has attracted increasing attention (Saien *et al.*, 2018). The interest underlying the periodate usage in decomposition of persistent organic pollutants are associated with its(I) relatively high oxidation potential ($E0 = 1.6$ V), (II) high dissolution capacity in water, (III) stability at room temperature and (IV) generation of free radicals (e.g. $IO_3^\bullet$, $IO_4^\bullet$) through reactions of intermolecular electron transfer (Lee *et al.*, 2014). Although the oxidation potential of periodate anion is acceptable however, its oxidation reactions are relatively slow at a room temperature and also serve selectively to oxide the organic compounds. The previous studies confirmed that periodate can be activated by ultraviolet (UV) irradiation as illustrated by equations of 1 to 3 and produce free radicals of $IO_3^\bullet$ and OH• which can degrade organic matters (e.g., 4-chlorophenol and dye), (see Equations 1 to 3) (Chia *et al.*, 2004; Lee *et al.*, 2004).

$$IO_4^- + hv \rightarrow IO_3^\bullet + O^{\bullet-} \qquad (1)$$

$$O^{\bullet-} + H^+ \rightarrow OH^\bullet \qquad (2)$$

$$IO_3^\bullet + 4\text{-}CP \rightarrow IO_3^- + \text{oxidized products} \qquad (3)$$

A great substitution to UV irradiation is ultrasonic (US) radiation. US radiation influence on molecules is related to nucleation, cavitations along with formation of micro-bubbles. The micro- bubbles produced provide areas of high pressure in the system which can generate $OH^\bullet$ radicals through dissociation of water. Therefore ultrasonic radiation is mainly used in numerous technologies for water purification (Dobaradaran *et al.*, 2018; Zhou *et al.*, 2015; Ammar, 2016). The generated $OH^\bullet$ radicals can non- selectively degrade the organic compounds, therefore they reduce the selective nature of periodate in degradation of organic compounds. Also, the main advantage of this method is high ability to degrade hazardous material to non-hazardous end products (Lee *et al.*, 2014; Harrabi *et al.*, 2018). The combination of ultrasonic waves with oxidants like IO_4^- can accelerate the removal of organic components from aqueous solutions (Seid-Mohamadi *et al.*, 2015).

Moreover, it has been proven that addition of Nano zero valent iron (nZVI) along with an oxidant (e.g., persulfate, hydrogen peroxide, etc.) in aqueous solutions can enhance the elimination of organic compounds by increasing the generation of powerful free radicals such as $OH^\bullet$ and $SO_4^\bullet$ (Harrabi *et al.*, 2018; Zhou *et al.*, 2008). The most important feature of nZVI is its high surface area which can accelerate the production of oxidants (Baziar *et al.*, 2018b). However, it is reported that the formation of iron oxide layers (passive layers) on the surface of nZVI may dramatically reduce the reactivity of nZVI and retard the generation free radicals (Song *et al.*, 2019). Hence, in the present work we evaluate the role of US radiation as a destructive agent of iron passive layer, as well as nZVI loading and periodate dosage as factors that can improve the performance of US/nZVI/IO_4^- system for degradation of phenol.

2. Materials and methods

2.1. Chemicals

The chemicals used in this study are as follows: phenol (99.8%; Merck Co.), Sodium periodate (99%; Sigma-Aldrich), potassium ferricyanide (99%; Merck Co.), 4-aminoantipyrine (98%; Merck Co.), Nanoparticle Zero Valent Iron powder (97%; particle size 30-60 nm; Merck Co.), KH_2PO_4 (>99%, Sigma-Aldrich), K_2HPO_4 (>98%; Sigma–Aldrich), NH_4OH (Merck Co.), H_2SO_4 and NaOH (Merck Co.).

2.2. Experimental procedure

All experimental tests were performed in an ultrasonic stainless steel reactor (LUC-model 405) with dimensions of 15 cm × 13 cm × 25 cm and with a total volume of 5 L. Figure 1 shows the schematic diagram of used ultrasonic reactor which was operated at a fixed frequency (40 kHz), temperature (33±1) and power (350 W) during the all experimental tests. The ultrasonic reactor used in this study consists of three parts: (i) turbulent regime tank, (ii) ultrasonic generator, (iii) transformer.
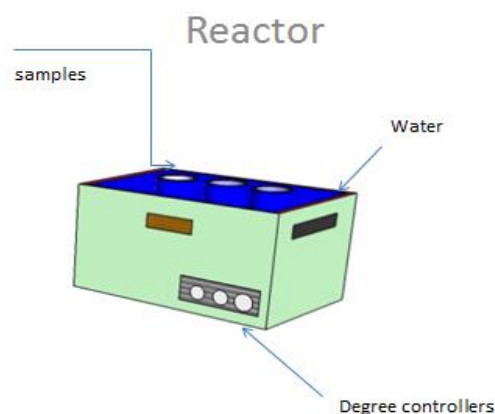

Figure 1. The schematic diagram of the ultrasonic reactor

To study the phenol degradation, the nZVI and sodium periodate with pre-designated concentrations (nZVI 0.5-5 mM and sodium periodate 1-7 mM) were mixed with an appropriate concentration of phenol (25-200 mg/L) in a beaker with a final volume of 100 mL. Then the solution pH (3-11) was adjusted with H_2SO_4 and NaOH (0.1 mol/L). The final solution was transferred to the ultrasonic stainless steel reactor (to get exposure with ultrasound waves) and stirred by a magnetic stirrer to obtain a homogenous solution within the process reaction times of 0-120 min. The initial and final concentration of phenol in samples was measured using UV-visible spectrophotometer at a wavelength of 500 nm (Deng *et al.*, 2014). The removal efficiency of the developed system in various operation conditions was determined by Equation (4).

$$Removal\,(\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (4)$$

Here, C_i and C_f are related to the initial and final concentration of phenol in the developed system, consecutively. It is noted that, prior to phenol measurement in the samples, they were centrifuged for 5 min at a rotational speed of 1000 rpm to remove the nZVI.

3. Results and discussion

3.1. Effect of pH in $Us/IO_4^-/Fe^\bullet$ system

The effect of pH on phenol degradation in the $Us/IO_4^-/Fe^\bullet$ system was studied by changing its level between 3 and 11. It is quite obvious that in AOPs reactions the presence of several oxidants in the process increases the power of degradation. It is clear from Figure 2, the performance of $Us/IO_4^-/Fe^\bullet$ system was dependent upon the solution pH and it had significant influence in the range studied of 3-11. As the solution pH was increased the degradation percentage of phenol decreased. At pH value of 3 and contact time equal to 60 min the highest degradation percentage (88.4%) was observed. Alkaline pH 11 had the lowest removal percentage (49%) in this study. The removal percentage of phenol was further investigated up to 120 minutes of contact time; it was found that after 60 min treatment, the removal percentage was changed slightly, so the optimum contact time was considered to be 60 min which also applied to the next steps of the experiment.
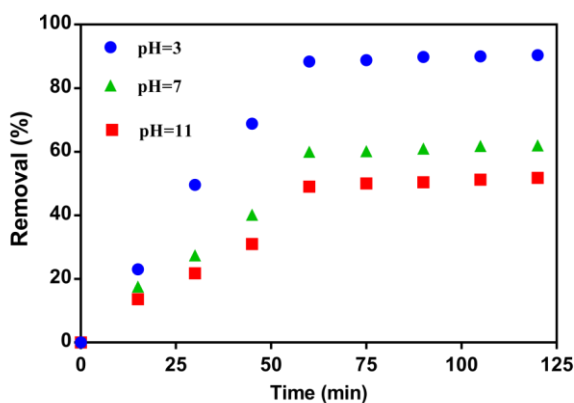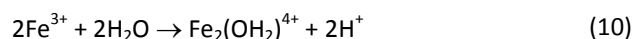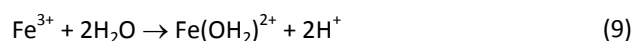

Figure 2. Effect of pH on the phenol degradation by $Us/IO_4^-/Fe^\bullet$ system. IO_4^- 5 mM, NZVI 2 mM, phenol 50 mg/L

It is confirmed that the lower solution pH has more positive influence on phenol degradation than neutral and alkaline pHs in the $Us/IO_4^-/Fe^\bullet$ system. This might be due to the increasing concentration of hydrogen ions (H^+) in the system at lower solution pH, and therefore greater generation of $OH^\bullet$ and $IO_3^\bullet$ radicals as the possible oxidants (see Equations 5 to 7) (Lee et al., 2014).
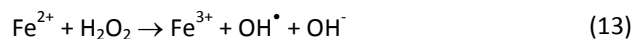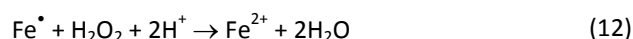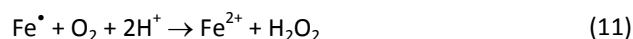
$$IO_4^- + H^\bullet \rightarrow IO_3^- + OH^\bullet \qquad (5)$$

$$IO_3^- + H^\bullet \rightarrow IO_2^- + OH^\bullet \qquad (6)$$

$$IO_4^- + H^\bullet \rightarrow IO_3^\bullet + OH^- \qquad (7)$$

Basically, in the aqueous solutions H^+ ions are reduced to $H^\bullet$ in the presence of $Fe^\bullet$, also pH than 5 the $Fe^\bullet$ convert to $Fe^\bullet(OH)3$ and precipitates, thus compounds that have been attached to the nanoparticles are also deposited and removed from the solution (Deng et al., 2014). As a result, a large amount of $H^\bullet$ is generated by $Fe^\bullet$ in acidic condition (pH = 3) and $H^\bullet$ iseffective in generation of $IO_3^\bullet$ and $OH^\bullet$ free radicals. These free radicals are responsible for phenol degradation. However, the removal percentage was less in the basic and neutral pH than the acidic pH. This performance can be due to the formation of iron based oxy-hydroxides in the system, like $FeOH^{2+}$, $Fe(OH_2)^{2+}$ and $Fe_2(OH)_2^{+4}$, which prevent the periodate activation as well as production of hydroxyl radicals (see Equations 8-10) (Schrick et al., 2002; Hussain et al., 2012).

$$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+ \qquad (8)$$

$$Fe^{3+} + 2H_2O \rightarrow Fe(OH_2)^{2+} + 2H^+ \qquad (9)$$

$$2Fe^{3+} + 2H_2O \rightarrow Fe_2(OH_2)^{4+} + 2H^+ \qquad (10)$$

Generally, two reaction pathways are assumed for free radical generation at the pH values ranging between acidic and neutral. The first is bringing the $H^\bullet$ in an acidic condition and second is bringing in the 1 electron transfer in a neutral condition by adjusting the initial solution pH in the process. However, the latter is not completely understood and there has not been an explanation for it recently (Lee et al., 2014).

In addition, in an acidic pH, $Fe^\bullet$ can enhance the degradation of phenol in the presence of dissolved O_2 with a mechanism of 2- electron transfer and formation of hydrogen peroxide. The generated hydrogen peroxide can also reduce to H_2O with a new reaction of 2- electron transfer. Next, the interaction between the hydrogen peroxide and ferrous iron (Fe^{2+}) can form $OH^\bullet$ radicals. (see Equations 11 to 13) (Hussain et al., 2014).

$$Fe^\bullet + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \qquad (11)$$

$$Fe^\bullet + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \qquad (12)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \qquad (13)$$

3.2. Effect of periodate concentration on the $Us/IO_4^-/Fe^\bullet$ system

The effect of periodate concentration on the performance of $Us/IO_4^-/Fe^\bullet$ system was investigated by adjusting the concentration from 1 mM to 7 mM and keeping $Fe^\bullet$ concentration at 2 mM with a reaction time ranging between 0-60 min. As illustrated in Figure 3, by increasing the periodate concentration from 1 mM to 2 mM, the phenol removal efficiency increased from 86.2% to 93.6%. However, further increasing the periodate concentration had negative influence on the system performance and the removal efficiency decreased. It is clear that the periodate concentration and its activation process play important roles in the enrichment of periodate reactive species (like $IO_4^\bullet$ and $IO_3^\bullet$) and the corresponding removal efficiency. When an adequate amount of periodate is fed

to the system, in the presence of an activator, the removal efficiency increases. This trend can be explained by the production of free radicals in large enough amounts to degrade the organic compound. Although higher periodate concentrations (more than 2 mM) produce higher amounts of radicals, the generated radicals can react with each other or with IO_4^- in a radical destructive reaction. Therefore, these reactions can reduce overall removal efficiency. Equation (14) presents an example of scavenging reaction which can occurr in the $Us/IO_4^-/Fe^{\bullet}$ system at an excess level of periodate concentration (Temiz *et al.*, 2016).
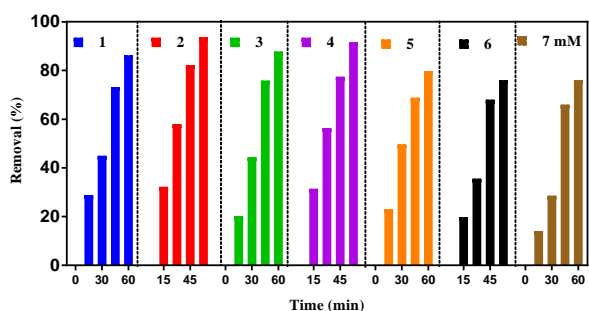
$$OH^{\bullet} + IO_4^{\,-} \rightarrow OH^- + IO_4^{\bullet} \qquad (14)$$

Figure 3. Effect of periodate concentration on the phenol degradation by $Us/IO_4^-/Fe^{\bullet}$ system. pH 3, NZVI 2 mM, phenol 50 mg/L

3.3. Effect of NZVI concentration on the $Us/IO_4^-/Fe^{\bullet}$ system

Figure 4 presents the phenol degradation under various $Fe^{\bullet}$ concentrations in the $Us/IO_4^-/Fe^{\bullet}$ system. As seen, the phenol degradation was extensively impacted by $Fe^{\bullet}$ loading and the phenol degradation percentage improved from 0% to 96.6% when $Fe^{\bullet}$ concentration increased from 0 to 3 mM in the system. This pattern can be explained by: (i) an increase in the total surface area with increasing the $Fe^{\bullet}$ loading, which creates a contribution to the increase in the iron corrosion, (ii) an increase in the corrosion products (like Fe^{2+}, Fe^{3+}, etc.) by increasing the $Fe^{\bullet}$ loading in an acidic medium that can produce free radicals to decompose the phenol (Baziar *et al.*, 2018a). However, further increasing the $Fe^{\bullet}$ loading (more than 3 mM) led to the reduction of system performance and, as the result, the removal percentage of phenol decreased.
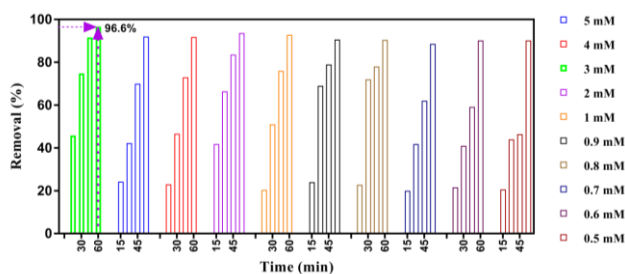

Figure 4. Effect of NZVI concentration on the phenol degradation by $Us/IO_4^-/Fe^{\bullet}$ system. pH 3, periodate 2 mM, phenol 50 mg/L

As mentioned above, $Fe^{\bullet}$ can decompose an organic pollutant through transfer of two electrons to the dissolved oxygen to generate hydrogen peroxide (Equation 11). The hydrogen peroxide formed can be converted to H_2O with another transfer of two electrons from $Fe^{\bullet}$ (Equation 12). The products of reactions (H_2O_2 and Fe^{2+}) can be combined together to produce the Hydroxyl free radicals. However, with excessive loading (concentration) of $Fe^{\bullet}$, a large amount of Fe^{2+} is produced. It can scavenge hydroxyl free radical via following reaction (Tang *et al.*, 2008):

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^- \qquad (15)$$

Therefore, the obtained results propose that, if the dosages of $Fe^{\bullet}$ and periodate exceed the optimal value, the removal efficiency decreases subsequently. This work demonstrated that the addition of sufficient dosages of the $Fe^{\bullet}$ and periodate were greatly important in decomposing phenol in water solutions.

3.4. Effect of initial phenol concentration on $Us/IO_4^-/Fe^{\bullet}$ system

Figure 5 shows the performance of the developed system with phenol concentrations varying from 25 to 200 mg/L while other parameters were fixed at their optimum values. The highest removal percentage (99.6%) was obtained when the phenol concentration was 25 mg/L. As observed in Figure 5, by increasing the initial phenol concentration from 25 to 200 mg/L, the removal efficiency decreased from 99.6% to 20.4% within 60 min. Generally, when a high level of phenol concentration was fed into the system, the molecules of phenol could be adsorbed on the surface of Fe^o then these molecules, by decreasing the number of active sites on the surface of iron atom (Hansson *et al.*, 2012), reduce the activation of periodate as well as the generation of OH radicals. Therefore, the removal efficiency decreases due to the inadequate generation of free radicals in the system.
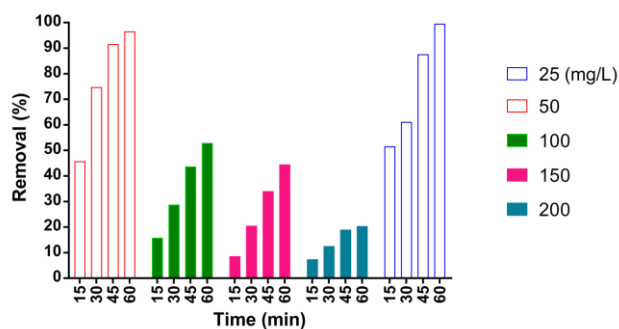

Figure 5. Effect of phenol concentration on the phenol degradation by $Us/IO_4^-/Fe^o$ system. pH 3, periodate 2 mM, NZVI 3 mM

In the next step of work, we compared the performance of $Us/IO_4^-/Fe^{\bullet}$ system with US/IO_4^- and $IO_4^-/Fe^{\bullet}$, and also with IO_4^- and US alone. In fact, the purpose of this stage of the study was to identify the function of each variable used in the system of $Us/IO_4^-/Fe^{\bullet}$ for phenol

decomposition. It is noted that the values of the parameters in the all systems were the same as the obtained optimal values of the parameters in the $Us/IO_4^-/Fe^•$ system. Figure 6 shows the performance of $Us/IO_4^-/Fe^•$ system with other developed treatment systems. As observed in Figure 6, merely 12% and 9.6% of phenol was decomposed within 60 min of treatment by US and IO_4 alone, respectively, while 33.6%, 47.8% and 96.6% of phenol was decomposed in the systems of $IO_4^-/Fe^•$, US/IO_4 and $Us/IO_4^-/Fe^•$ respectively. The experiment results showed that US and Fe^0 in the combined systems can play an outstanding role for enhancing the phenol decomposition. Generally, in the heterogeneous systems (similar to $US/IO_4^-/Fe$ treatment) the main influence of US is abrasion and pitting on the surfaces of catalyst (Dobaradaran *et al.*, 2018). US sweeps up the catalyst surfaces from attached intermediate products and it provides clean surfaces for next reactions. In addition, the aggregated Fe^0 particles could be dispersed by US waves, thus the surface of active sites in the system increases. Furthermore, US radiation can lead to the generation of hydroxyl radicals (Equation 16) through dissociation of water molecules by producing micro-bubbles which provide the areas of high pressure (Dobaradaran *et al.*, 2018).
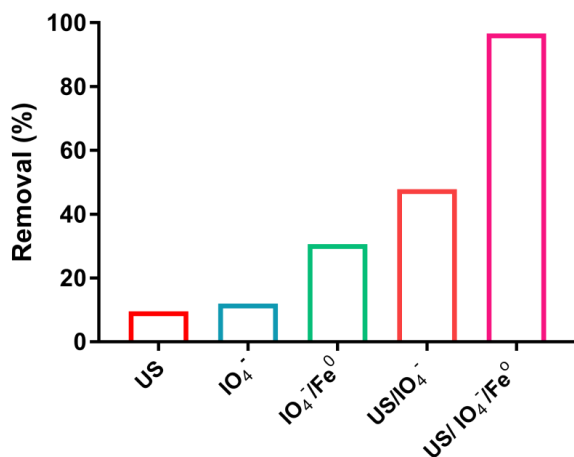
$$H_2O + US \rightarrow OH^• + H^• \qquad (16)$$

Figure 6. Effect of NZVI on periodate activation in the absence of ultrasonic waves on the phenol degradation. pH 3, periodate 2 mM, NZVI 3 mM, phenol concentration 50 mg/l, duration 60 min

3.5. Effect of CaCl$_2$ on the degradation of phenol in Us /IO$_4^-$/Fe$^•$ system

In the natural water environments, the activation of IO_4^- may be affected due to the presence of background ions. Hence, we investigated the influence of CaCl$_2$, a compound or salt that can easily dissolve in aqueous solutions and generate ions of calcium and chloride. Three individual tests were performed to determine the effect of CaCl$_2$ on the performance of $Us/IO_4^-/Fe^•$ system

by adjusting the CaCl$_2$ concentration in the values of 0.13, 0.5, and 1.03 g/L. As presented in Figure 7, the selected concentrations posed a little effect to the decomposition of phenol.
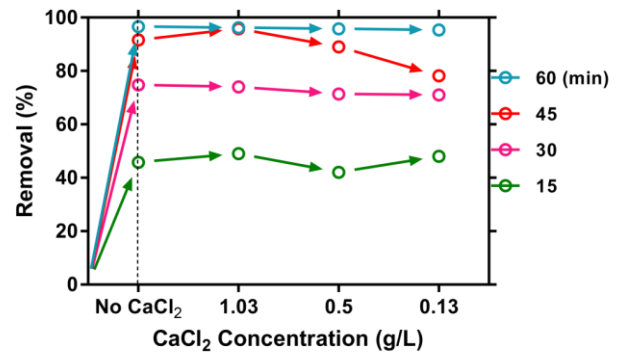

Figure 7. The impact of ion intensity on the decay of phenol in the $Us/IO_4^-/Fe^•$ system. pH = 3, periodate 2 mM, NZVI 3 mM, phenol concentration 50 mg/l, duration 60 min

3.6. COD removal in Us/IO$_4^-$/Fe$^•$ system

One of the most well-known methods for determination of persistent organic matter degradation in wastewater treatment is chemical oxygen demand (COD) (Baziar *et al.*, 2018c). Determination of COD in our work is highly important, because of its potential to oxidize the organic pollutants like phenol using dichromate. In fact, the degree of oxidation of the process is determined by the extent of reduced COD. This test was conducted to find out the effectiveness of the process in degradation of phenol at the optimum values of parameters as determined in the previous steps. Figure 8 illustrates the performance of $Us/IO_4^-/Fe^•$ on reduction of COD in a treatment test with three replications. As seen in this figure the performance of the developed system is about 85% in average. Therefore, it can be concluded that the process has high efficiency in eliminating COD. It is noted that for comparison we performed two separate tests using Us/IO_4^- and $IO_4^-/Fe^•$ processes in the same conditions. The results showed that Us/IO_4^- and $IO_4^-/Fe^•$ can remove COD up to 38 % and 29% on average, respectively.
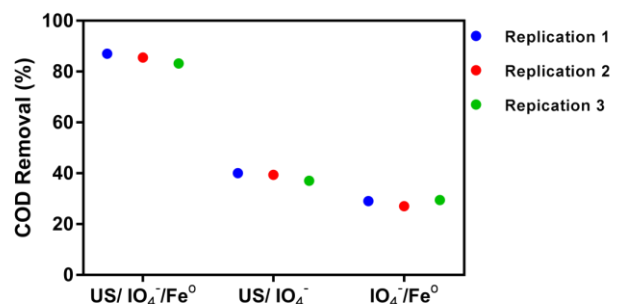

Figure 8. The impact of $Us/IO_4^-/Fe^o$ systems (combined and isolated) for COD removal. pH = 3, periodate 2 mM, NZVI 3 mM, phenol concentration 50 mg/l, duration 60 min

3.7. Proportion of OH radicals on degradation of phenol in the US/nZVI/periodate process

In this study, tert-butyl alcohol (TBA) with a concentration of 1 M was used to quench OH radicals in the US/nZVI/periodate process with the aim of identifying the contribution of OH radical on degradation of phenol. In the previous studies, it has been demonstrated that TBA with no alpha hydrogen can completely destroy the hydroxyl radicals in aqueous solutions (Baziar *et al.*, 2018b). It is marked from the laboratory radical scavenger test that the addition of TBA extensively decreased the decomposition of phenol. As already mentioned, the degradation of phenol in the optimized conditions of the process was 96.6% (without using radical scavenger). The addition of TBA, however, decreased the phenol decomposition to 43.2%. Therefore, it can be concluded that the contribution of hydroxyl radical to the degradation of phenol in optimal conditions is 56.4% and the share of other radicals (like IO_4, IO_3) is 43.2%.

3.8. Kinetic of phenol decomposition in the $Us/IO_4^-/Fe^\bullet$ system

In this experiment, the effects of different parameters such as periodate concentration, nZVI loading; pH and initial phenol concentration on the kinetic of phenol decomposition were studied using modified Langmuir–Hinshelwood model (Equation 17) (Dobaradaran *et al.*, 2018). Table 1 shows the constant of first-order reaction rate (k-value) and the determination coefficient (R^2- value) of each parameter used in the system. As observed in this table, the R^2- values of all experimental tests were above 0.8. These results support the conclusion that phenol degradation in the process of US/Periodate/nZVI follows a first-order kinetic model. In addition, it can be concluded that the reaction rate (k) is significantly dependent on the concentration of phenol. For instance, at phenol concentration of 25 mg/L, the decomposition rate of phenol was 0.0827 min^{-1}, while the reaction rate at phenol concentration of 200 mg/L was decreased to 0.0039 min^{-1}.

$$ln\left(\frac{C}{C.}\right) = -kt \qquad (17)$$

where k is the rate constant; C and C. are initial and final concentrations of phenol in the system.

Table 1. The effect of studied parameters on kinetics of phenol decomposition

Parameter	Value	Equation	k_0 (min^{-1})	R^2	$t_{1/2}$ (min)
Periodate (mM)	1 mM	y = 0.0329x - 0.1407	0.0329	0.959	21.06382979
	2 mM	y = 0.0456x - 0.2208	0.0456	0.9593	15.19736842
	3 mM	y = 0.036x - 0.2131	0.036	0.9484	19.25
	4 mM	y = 0.0404x - 0.1786	0.0404	0.9602	17.15346535
	5 mM	y = 0.0273x - 0.0783	0.0273	0.9907	25.38461538
	6 mM	y = 0.0252x - 0.1092	0.0252	0.9527	27.5
pH	3	y = 0.0347x - 0.1893	0.0347	0.9379	19.97118156
	7	y = 0.0144x - 0.0418	0.0144	0.9501	48.125
	11	y = 0.0105x - 0.027	0.0105	0.9491	66
Phenol (mg/L)	25	y = 0.0827x - 0.6247	0.0827	0.8083	8.379685611
	50	y = 0.0575x - 0.1556	0.0575	0.9895	12.05217391
	100	y = 0.0127x - 0.0139	0.0127	0.9965	54.56692913
	150	y = 0.01x - 0.0359	0.01	0.984	69.3
	200	y = 0.0039x + 0.0119	0.0039	0.9707	177.6923077
nZVI (mM)	0.5	y = 0.0336x - 0.2563	0.0336	0.8576	20.625
	0.6	y = 0.0353x - 0.2617	0.0353	0.8375	19.63172805
	0.7	y = 0.0339x - 0.2368	0.0339	0.8783	20.44247788
	0.8	y = 0.0396x - 0.1106	0.0396	0.964	17.5
	0.9	y = 0.0401x - 0.1289	0.0401	0.9767	17.28179551
	1	y = 0.0431x - 0.2923	0.0431	0.9234	16.07888631
	2	y = 0.0451x - 0.1151	0.0451	0.9846	15.36585366
	3	y = 0.0575x - 0.1556	0.0575	0.9895	12.05217391
	4	y = 0.0403x - 0.2702	0.0403	0.9116	17.19602978
	5	y = 0.0399x - 0.2847	0.0399	0.8811	17.36842105

4. Conclusion

The results of this study revealed that the US/Periodate/nZVI system is robust in degradation of phenol with an initial concentration of 50 mg/L by 5 mM nano zero valent iron, 3 mM periodate at an ultrasonic reactor with a fix frequency (40 kHz), temperature (33±1) and power (350 W) within 1 h. It is also established in the present work that phenol degradation by US/Periodate/nZVI system follows the first-order kinetics.

In addition, the results of COD removal showed that US/Periodate/nZVI system is effective in elimination of COD from aqueous solutions. It can be concluded that the developed system is a promising and effective method for degradation of phenol from water solutions.

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