Decolouration of H_2SO_4 leachate from phosphorus-saturated alum sludge using H_2O_2 and advanced oxidation processes in phosphorus recovery strategy

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ABSTRACT

As a part of attempt for phosphorus (P) recovery from P-saturated alum sludge, which was used as a low-cost P-adsorbent in treatment reed bed for wastewater treatment, decolouration of H_2SO_4 leachate obtained from previous experiment, possessing a great deal of P, aluminum and red-brown coloured materials (RBCMs), by using H_2O_2 and advanced oxidation processes (AOPs) was investigated. The use of H_2O_2 and AOPs in the forms of Fenton (H_2O_2/Fe^{2+}) and photo-Fenton ($UV/H_2O_2/Fe^{2+}$) were tested. The changes in colour and total organic carbon (TOC) were taken place as a result of mineralization of RBCMs. The results revealed that all of these three processes examined were efficient. It was found that about 98 % colour and 47 % TOC can be removed under photo-Fenton treatment after 8 hours of UV irradiation. Correspondingly, the reaction rates of H_2O_2 and Fenton systems were slow, but 100 % colour and 59 % TOC removal of H_2O_2 process and 100 % colour and 67 % TOC reductions of Fenton process can be achieved after 72 hours of reaction. The changes of structure and molecular weight/size of RBCMs were also evaluated by HPLC and UV-vis spectroscopic analysis. From the results, some chromophores of RBCMs such as aromatic groups were appeared to be easily degraded to the smaller refractory components. Hence, based on the experimental results and considering the investment and expediency of operation, H_2O_2 and Fenton oxidation could be suitable technologies for the treatment of the RBCMs derived from P-extraction stage by using H_2SO_4 leaching.

Keywords: Natural organic matter; peroxide; advanced oxidation process; Fenton reaction; colour; total organic carbon

Introduction

During the series of incessant succession of research projects at University College Dublin, Ireland aimed at investigating the beneficial reuse of a widely generated water industrial by-product, i.e. dewatered aluminium-coagulated drinking water treatment sludge, as a substrate in engineered wetlands for wastewater treatment,[1] the alum sludge-based engineered wetland systems have been developed particularly for enhanced phosphorus (P) removal. Such the development makes a new and novel way of (re)using the waste sludge as opposed to landfilling it.[2] In line with the P recovery study from the P-saturated sludge after use in the engineered wetlands, P desorption/extraction was investigated and the H_2SO_4 has been demonstrated as an efficient and cost-effective reagent for such kind of P extraction.[3] However, soluble organics including some humic substances in the sludge have also been found to be released to the H_2SO_4 solution during P extraction since the chemical oxygen demand (COD) and total organic carbon (TOC) are extremely high in the P extraction solution, exhibiting a red-brown colour. Thus, the released soluble organics is termed as "red-brown coloured materials" (RBCMs) in this paper. It is understood that the RBCMs were natural organic matter (NOM) derived from the source water and transferred to the sludge during the water purification processes such as coagulation, flocculation, sedimentation and filtration. Although the RBCMs may contain different kinds of organics, their dark colour is consistent with some humic substances, which are ubiquitous, heterogeneous biopolymers resulting from microbial and chemical transformations of organic debris and widely present in terrestrial and aqueous environments.[4-6] Without a doubt, certainly, such the RBCMs have to be removed in the P recovery process if the pure phosphorus compound is expected to be formed in the P recovery strategy.

Extensive research has been conducted worldwide for the removal of natural organic matters (NOM) from natural source water. The removal methods include enhanced coagulation,[7] membrane separation,[8] carbon adsorption [9] and advanced oxidation processes (AOPs).[10-13] AOPs have been emerged as the highly efficient methods for the decomposition of a wide range of pollutants since they are characterized by generation of very reactive hydroxyl radicals (HO•), with a non-selective and higher oxidation potential (2.8 V) than that of O_3 (2.07 V), H_2O_2 (1.78 V), MnO_4^- (1.69 V).[14-16] In addition, AOPs have been proven to oxidize NOM into innocuous end products such as CO_2 and H_2O, without producing other aqueous pollution problems. Therefore, AOPs are the cutting-edge technologies, which are increasingly adopted for the removal of many kinds of organic pollutants to meet the new challenges of water pollution control accompanied with the world economical and societal development.[17-21]

The objective of this study was to determine the feasibility and effectiveness of using single oxidants, i.e. H_2O_2, and the AOPs of Fenton (H_2O_2/Fe^{2+}) and Fenton/UV processes to degrade the RBCMs which exist in the H_2SO_4 leachate during P extraction in our previous study.[3] The high RBCMs-containing solution was subjected for several tests to evaluate the effectiveness of their removal/degradation. The role of reaction time and initial concentrations of Fe^{2+} and H_2O_2 to influence the RBCMs degradation was evaluated. Furthermore, changes on structure and molecular weight of the RBCMs in the P-extraction solution were investigated by HPLC (high performance liquid chromatography) and UV-via spectroscopic analysis, which provided have given the insight into of the reactions.

Materials and Methods

Materials

The High RBCMs-containing solution studied was the leachate from P-saturated alum sludge, which was used as substrate in laboratory scale engineered wetland for an animal farm wastewater treatment. The leachate/solution was obtained during P desorption study by using H_2SO_4 leaching at a dose of 0.063 M.[3] By using inductively coupled plasma-mass spectrometry (ICP-MS), Hach spectrophotometer (DR/2800) and pH meter (ATI ORION, model 720A), the sample solution was characterized and the results were listed in Table 1. Analytical grade hydrogen peroxide solution (30 %, w/w) and ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) were used and they were purchased from Riedel-deHaën Chemical as received.

[Table 1 here]

Experimental procedure

The experiments were carried out in a room temperature. A batch of 100 ml samples was put into a series of 250 ml flask added with different volume (0.5-10 ml) of hydrogen peroxide (H_2O_2) or different quantity of Fenton reagents. Thereafter, the flasks were placed on an orbital shaker (SSL1, Bibby Sterilin LTD, UK) at 220 rpm for a certain period shaking. Meanwhile, samples were taken from the flask at some specific shaking time for colour measurement

Photodegradation tests were conducted in a Pyrex glass beaker of 250 ml capacity, as shown in Fig.1. The reaction mixture inside the beaker, consisting of 100 ml sample solution and the precise amount of Fenton reagent, was continuously stirred with a magnetic bar. The sample solution was illuminated with a shortwave ultraviolet lamp (Model R-52G, UVP, USA), which is a highly uniform 254 nm UV source with high-intensity of 1.25 mW/cm^2 at 6 inches with the filter. The beam was parallel and the length between lamp and surface of the solution was kept 12 cm. The lamp was warmed up for 10 minutes to reach constant output. Samples were taken at a regular time interval to determine the color removal.

Pre-test has shown an insignificant change of pH (in order of 0.1−0.3 units) during the reaction process. Therefore there was no pH re-adjustment during the experiments reported.

All the experiments were repeated twice or three times and the results were shown in average value.

[Figure 1 here]

Analytical techniques

Measurements of colour were performed as per standard method using the HACH spectrophotometer (model DR-2800) according to standard method. H_2O_2 residual was roughly monitored by Merchkoquant peroxide test strips (0.5−25 mg/L). In order to monitor the mineralization of RBCMs, measurements of TOC (100−700 mg/L) of sample solution, were conducted using the same HACH DR-2800 spectrophotometer following the sample digestion at 105 ^{o}C for 2 hours in a HACH DRB200 digester.

UV-vis spectroscopic measurements of the samples were performed on a Unicam heλiosα UV-vis Spectrophotometer using 1 cm quartz cells. Specific UV absorbance at 254 nm, 280 nm and 400 nm (defined as UV_{254}, UV_{280} and $Color_{400}$) were used to represent the concentrations of TOC, the normalized aromatic moieties and the color of the solution, respectively. To obtain more insight into the nature of RBCMs before and after treatment, the change of molecular size of RBCMs was measured by HPLC. The system consists of a Waters 1515 isocratic pump, a Waters 2487 UV dual λ detector operated at 254 nm, A PL Aquagel-OH 40 (300×7.5 mm) column. The mobile phase is 20 mM phosphate buffer solution (1.36g/L KH_2PO_4, 3.58 g/L Na_2HPO_4, pH=6.85). The eluent flow rate was 1.3 mL/min. 10 μL samples were injected into the system manually

Results

RBCMs degradation by different systems

H_2O_2 oxidation

Fig. 2 shows the RBCMs degradation in the form of colour removal of sample with reaction time at different H_2O_2 concentrations. It can be seen from Fig. 2 that, during its initial stage, the percentage decrease of color rapidly increased with increasing initial H_2O_2 concentration. It was observed that after one hour, the colour removal by 0.05, 0.10, 0.19, 0.38, 0.55, 0.73 and 0.89 M H_2O_2 was 5.9 %, 9.0 %, 10.1 %, 24.2 %, 29.5 %, 36.8 % and 38.2 %, respectively. But after 24 hours, there is no significant difference of color removal efficiencies with various H_2O_2 concentrations tested. After 72 hours, over 99 % color removal was achieved regardless of the H_2O_2 concentrations adopted. Obviously, during the first 8 hours, the increase of the initial H_2O_2 concentration was mailnly due to speed up the reaction. After ample reaction time and also at the end of the reaction, nearly all the color has been removed/degraded and thus the reactions under different H_2O_2 concentrations become the same. In view of using fewer reagents, the H_2O_2 concentration of 0.05 M and 0.10 M were adopted in subsequent experiments.

[Figure 2 here]

Residual H_2O_2 and TOC removals at different initial H_2O_2 concentrations were measured at 24 hours, 48 hours and 72 hours, respectively, and the results were showed in Table 2. It can be seen that when initial concentration is 0.05 M, H_2O_2 was fully consumed after 72 hours, corresponding TOC removal was found 58.8 %. This indicates a significant removal/degradation of RBCMs which have been mineralized to CO_2 and H_2O. As compared with the case of 0.05 M H_2O_2 used, when H_2O_2 initial concentration is 0.10 M, there was still around 0.74 mM H_2O_2 left in the system after 72 hours. However, the TOC remains the same level of removal under the two H_2O_2 concentrations.

[Table 2 here]

Fenton treatment

The results of the Fenton treatment for colour removal with and without stirring were illustrated in Fig. 3. The dosage of Fenton reagent was 0.5 mM for Fe^{2+} and 0.05 or 0.1 M for H_2O_2 in 100 ml sample. As shown in Fig. 3, there is little difference between stirring (at 220 rpm) and non-stirring during the Fenton reaction regarding the colour removal. There is also no obvious trend of colour removal with the H_2O_2 dosage between 0.05 M and 0.1 M. However, it is evident that the colour removal was enhanced with Fenton reaction time especially in the first 8 hours of test. The colour removal efficiency remains insignificant change after 24 hours of reaction, at that time and it was noted that over 95 % of colour was removed during this period. It should be noted that a negative removal of colour, as shown in Fig. 3, was appeared in the first hour of reaction since Fe^{2+} was oxidized by H_2O_2 to Fe^{3+} which exhibited brown/yellow colour at the beginning of reaction.

[Figure 3 here]

Table 3 provides the results of Fenton treatment on TOC removal. It is very interesting to point out that although there is no obvious difference on colour removal between stirring and non-stirring, stirring clearly benefits the TOC removals. As shown in Table 3, stirring can enhance the speed of H_2O_2 exhaustion and therefore it leads to additional 8 % (on average) TOC removals from 24 hours to 72 hours reaction. In particular, this has been highlighted in the case of initial H_2O_2 of 0.1 M being adopted. RBCMs degradation by Fenton reaction can be simply described by equation 1.

$$\text{RBCMs} + H_2O_2 + Fe^{2+} \rightarrow \cdots\cdots\rightarrow \text{RBCM}_{\text{mineralized}} + CO_2 + H_2O + Fe^{3+} \quad (1)$$

194 It is clear that the part of the RBCMs can be mineralized to CO_2 and H_2O. Stirring is therefore
195 beneficial for continuous reaction by blowing CO_2 from the solution, leading to higher TOC
196 (RBCMs) removal. Thus, stirring was adopted in the ensuing experiments
197 [Table 3 here]
198
199 To further clarify the influence of H_2O_2 and Fe^{2+} dosages on RBCMs degradation, Fig. 4 and
200 Table 4 provides the results of Fenton treatment with two levels of H_2O_2 and three levels of
201 Fe^{2+} dosages. As expected, the color removal increased with increasing concentration of Fe^{2+},
202 as shown in Fig. 4. This can be explained by the production of hydroxyl radical (HO•) related
203 to Fe^{2+} concentration. When the initial concentration of Fe^{2+} is less than 0.5 mM, the
204 production rate of hydroxyl radical has a linear relation with Fe^{2+} in the first stage of Fenton
205 process.[22] This can also be confirmed by the decrease of H_2O_2 which is showed in Table 4.
206 Higher Fe^{2+} concentration will accelerate H_2O_2 to produce HO•. Interestingly, it is noted from
207 Fig. 4 that, when the Fe^{2+} concentrations remain the same levels, addition of H_2O_2 of 0.1 M
208 shows the less color removal efficiency than that of 0.05 M within 8 hours. This would be due
209 to self-decomposition of H_2O_2 to O_2 and H_2O, and the recombination of HO• radicals.[23]
210 However, it can be seen from Fig. 4 that, after 24 hours reaction, both 0.05 M and 0.1 M H_2O_2
211 showed similar ability for colour removal. It should be pointed out that during the final stage of
212 the Fenton reaction, higher Fe^{2+} would have a negative effect on color removal. It may be
213 derived from the oxidation of residual Fe^{2+} to Fe^{3+} which exhibited yellow in color in the
214 solution.
215 [Figure 4 here]
216 [Table 4 here]
217

In regard to TOC removal, it has increased with increasing reaction time but higher Fe^{2+} seems to have adverse influence on TOC removal especially in longer time reactions, as shown in Table 4. The maximum TOC removal of 67.0 % was achieved at 72 hours by addition of 0.1 M H_2O_2 and 0.125 mM Fe^{2+}. On such condition, the color was fully eliminated.

Photo-Fenton treatment

Fig. 5 and Table 5 show the results of colour and TOC removal during photo-Fenton process. The blank, i.e. the only UV irradiation, was conducted, which indicates that there is no use for enhancing color removal under the current UV lamp. Comparing the results with those shown in Fig. 4, the similar trends were observed. However, it is obviously noted that the photo-Fenton treatment significantly improves the color removal. After 8 hours UV irradiation, 98.0 % color and 47.2 % TOC were removed by addition of 0.05 M H_2O_2 and 0.5 mM Fe^{2+}.

[Figure 5 here]

[Table 5 here]

UV-vis spectroscopic analysis

The UV-vis absorption spectra provide a useful tool to identify the change of structural characteristics and molecular weight of RBCMs. Such investigations of the selected samples before and after the different treatment processes were carried out and the results jointly illustrated in Fig. 6. The three treated samples (S1-S3) were collected from each of the following treatment processes at the optimal testing conditions which indicate in the legend of Fig. 6: H_2O_2 oxidation (S1), Fenton reaction (S2) and photo-Fenton treatment (S3). It is well known that the UV-vis spectra of RBCMs are broad, featureless and monotonously decrease with increasing wavelength. For the original sample (S0), it has a high absorbance between 200−330 nm. After 330 nm, the absorbance decreases sharply with increasing wavelength, as shown in Fig. 6. Notably, compared with S0, the significant decrease of absorbencies of S1, S2

and S3 after treatments can be observed in Fig. 6. It should be pointed out that the S3 was tested at a high Fe^{2+} concentration with short reaction time, this may cause the S3 curve being above the S1 and S2 in Fig. 6 since the UV illuminating can promote to produce a great deal of Fe^{3+} which has a similar absorbency characteristics with RBCMs in 200−400 nm regions, thus resulting in a negative effect of the UV-vis absorption spectra. As per literature, various absorption at wavelengths of 250, 254, 270, 280, 300, 365, 400, 436 and 465 nm as well as ratios like Abs_{250}/Abs_{365}, Abs_{465}/Abs_{665} have been cited for the spectral differentiation of NOM.[24] Among them, absorbencies at 254 nm (UV_{254}) and 400 nm ($Color_{400}$) were interchangeably measured with TOC and colour, respectively.[6,25,26] The range of 260−290 nm indicates the occurrence of π-π* electron transitions for phenolic substances, aniline derivatives, benzoic acids, polyenes and polycyclic aromatic hydrocarbons.[27] Moreover, since many of these substances are precursors or components of certain types of NOM, the value of absorptivity at 280 nm (UV_{280}) may yield important clues regarding the degree of aromaticity, source functions, extent of humification and possible molecular weight.[28] Thus, similarly in this study, absorptivity at 280 nm is specially viewed as an indication of the structural feature of RBCMs. It can be seen from Fig. 6 that the shoulder in the range of 260−290 nm of S0 disappeared as a result of the treatments especially in H_2O_2 oxidation and Fenton process. These results suggest that some unsaturated components, such as aromatic moieties in the RBCMs, may well be degraded during these treatments.

The attached diagram within Fig. 6 is the plot of ΔlogK corresponding to S0, S1, S2 and S3. The ΔlogK is a major parameter, which is increased with the molecular size of NOM and free radical concentration.[29] The value of ΔlogK can be calculated by subtracting the logarithm of the absorptivity at 600 nm from that at 400 nm. As shown in Fig. 6, the obvious decreases in ΔlogK values of all treated samples especially for S2 were observed, providing hard evidence of the fact that some RBCMs were broken down into smaller molecules after these treatments.

As a visible appearance, Fig. 7 shows the original and treated samples marked as S0, S1, S2 and S3 with previous denotation.

[Figure 6 here]

[Figure 7 here]

Result of HPLC measurement

HPLC was employed to monitor the molecular size of the RBCMs before and after the treatment based on the principle of size-exclusion. It is understood that the large molecular size will be detected first followed by the small molecular size of the RBCMs. Similarly, big peak/absorbance indicates the strong amount of RBCMs and small peak refers to the light amount of the RBCMs. From Fig. 8, it is seen clearly that the RBCMs before treatment (S0) possess heavy mass with big molecular size while the RBCMs after treatment (S2) exhibit small molecular size with low amount, indicating the breakdown of the RBCMs by Fenton reaction.

[Figure 8 here]

Discussion

Although the degradation of NOM has been investigated extensively in the literature, it is noted that, NOM came from either some industrial products or isolated from special nature organic materials as per the investigations reported. Hence, the components of NOM are relatively simple and the concentrations are lower than the samples investigated in this study. As described earlier, the samples studied currently were derived from a novel study aimed at reusing the dewatered alum sludge cake as P adsorbent and biofilm carrier in constructed wetland for P-rich wastewater treatment.[2,3] After a long time operation in wetland of reuse, the alum sludge was finally saturated by P from the wastewater. In order to not only decrease

293 the risk of disposal of P-saturated alum sludge but also try to recovery P from it as a recycled
294 resource, extraction by using H_2SO_4 was proved to be an efficient and economic method for P
295 release. [3] However, RBCMs and metals such as Al, Ca, Mg and Fe were also released into
296 solution at the same time, forming a special sample with strong colour, low pH, high
297 concentrations of P, Al, RBCMs and other components (see Table 1). Therefore, there is a
298 necessity to remove colour and RBCMs from the H_2SO_4 extracted solution during the attempt
299 of obtaining the pure phosphate as final target in P recovery.

300 H_2O_2 oxidation was tested firstly because the nature of H_2O_2 is a strong (oxidation potential
301 =1.78 V), but not very specific oxidizing agent. As a result, high yields of degradation products
302 are expected. However, the results show that the reaction time is the key factor for colour and
303 TOC removal. The reason behind is that most substances do not react rapidly with H_2O_2 and, in
304 order to achieve oxidation, activation of H_2O_2, such as transition metal, alkaline conditions, is
305 required.[30] Whereas, H_2O_2 oxidation was carried out in this study at very low pH
306 (approximately 2). This may have caused the slow reaction and thus a long time reaction is
307 necessary.

308 The Fenton reagent has been shown to be effective in the degradation of a wide spectrum of
309 organic and inorganic pollutants.[31-33] More recently, Watts and Teel [34] reported an important
310 reaction during Fenton process:

311 $$HO_2\bullet \rightarrow O_2\bullet^- + H^+ \qquad (2)$$

312 These propagation reactions produce a pool of radicals with different reactive properties.
313 Hydroxyl radical (HO•) and perhydroxyl radical (HO_2•) are both oxidant although the latter is
314 relatively weak. Superoxide radical ($O_2\bullet^-$) is a weak reductant and nucleophile in aqueous
315 systems which may be responsible for an enhanced treatment of contaminants when they don't
316 react with hydroxyl radicals.[34] As a result, Fenton treatment can be used widely for
317 degradation of many kinds of pollutants.

Because Fe^{3+} ions exist mostly as hydroxyl complexes and soluble Fe^{2+} salts tend to co-precipitate with Fe^{3+} oxyhydroxides if ions are present at neutral pH, Fenton reaction is therefore most effective in acidic solution (pH~3) which keeps Fe^{3+} species soluble. [5] The pH of the samples in this study is around 2.1, thus it is suitable for Fenton reaction. As reported in Fig. 2 & 4 and Table 2 & 4, compared with H_2O_2 oxidation, Fenton reaction can increase distinctly the rate of colour removal within initial 8 hours. The possible reason maybe lies in the enhanced mass of radicals including HO•, HO_2• and O_2•$^-$ being produced and reacted quickly with some easily destroyed chromophores of RBCMs, such as aromatic ring in the first stage. However, the rate of radicals production becomes slow and the left components of RBCMs become difficult to be destroyed with increasing reaction time. Therefore, the overall colour and TOC removal efficiencies can't be improved significantly. It should be pointed out that, firstly, at low H_2O_2 concentration of 0.5 M, the H_2O_2 oxidation was slightly better than Fenton reaction for TOC removal (see Table 2, 4). The reason was assumed that, because of catalysis of Fe^{2+}, there are not only high oxidants of H_2O_2 and HO• but also weak oxidant of HO_2• and weak reductant of O_2•$^-$ in the reaction system. Thus, in low concentration of H_2O_2, the negative effect of HO_2• and O_2•$^-$ is striking, leading to H_2O_2 being slightly better than Fenton on total ability of oxidation. Secondly, the high concentration of Fe^{2+} brings a negative effect on TOC removal though it is positive for production rate of HO• in first stage of Fenton process. The supposed reason is that the excessive Fe^{2+} can be adsorbed by RBCMs due to the capability of RBCMs to complex metal ions [35] to form complex which is more difficult to be broken down into CO_2 and H_2O than RBCMs.

A combination of H_2O_2 and UV irradiation with Fe^{2+}, a so-called photo-Fenton process, can significantly enhance the decomposition of many refractory organic compounds. The main mechanism of photo-Fenton process is as follows:

$$H_2O_2 + Fe^{2+} \rightarrow Fe(OH)^{2+} + HO\bullet \quad (3)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO\bullet \qquad (4)$$

The acceleration for decomposition of organic compounds is believed to be in order to photolysis of iron aquacomplex, $Fe(H_2O)_5(OH)^{2+}$ (respected hereafter by $Fe(OH)^{2+}$), to providing a new important source of HO• radicals.[36,37] It is also confirmed from the results of this study that photo-Fenton showed the highest efficiency for colour removal. After 8 hours irradiation, 97.8 % colour was removed whereas only 54.7 % and 81.1 % colour were removed by H_2O_2 and Fenton processes, respectively, at the same reaction period of 8 hours. In addition, the high TOC removal of 47.2 % was also achieved in the same time.

Comparing the three processes tested in the current study, they are all based on the H_2O_2 oxidation actually. UV and Fe^{2+} act as the activator for improving the oxidation ability of H_2O_2. As per the results and the discussion, the photo-Fenton system showed the highest ability on colour and TOC removals. But considering the investment and danger of UV irradiation for operator, UV-assisted systems may not be the convenient and economical choice. Compared with H_2O_2 oxidation, Fenton system can increase TOC removal from 58.6 % to 67.0 % but a small quantity of ferrous salts addition is required. However, the main advantage of H_2O_2 oxidation is that it doesn't bring any additional compound to the system.

Conclusions

The H_2SO_4 leachate samples, consisting of a large amount of RBCMs, phosphate and aluminium, were treated by H_2O_2, Fenton and photo-Fenton systems, respectively, for the purpose of degradation of RBCMs in regard to colour and TOC. The results of colour and TOC removals showed that all of the three processes are efficient. Among them, photo-Fenton is the most efficient process because around 98 % colour and 47 % TOC were removed after 8 hours reaction. For H_2O_2 and Fenton systems, the reaction rate is comparatively slow and the reaction

time is the key factor for colour and TOC removals although 100 % colour and 58.6 % TOC could disappear by using H_2O_2 while 100% colour and 67.0 % TOC could be eliminated by using Fenton oxidation, both in 72 hours of reaction. It was found that higher concentration of H_2O_2 (0.1 M) is favourable than that of 0.05 M for colour removal. However, excessive Fe^{2+} brings a negative effect on TOC removal. Bearing in mind of the main objective of this study, it lies in seeking a RBCMs reduction approach which is efficient and easy to operate in practice. Therefore, considering the investment and danger of UV irradiation, H_2O_2 and Fenton system could be suitable methods for practical operation.

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Table 1 The characteristics of the sample (P-extraction leachate)

pH	Color (Pt-Co units)	Chemical oxygen demand (COD) (mg/L)	Total organic carbon (TOC) (mg/L)	Phosphorus (as PO_4^{3-}) (mg/L)	Aluminum (Al) (mg/L)	Calcium (Ca) (mg/L)	Magnesium (Mg) (mg/L)	Iron (Fe) (mg/L)
~2.1	4100	1026	430	720.6	346.4	74.8	10.88	8.98

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Table 2: H_2O_2 residual and TOC removal at different H_2O_2 concentrations

H_2O_2	Residual H_2O_2 (mM)			TOC removal (%)		
	24 hrs	48 hrs	72 hrs	24 hrs	48 hrs	72 hrs
0.05 M	> 0.74	> 0.74	0	45.58	52.79	58.84
0.1 M	> 0.74	> 0.74	0.74	38.37	48.79	58.60

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Table 3: Results of H_2O_2 residual and TOC removal during Fenton reagent treatment

	Residual H_2O_2 (mM)			TOC removal (%)		
	24 hrs	48 hrs	72 hrs	24 hrs	48 hrs	72 hrs
0.05 M H_2O_2 (NS)	0.15−0.29	0.15	0	38.84	41.40	44.56
0.05 M H_2O_2 (S)	0	0	0	49.30	49.77	51.40
0.10 M H_2O_2 (NS)	> 0.74	0.29−0.74	0	43.49	50.47	58.03
0.10 M H_2O_2 (S)	> 0.74	0	0	57.67	62.56	64.42

Note: $C_{Fe^{2+}}$ = 0.5 mM; NS: non stirring; S: stirring (at 220 rpm)

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Table 4 Residual H_2O_2 and TOC removal using different H_2O_2 and Fe^{2+} dosages

H_2O_2 (M)	Fe^{2+} (mM)	Residual H_2O_2 (mM)			TOC removal (%)		
		24 hrs	48 hrs	72 hrs	24 hrs	48 hrs	72 hrs
	0.500	0	0	0	49.30	49.77	51.40
0.05	0.250	0.06	0	0	51.16	53.72	54.74
	0.125	> 0.74	0	0	46.28	53.95	54.88
	0.500	> 0.74	0	0	57.67	62.56	64.42
0.10	0.250	> 0.74	> 0.74	0	47.67	65.39	66.28
	0.125	> 0.74	> 0.74	0.15−0.29	40.47	57.44	66.98

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Table 5: H_2O_2 residual and TOC removal after 8 hrs photo-Fenton treatment

H_2O_2 (M)	0.05			0.10		
Fe^{2+} (mM)	0.500	0.250	0.125	0.500	0.250	0.125
Residual H_2O_2 (mM)	0.15−0.29	0.74	> 0.74	> 0.74	> 0.74	> 0.74
TOC removal (%)	47.21	36.05	24.65	43.26	33.49	25.58

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Figure captions

Fig. 1 Schematic diagram of the photo reactor

Fig. 2. The removal of color at different H_2O_2 concentrations

Fig. 3. Results of color removal via Fenton treatment

Fig. 4. Effect of different H_2O_2 and Fe^{2+} dosages on color removal

Fig. 5. Colour removals during photo-Fenton process

Fig. 6. UV-vis absorption spectra and ΔlogK before and after the different treatments

Fig. 7. The visible observation of the samples before and after different treatments: S0, original sample; S1, H_2O_2 oxidation; S2, Fenton reaction; and S3, photo-Fenton treatment

Fig. 8. Results of RBCMs molecular size monitoring before and after Fenton reaction by HPLC

618 Figure 1

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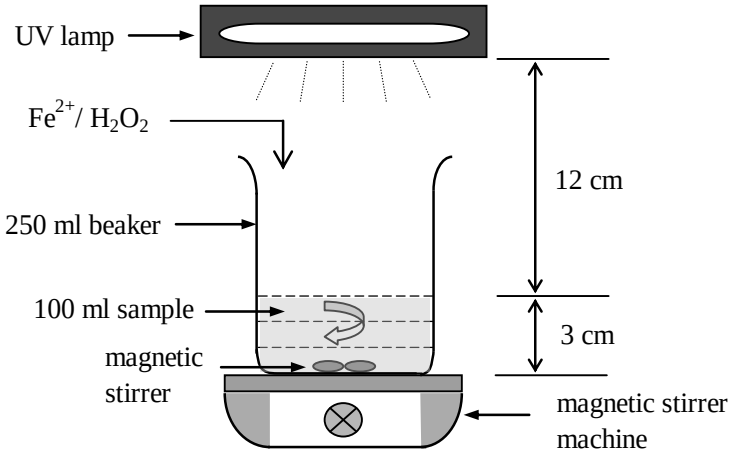

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637 Figure 2

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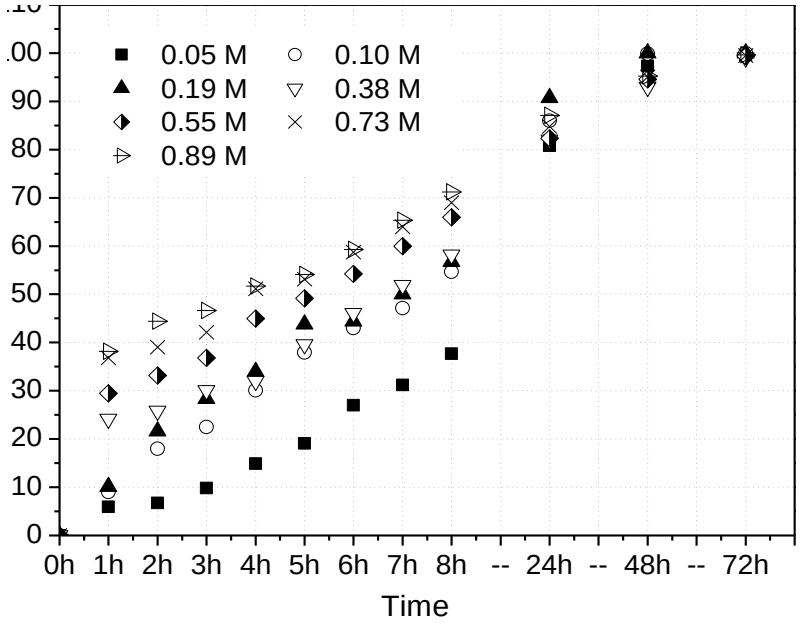

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653 Figure 3

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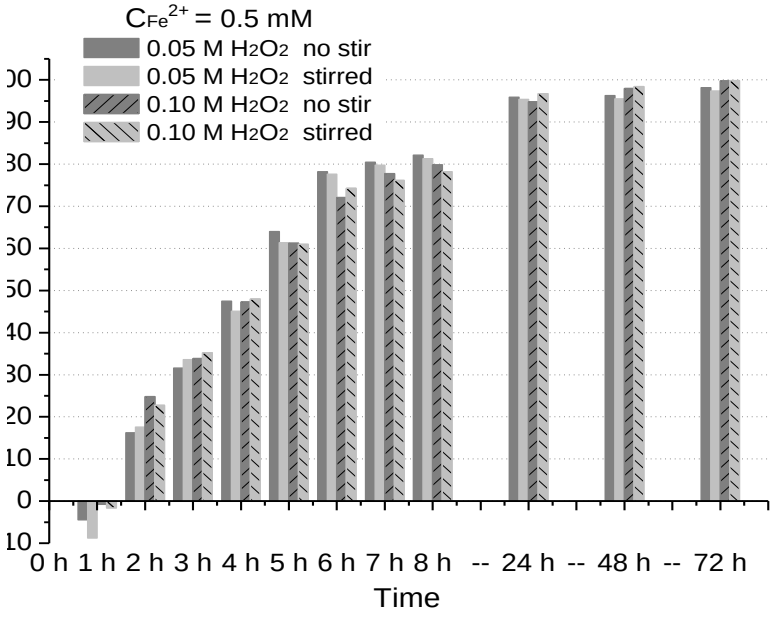

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670 Figure 4

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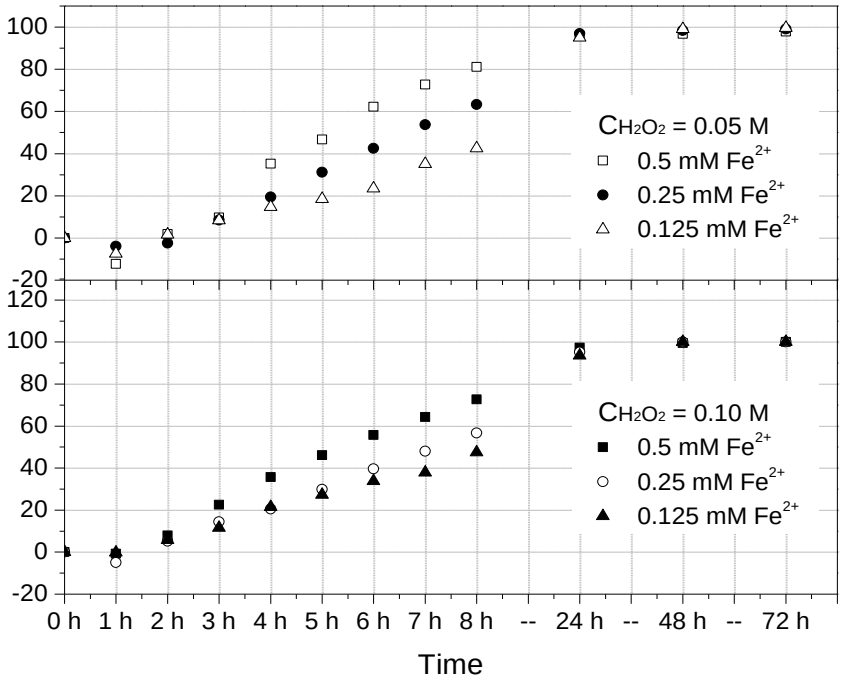

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685 Figure 5

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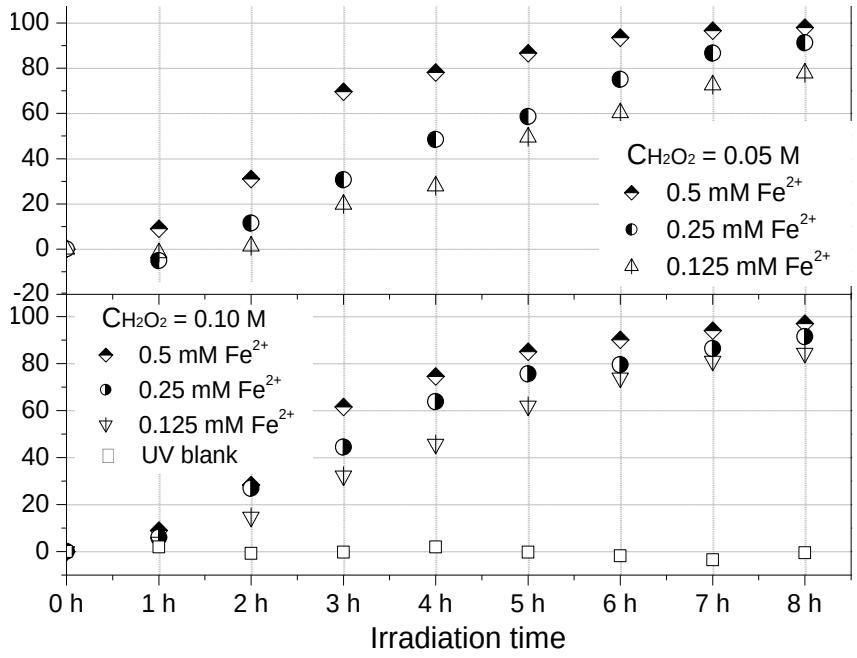

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701 Figure 6

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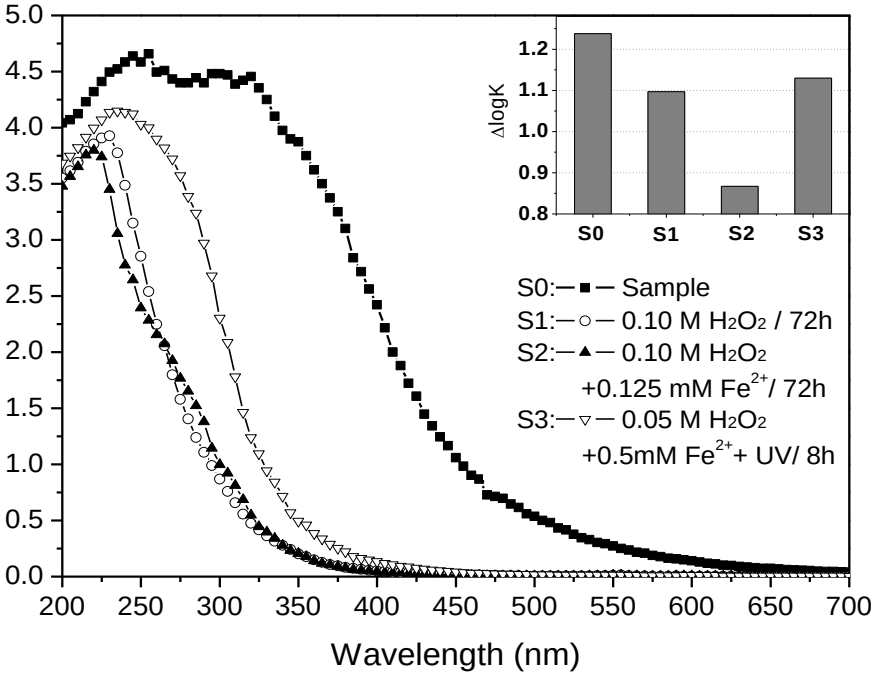

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Figure 7

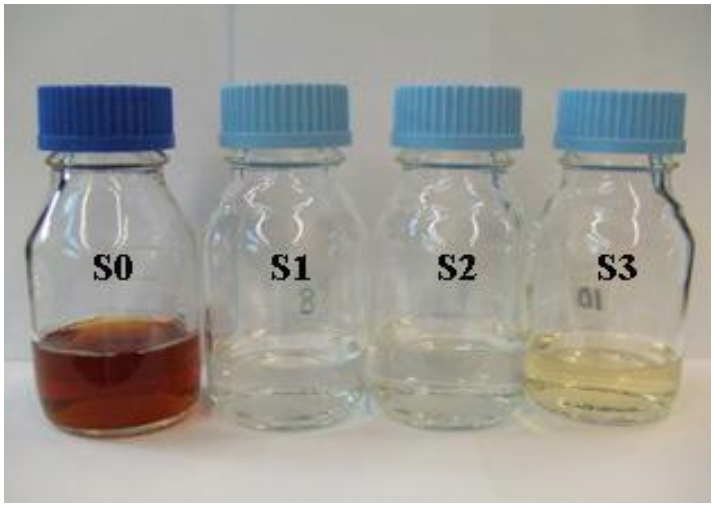
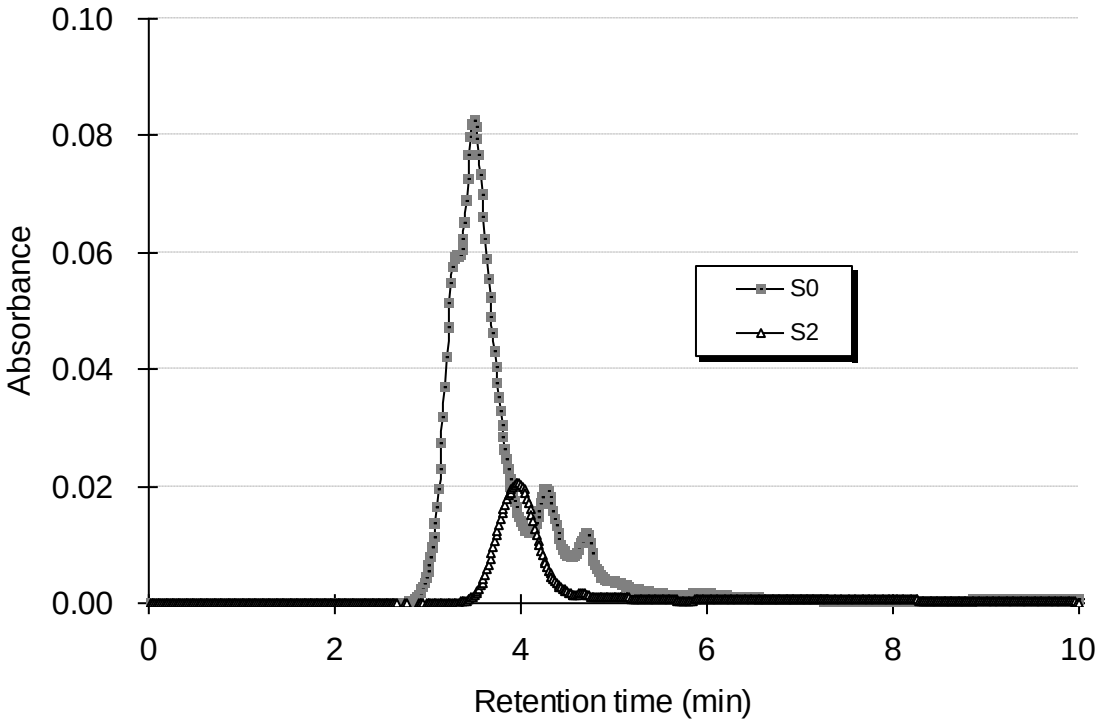


Figure 8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Retention time (min)
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