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Comparison of anaerobic pre-treatment and aerobic post-treatment coupled to photo-Fenton oxidation for degradation of azo dyes

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ABSTRACT

Photo-Fenton oxidation was used for treatment of synthetic textile wastewater as stand alone treatment, as pre-treatment before aerobic biological treatment and as post-treatment after anaerobic biological treatment. The processes were compared with regards to decolorization, chemical oxygen demand (COD) reduction and chemical consumption. When applying photo-Fenton alone for treatment of Remazol Red RR (100 mg/l), optimal conditions were 3.0 mM H_2O_2 and 0.25 mM Fe^{2+}. These conditions resulted in complete decolorization and a residual COD of 2.9 mg/l. When reducing the H_2O_2 dose to 1 mM, residual COD was 22 mg/l. In the combined photo-Fenton/aerobic treatment complete decolorization and COD removal was achieved at 3 mM H_2O_2 and 0.25 mM Fe^{2+}, while 9 mg/l of residual COD remained at the H_2O_2 concentration 1 mM. When applying photo-Fenton as post-treatment after the anaerobic step, the residual COD was 14 mg/l independent of the H_2O_2 concentration being set to 1 or 3 mM, however the Fe^{2+} concentration needed to be increased to 2 mM, due to complex formation with the phosphate added as a macronutrient. Phytotoxicity tests showed higher residual toxicity after the photo-Fenton treatment alone than after the combined processes. Our results thereby show that incorporation of a biological step leads to improved mineralization and reduced residual toxicity at lower H_2O_2 doses.

1. Introduction

Textile industries consume large amounts of water in the dyeing process and the resulting wastewaters are highly polluted with dyes, salts and other organic compounds. Azo dyes are the most commonly used dyes and due to their recalcitrant nature degradation by conventional wastewater treatment methods is difficult. If not properly treated their release can lead to reduced photosynthesis in receiving waters and they can be partially degraded under anaerobic conditions to form aromatic amines. Some of these amines are known carcinogens [1]. Common methods for treatment of textile wastewaters are precipitation or adsorption sometimes followed by biological treatment. These methods do however only transfer the pollutants from one phase to another, and the disposal of the hazardous sludge formed remains an unsolved problem. It is thereby crucial to find methods leading to complete degradation [2]. A commonly suggested treatment for textile wastewater is the combined anaerobic–aerobic biological process [3,4]. Even though most azo dyes are recalcitrant under aerobic conditions, reductive cleavage of the azo bond leading to decolorization and formation of aromatic amines can be achieved under anaerobic conditions. These amines are not further degraded under anaerobic conditions; nevertheless mineralization can be achieved when altering to aerobic conditions. The drawback of this treatment is that complete degradation cannot be guaranteed for all amines [5–7].

Advanced oxidation processes (AOPs) are based on the generation of highly reactive radicals (e.g. $HO^{\bullet}$) capable of degrading a wide range of pollutants [8–11]. Many AOPs have been evaluated for dye degradation such as ozonation [12], photocatalysis [13], H_2O_2/UV treatment [14] and Fenton or photo-Fenton processes [15]. In cost evaluations of different AOPs, Fenton's reagent and solar photo-Fenton have shown a good combination of effectiveness and operating costs [16,17].

The Fenton oxidation is a reaction where a mixture of ferrous iron and hydrogen peroxide is used. While being oxidized to ferric iron, ferrous iron catalyses the generation of hydroxyl radicals from hydrogen peroxide. The radicals attack the organic compound leading to degradation. The reaction is carried out in an acidic solution where Fe^{3+} does not precipitate. The Fenton reaction can be improved by combining it with radiation (UV or visible till 580 nm), which contributes to recycling of ferric ions, and to some extent also photolysis of hydrogen peroxide [9,18,19].

As with many other AOPs the main disadvantages are the high chemical requirement and energy consumption. Due to high operating costs, full-scale technical applications are still scarce. By combining the photo-Fenton treatment with a biological step, the

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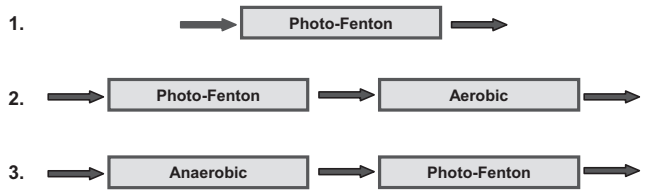

Fig. 1. Schematic diagram of the treatment methods.

chemical dosage as well as the cost could be reduced [20]. The process economy could be further improved by using solar energy as radiation source instead of UV-light [9,20,21]. When using an integrated photo-Fenton/biological system two approaches can be considered. In the first approach photo-Fenton is used as pre-treatment to break recalcitrant structures after which the more easily degradable intermediates could be degraded in a biological step [20,22,23]. In the second approach a biological pre-treatment is used to reduce biological oxygen demand (BOD), limiting the photo-Fenton treatment for recalcitrant molecules and not wasting chemicals on removal of biodegradable compounds [7,24,25]. Studies comparing photo-Fenton as pre- and post-treatment are however few. This work was therefore conducted to compare the feasibility of anaerobic/photo-Fenton treatment with photo-Fenton/aerobic treatment for degradation of the azo dye Remazol Red RR. The influence of pH and reagent concentrations was studied and the two processes were then compared with regards to decolorization, chemical oxygen demand (COD) reduction and chemical consumption. Finally a phytotoxicity test was conducted to measure residual toxicity.

2. Materials and methods

2.1. Experimental set-up

Three different treatments were conducted: photo-Fenton as stand alone treatment, photo-Fenton combined with aerobic biological post treatment and anaerobic pre-treatment followed by photo-Fenton (Fig. 1).

2.2. Inoculum

Aerobic sludge (total suspended solids 3.1 ± 0.1 g/l and volatile suspended solids 2.5 ± 0.1 g/l) and anaerobic sludge (total solids 1.6 ± 0.1% and volatile solids 1.3 ± 0.1%) was collected from Källby municipal wastewater treatment plant in Lund, Sweden.

2.3. Chemicals

The azo dye Remazol Red RR was provided by a textile factory in Tirupur, India, and used without further purification. H_2O_2 30% (Merck, Germany) and $FeSO_4 \cdot 7H_2O$ (ICN Biochemicals Inc, USA) were used for the photo-Fenton experiments.

Anaerobic medium was prepared by adding 10 ml of mineral salts solution, 1 ml of trace element solution, 1 ml of vitamin solution, 1 ml of ultra trace element solution and 1.5 ml of cysteine stock solution and diluting to 1.0 l with distilled water. pH of the medium was adjusted to pH 7 using 1 M H_2SO_4. The mineral salts solution contained (g/l): K_2HPO_4 53.5, NH_4Cl 30, NaCl 30, $CaCl_2 \cdot 2H_2O$ 11, $MgCl_2 \cdot 6H_2O$ 10. The trace element solution contained (mg/l): $FeCl_2 \cdot 4H_2O$ 2000, H_3BO_3 50, $ZnCl_2$ 50, $CuCl_2 \cdot 2H_2O$ 38, $MnCl_2 \cdot 2H_2O$ 41, $(NH_4)_6Mo_7O_{21} \cdot 4H_2O$ 5, $AlCl_3 \cdot 6H_2O$ 9, $CoCl_2 \cdot 6H_2O$ 5, $NiSO_4 \cdot 6H_2O$ 10, EDTA (salt) 50. Vitamin solution (mg/l): pyridoxamine 175, nicotinic acid 100, D-pantothenic acid Ca-salt 100, cyanocobalamin 54, 4-aminobenzoic acid 49, Pyridoxine·HCl 101, D-biotin 20, lipoic acid 50, folic acid 22, riboflavin 49, thiamin·HCl 56. Ultra trace element solution (mg/l): $Na_2SeO_3 \cdot 5H_2O$ 130, $NaWO_4 \cdot 2H_2O$ 690. The concentration of the cysteine stock solution was 23.4 g/l. Glucose was used as a carbon source at 150 mg/l.

The aerobic medium was prepared according to Jonstrup et al. [26].

2.4. Photo-Fenton

The photo-Fenton experiments were conducted using a solution of Remazol Red RR with the concentration 100 mg/l in 15 ml glass tubes filled with 10 ml of the dye solution. For optimization of Fe^{2+} concentration, 0.0125, 0.025, 0.05, 0.125, 0.25, 0.5 and 1 mM were tested, while the H_2O_2 concentration was set at 3 mM. For optimization of H_2O_2 concentration, 0.003, 0.01, 0.03, 0.3, 3, 30 and 300 mM were tested together with the optimal Fe^{2+} concentration. The samples were irradiated with an 18 W UV–vis blue-lamp (Sylvania Reptistar, Sylvania, USA, 30% UVA, 5% UVB) placed on 15 cm distance and stirring was provided at 50 rpm using a rocking table. To compare the efficiency of the photo-Fenton reaction with the Fenton reaction, one set of unirradiated samples were prepared containing optimal concentrations of H_2O_2 and Fe^{2+}. Controls for photolysis were prepared adding only dye solution and no reagents. The experiment was performed in triplicates.

2.5. Combined photo-Fenton/aerobic treatment

A solution of Remazol Red RR at a concentration of 100 mg/l was treated by photo-Fenton oxidation at pH 5 using 0.25 mM Fe^{2+} and four different H_2O_2 concentrations: 0.5, 1, 2 or 3 mM. Consumption of hydrogen peroxide was measured during the treatment. After treatment, nutrients for the aerobic biodegradation were added and pH adjusted to pH 7 using 0.1 M NaOH. Serum bottles (120 ml) were filled with 30 ml of treated dye solution and inoculated with 1 ml of activated sludge. The samples were incubated at room temperature and agitated at 150 rpm during 14 days. Controls for biomass adsorption were prepared containing the treated dye solution, nutrients and 1 ml of activated sludge, which had been autoclaved for 45 min. The experiment was performed in triplicates.

2.6. Combined anaerobic/photo-Fenton treatment

Serum bottles (120 ml) were filled with 70 ml of anaerobic medium containing 100 mg/l of Remazol Red RR. The efficiency of the photo-Fenton oxidation can be reduced in the presence of phosphate, added to the medium as a macronutrient, due to precipitation of ironphosphate which reduces the amount of iron available for the reaction [7]. Different phosphate concentrations were thus evaluated. The amount of PO_4^{3-} added as K_2HPO_4 was 0 mg/l, 147 mg/l or 294 mg/l, the two latter amounts corresponding to half of the amount and the total amount prescribed in the anaerobic medium. pH was adjusted to pH 7 using 1 M NaOH. The bottles were flushed with nitrogen gas for 4 min to remove oxygen and sealed with thick butyl stoppers and aluminum crimps. The anaerobic atmosphere of the gas phase was confirmed by gas chromatography and finally each bottle was inoculated with 1.5 ml of anaerobic sludge using a syringe. The samples were incubated at room temperature for 5 days. Controls for evaluation of biomass adsorption contained medium with dye and 1.5 ml of anaerobic sludge, which had been autoclaved for 45 min. After 5 days treatment the samples were centrifuged to separate the sludge. The supernatant was collected and pH was adjusted to 5 using 1 M H_2SO_4. The photo-Fenton treatment was conducted using 0.25, 0.5,

1 and 2 mM of Fe^{2+} and 1, 2 or 3 mM of H_2O_2. The experiment was performed in triplicates.

2.7. Phytotoxicity test

The phytotoxicity of the treated solutions was evaluated in a test using seeds of *Lepidium sativum*. The photo-Fenton treatment was conducted using optimal reagent concentrations and samples were collected after 0, 5, 15, 30, 60 and 120 min of treatment. Samples were also collected after the combined photo-Fenton-aerobic treatment and the combined anaerobic-photo-Fenton treatment. Remaining H_2O_2 was removed using 50 mg/l of catalase. The pH of the treated solutions was adjusted to pH 7 using 0.1 M NaOH and 2 ml of sample was added to glass Petri dishes (Ø 5 cm) containing a filter paper and 5 evenly distributed seeds of *L. sativum*. Tap water was used as control. The Petri dishes were incubated in the dark. After 5 days the length of the stem was measured. The stem length has been reported to give more reproducible results than the root length when determining inhibition [27]. Growth inhibition was calculated according to Eq. (1) and Grubb's test was used to detect potential outliers.

$$\text{Inhibition}\,(\%) = \left[\frac{\text{Control} - \text{Sample}}{\text{Control}}\right] \times 100 \quad (1)$$

2.8. Analytical methods

The O_2 gaseous concentrations were measured to confirm anaerobic conditions by withdrawal of 150 μl of gas sample and injection on a gas chromatograph with a thermal conductivity detector (Agilent Technologies 6890 N) equipped with Haysep N 80/100 mesh and molecular sieve 5A 60/100 columns separated with valves. Helium was used as carrier gas with a flow rate of 28 ml/min. Temperatures of detector, injector and column were 150, 105 and 60 °C, respectively.

Absorbance was measured at the wavelengths of maximum absorbance both in the visible (516 nm) and in the UV range (290 nm) using an Ultraspec 1000 UV–vis spectrophotometer (Pharmacia Biotech, Sweden). Spectrophotometric scanning between 200 and 800 nm was also performed using a 1601PC UV–vis spectrophotometer (Shimadzu, Japan). The samples were centrifuged at 13,000 × *g* for 10 min (Biofuge 13, Heraeus, Germany) prior to analysis and absorbance of the supernatant was measured. During the photo-Fenton treatment, 0.5 ml of sample was withdrawn and 0.5 ml of sodium sulfite solution (3.8 g/l) was used to quench remaining H_2O_2 and stop the reaction before absorbance measurements. Dilution with distilled water was done when necessary.

COD and PO_4^{3-} were determined using Dr Lange lab kits (LCK 114 and LCK 348, Hach Lange, Germany) and analysed with a LASA 100 spectrophotometer. Since hydrogen peroxide can contribute to measured COD values, an equation developed by Kang et al. [28] Eq. (2) was used to eliminate the interference. This equation can be used at H_2O_2 concentrations lower than 200 mg/l (5.88 mM).

$$\text{COD}(\text{mg/l}) = \text{COD}_\text{m} - 0.4706\,[\text{H}_2\text{O}_2]. \quad (2)$$

Hydrogen peroxide concentration was determined using a modified version of a spectrophotometric assay by Elovson Grey et al. [29]. The assay was performed in a quartz cuvette adding 660 μl distilled water, 100 μl glacial acetic acid, 40 μl sample and 200 μl 6% (w/v) KI. The shift in absorbance at 360 nm was measured during 2 min. The hydrogen peroxide concentration was calculated using a standard curve with a linear relationship in the range 0.01–3 mM.

3. Results and discussion

3.1. Optimization of photo-Fenton parameters

The Fe^{2+} concentration was varied between 0.0125 and 1 mM. Complete decolorization was achieved at the concentrations between 0.125 and 1 mM within 15 min (data not shown). Complete decolorization was also achieved at 0.05 mM Fe^{2+}, although it required almost 1 h. The reduction of the peak in the UV range, abs_{290}, was affected by the Fe^{2+} concentration to a higher extent. At 0.25 mM, abs_{290} was reduced by 94% in 1 h, while lower reduction efficiencies were shown at both lower and higher concentrations.

The H_2O_2 concentration was varied between 0.003 and 300 mM. Complete decolorization was achieved within 15 min at H_2O_2 concentrations between 0.5 and 300 mM, but not at lower H_2O_2 concentrations independently of treatment time (data not shown). The most efficient reduction of abs_{290} (93%) was obtained at a H_2O_2 concentration of 3 mM. Lower efficiencies were observed both at lower and higher concentrations. Emami et al. [30] reported recombination of hydroxyl radicals and radical scavenging effect of H_2O_2 at high H_2O_2 concentrations, which had a negative impact on decolorization efficiency. Optimal concentrations were thereby determined to be 0.25 mM Fe^{2+} and 3 mM H_2O_2.

An important observation was that the UV peak was never completely reduced at any of the tested concentrations. This could be due to the absorptive character of the Fenton reagents or the formation of organic complexes with iron and degradation intermediates [21]. The absorptive character of the reagents might thereby explain the reduced efficiency at the highest reagent concentrations. Measurements of absorbance in the UV range can thereby be considered as a qualitative rather than a quantitative parameter and needs to be complemented with COD analyses to confirm degradation yields.

No difference in decolorization efficiency was observed between the Fenton and photo-Fenton reaction. The photo-Fenton reaction was however slightly more efficient for reduction of aromatic structures. After 1 h of treatment, photo-Fenton resulted in 93% reduction of abs_{290} compared to the Fenton reaction reaching 89%, indicating that the UV light enhanced the efficiency of the Fenton reaction. These results are in agreement with those by Lucas and Peres [15] who observed little difference in terms of decolorization of Reactive Black, but more significant effect on mineralization. In the photolysis control, 3% decolorization was observed after 1 h, which shows that no significant degradation took place without addition of the Fenton reagents.

According to literature pH 3 is optimal for the photo-Fenton reaction [21,31]. This pH is however not compatible with a biological treatment and is far lower than the pH of the dye wastewater, which usually is in the alkaline range. It would thus be beneficial to run the reaction at a higher pH. pH values between pH 3 and 8 were evaluated and the decolorization is shown in Fig. 2. Complete decolorization and 93% reduction of abs_{290} was observed at pH 3–6. At pH 3 the samples were completely decolorized within 15 min, while 30 min were required at pH 4–5 and almost 1 h at pH 6. At pH 7 and 8 the reaction was slow initially, after which it was improved. After 8 h 100% decolorization and 80% abs_{290} reduction was reached at pH 7, while 70% decolorization and 35% abs_{290} reduction was reached at pH 8. pH was measured at the end of the treatment and the results showed that pH had decreased during the reaction. The sample set at pH 3 remained at pH 3 while the pH of the sample set at pH 4 decreased to 3.5 and the other samples decreased to a final pH of 5. The decrease in pH is due to the release of protons from the hydrogen peroxide during the photo-Fenton reaction. This might explain why the reaction was efficient also at higher pH, but only after a longer time.

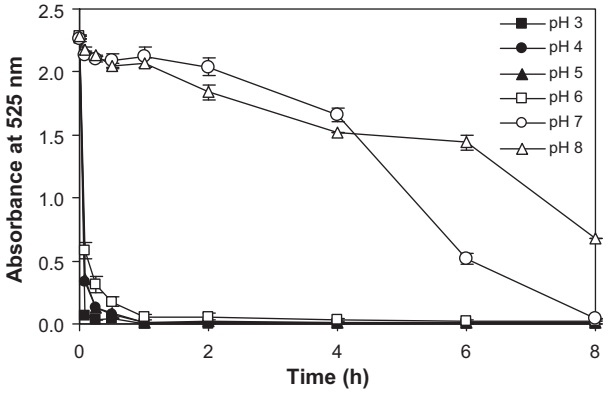

Fig. 2. Influence of initial pH on the decolorization of Remazol Red RR during photo-Fenton treatment. Remazol Red RR 100 mg/l, H_2O_2 3 mM and Fe^{2+} 0.25 mM.

3.2. Phytotoxicity test

A phytotoxicity test was conducted on solutions exposed to photo-Fenton treatment for 0–120 min. Lower growth inhibition was detected for the untreated dye than for its degradation products. A growth inhibition of 16% was observed for the untreated solution, while it increased to 45% after 5 min treatment to then decrease with treatment time to 43%, 41%, 24% and finally 16% after 15, 30, 60 and 120 min, respectively.

3.3. Combined photo-Fenton/aerobic treatment

To reduce chemical consumption, the H_2O_2 dose was varied to find the minimum concentration required for sufficient improvement of biodegradability. Focus was put on the H_2O_2 since it contributes to a significantly higher environmental impact than the Fe^{2+} [20]. Furthermore it is beneficial not to have excessive amounts of H_2O_2 remaining that might inhibit the biological step. Complete decolorization was achieved already during the photo-Fenton treatment at all the tested concentrations. Abs_{290} was reduced by 99% at 3 mM, 97% at 2 mM, 92% at 1 mM and 73% at 0.5 mM. COD was measured during the photo-Fenton reaction and the obtained values were corrected according to Eq. (2) to eliminate the interference of residual hydrogen peroxide. The main COD reduction took place within the first half an hour after which only a slight further reduction was observed (Fig. 3). This is in agreement with the trend of the hydrogen peroxide consumption (Fig. 4), which shows that most of the hydrogen peroxide was consumed already during the first half an hour of the treatment and only a minor amount remained at the start of the aerobic post-treatment. At 3 mM H_2O_2,

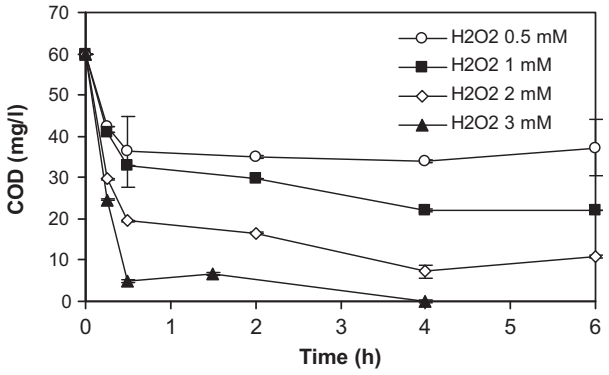

Fig. 3. COD reduction during photo-Fenton treatment of Remazol Red RR at 100 mg/l, using 0.25 mM of Fe^{2+} at pH 3.

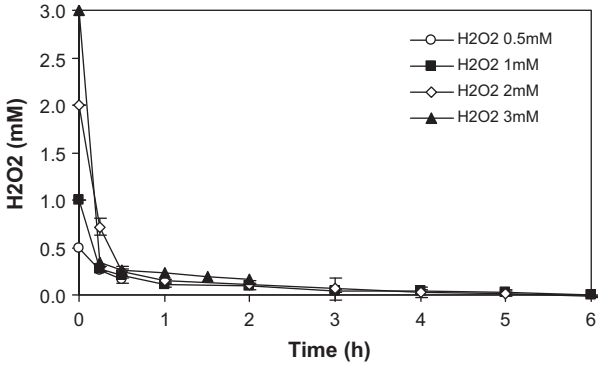

Fig. 4. Reduction of hydrogen peroxide concentration during the photo-Fenton treatment. Remazol Red RR 100 mg/l, Fe^{2+} 0.25 mM, H_2O_2 0.5–3 mM and pH 3.

95% COD reduction was achieved, while 82, 63 and 28% reduction were achieved at the concentrations 2, 1 and 0.5 mM, respectively. The values correspond to residual COD concentrations of 2.9, 11, 22 and 37 mg/l.

The total COD reduction after the combined photo-Fenton/aerobic process is presented in Fig. 5. In the samples with 3, 2, 1 and 0.5 mM of H_2O_2 the COD reduction was 100, 83, 86 and 58%, respectively. Complete reduction was achieved at 3 mM, although almost the entire part occurred already in the photo-Fenton step. Comparable COD reductions were obtained at the H_2O_2 concentrations of 1 and 2 mM; however a higher degree of COD reduction took place in the biological step at 1 mM. The remaining COD was 9.0, 9.2 and 24 mg/l in the samples treated with 2, 1 and 0.5 mM H_2O_2, respectively. No COD reduction was observed in the biomass adsorption controls.

The growth inhibition observed in the phytotoxicity test after the combined treatment was 1% at 0.5 mM H_2O_2, while no inhibition was detected after the treatment with higher H_2O_2 concentrations. This shows that the combined photo-Fenton/aerobic treatment is highly efficient both in terms of mineralization and detoxification of the treated dye. Furthermore, lower phytotoxicity was observed than when photo-Fenton oxidation was used alone.

3.4. Combined anaerobic/photo-Fenton treatment

Complete decolorization was achieved in the anaerobic treatment within 5 days at all the tested phosphate concentrations (Fig. 6). Absorbance was reduced by 11% in the biomass adsorption controls, which shows that adsorption only played a minor role as decolorization mechanism. Phosphate concentrations were measured after the treatment and the obtained values were 49, 110 and 232 in the samples with 0, 147 and 294 mg/l of PO_4 addition,

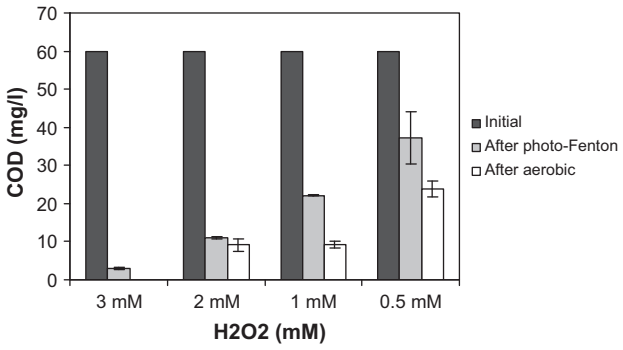

Fig. 5. COD reduction in the combined photo-Fenton/aerobic treatment as a function of H_2O_2 concentration. Remazol Red RR 100 mg/l, Fe^{2+} 0.25 mM.

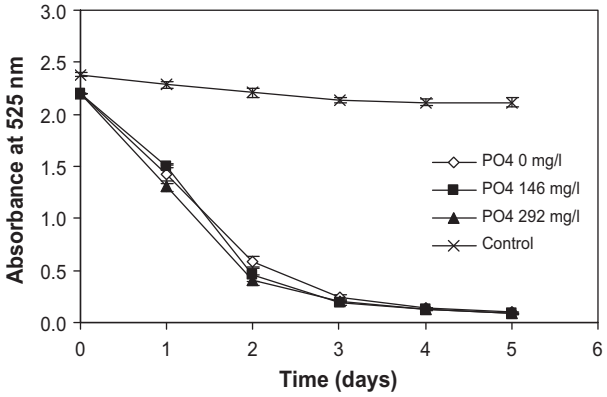

Fig. 6. Anaerobic decolorization of Remazol Red RR (100 mg/l) at varying phosphate additions.

respectively. The phosphate contribution from the added anaerobic sludge was determined to be 20 mg/l. A decrease in phosphate concentration was expected due to phosphate consumption during biomass growth. The increase at the lowest concentration could however be due to release of phosphate from decaying biomass. No reduction in UV absorbance was observed, although there was a shift in wavelength of maximal absorbance, from 290 nm to 267 nm (Fig. 7). The COD reduction after anaerobic treatment was comparable in all samples, from 222 mg/l to 69, 64 and 63 mg/l in the samples with 0, 146 and 292 mg/l of phosphate addition, respectively. The contribution of the dye to the initial COD was 60 mg/l, while the anaerobic medium, and glucose in particular, contributed to approximately 160 mg/l. Since the anaerobic treatment only results in azo bond cleavage and no further degradation, the COD reduction in this step was correlated to consumption of glucose. Since all the tested phosphate concentrations resulted in comparable decolorization and COD reduction yields, the samples without phosphate addition were chosen for further photo-Fenton treatment.

No degradation was achieved in the photo-Fenton treatment when adding 0.25 mM of Fe^{2+} and 0.5–3 mM of H_2O_2 to the anaerobically pre-treated solutions. This could be explained by less iron being available for the photo-Fenton reaction due to precipitation of ironphosphate. This phenomenon has also been reported by Garcia-Montano et al. [7] when using photo-Fenton as post-treatment of an anaerobically treated dye solution. The Fe^{2+} concentration was thus increased and 0.5, 1 and 2 mM Fe^{2+} were evaluated with 1, 2 or 3 mM H_2O_2 (Fig. 8a). Also 0.5 mM Fe^{2+} proved to be insufficient to obtain any further degradation. At the

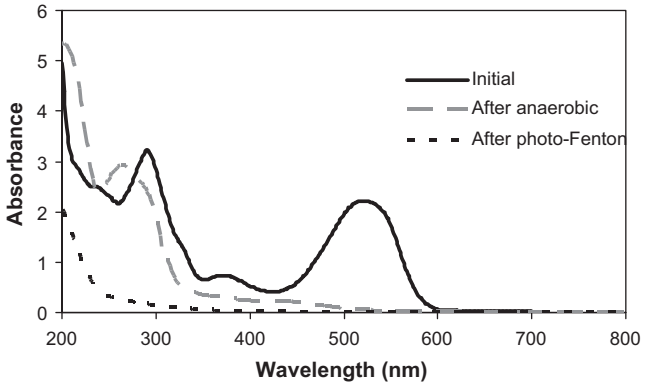

Fig. 7. UV–vis scanning between 200 and 800 nm of the initial dye solution, after anaerobic treatment (sample with no phosphate addition) and after photo-Fenton (Fe^{2+} 1 mM and H_2O_2 2 mM, pH 5).

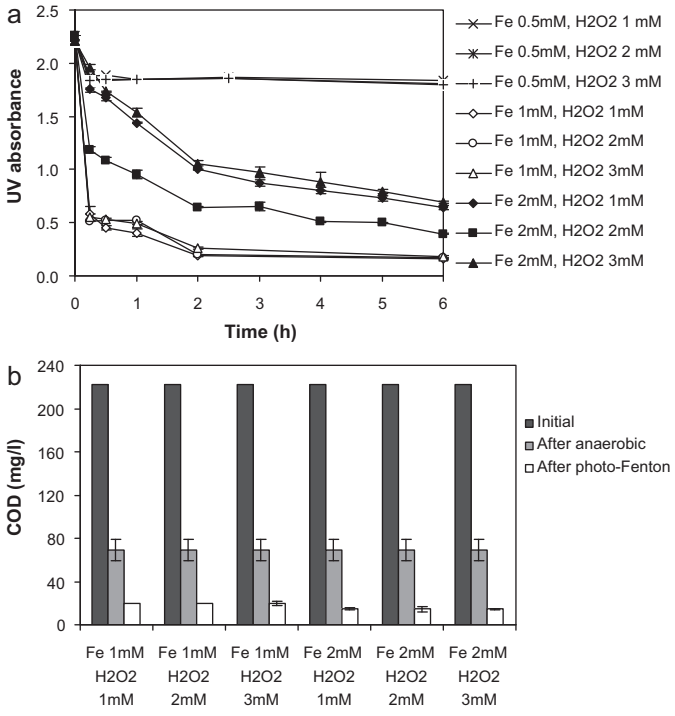

Fig. 8. (a) UV absorbance measured at 290 nm before treatment and at 267 nm after anaerobic and photo-Fenton treatment and (b) residual COD, as a function of Fe^{2+} and H_2O_2 concentrations.

Fe^{2+} concentration 1 mM, 90% reduction of abs_{267} was obtained within 2 h and 92% within 6 h, with insignificant difference between the hydrogen peroxide concentrations tested. When increasing the Fe^{2+} concentration to 2 mM, the absorbance reduction was 71% within 2 h and 82% within 6 h when combined with 2 mM H_2O_2. The efficiency was lower at 1 and 3 mM H_2O_2, 55 and 52% after 2 h and 71 and 69% after 6 h, respectively. The lower efficiency at the higher reagent concentrations could as previously mentioned be due to the radical scavenging effect of H_2O_2 at high concentrations, or the absorptive character of the reagents.

The COD reduction after the combined anaerobic/photo-Fenton treatment is presented in Fig. 8b and it can be seen that residual COD was comparable at 1 and 2 mM Fe^{2+} with a total COD reduction of 91% and 93%, respectively. It is worth to note that although the absorbance reduction indicated a more efficient process with the Fe^{2+}concentration 1 mM (Fig. 8a), the COD measurements revealed that the degradation was slightly more efficient at the higher iron concentration. This confirms that the absorptive character of the reagents might give the impression of a less efficient process, if only relaying on absorbance measurements. The H_2O_2 concentration had very little effect on the final COD reduction at respective iron concentration, although the reduction was slightly faster at 2 mM H_2O_2 than at the other concentrations. This indicates that the iron concentration is the limiting parameter when applying the photo-Fenton oxidation on water containing phosphate ions.

However it needs to be taken into consideration that initial COD was significantly higher (222 mg/l) in this treatment than in the photo-Fenton/aerobic treatment. It is thereby more fair to compare the treatments in terms of residual COD levels. Remaining COD at the Fe^{2+} concentration 1 mM and H_2O_2 concentrations 1–3 mM was approximately 20 mg/l, and 14 mg/l at the Fe^{2+} concentration 2 mM and H_2O_2 concentrations 1–3 mM.

In the study by Garcia-Montano et al. [7] only 59% dissolved organic carbon (DOC) removal was obtained even though significantly higher Fe^{2+} and H_2O_2 concentrations were tested. It was

suggested that the solution from the anaerobic treatment could be pre-treated to remove phosphate ions or that the dose of Fenton reagents could be increased. Our results show that these measures are not necessary. The efficiency of the treatment can instead be increased by decreasing the phosphate addition. Phosphate levels in textile wastewaters are very low, around 1 mg/l [17,32], hence almost the entire phosphate content will result from the amount required by the anaerobic process. In this study it was shown that high decolorization could be achieved at phosphate levels around 50 mg/l.

In the phytotoxicity test 0, 10 and 5% growth inhibition was observed at the Fe^{2+} concentration 1 mM with 1, 2 or 3 mM H_2O_2. At the higher iron concentration (2 mM Fe^{2+}) and 1, 2 or 3 mM H_2O_2, 0, 9 and 0% growth inhibition was observed. Residual H_2O_2 or degradation products could contribute to the measured phytotoxicity; it did however not show any correlation with the concentrations. The inhibition levels can be considered very low and are furthermore lower than the observed levels of the initial dye solution and after the photo-Fenton treatment.

Comparing the results obtained in the different treatments it can be concluded that integration of a biological step reduces the H_2O_2 consumption in the photo-Fenton treatment. When applying photo-Fenton as stand alone treatment 0.25 mM of Fe^{2+} and 3 mM of H_2O_2 were required to reach 3 mg/l residual COD. When decreasing the H_2O_2 dose to 2 mM, a final COD level of 11 mg/l was reached, while residual COD was 22 mg/l at 1 mM H_2O_2 dose. In the combined treatments, comparably lower residual COD levels were achieved. After the photo-Fenton/aerobic treatment 9 mg/l COD remained using the reagent concentrations of 1 mM H_2O_2 and 0.25 mM of Fe^{2+}. In the anaerobic/photo-Fenton treatment there was however a need of increasing the iron concentration from 0.25 mM to 1 mM, due to precipitation between iron and residual phosphate from the anaerobic step. After the anaerobic/photo-Fenton treatment at 1 mM H_2O_2 and 1 mM Fe^{2+}, residual COD was 20 mg/l. By increasing the Fe^{2+} concentration to 2 mM, the results improved further to a residual COD of 14 mg/l.

In conclusion the combined photo-Fenton-aerobic treatment gave the best results based on final COD levels at the lowest reagent dosage. Nevertheless, it needs to be taken into consideration that the initial COD was significantly higher in the anaerobic/photo-Fenton treatment due to the glucose added as electron donor for the anaerobic decolorization. When treating real textile wastewater a cheaper electron donor such as ethanol [33] or molasses [34] could be used if the amount of organic compounds present in the wastewater is too low. Even though the combined photo-Fenton/aerobic process reached higher mineralization levels in this study, the anaerobic/photo-Fenton treatment might be more competitive when treating real textile wastewater containing other contaminants than the dye. Average BOD and COD concentrations in textile wastewater are according to literature 100–1200 mg/l and 230–4000 mg/l respectively [35–39]. When using photo-Fenton for pre-treatment, reagents will be consumed not only for biodegradability improvement, but also for BOD removal. By using an initial anaerobic step biodegradable compounds could first be removed, saving the Fenton reagents for degradation of the more recalcitrant compounds. Thereby it remains to compare the obtained results with studies on real wastewater.

4. Conclusions

Photo-Fenton and combined photo-Fenton biological processes were used for treatment of Remazol Red (100 mg/l) achieving high decolorization and mineralization yields, as seen by reduction of absorbance and COD. By incorporation of aerobic post-treatment or anaerobic pre-treatment, the efficiency of the process could be increased at low H_2O_2 dosage. Furthermore lower residual toxicity was achieved when combining photo-Fenton with biological treatment. These results show that combining biological steps with the photo-Fenton step can be beneficial for the total treatment process. Based on the results in this study the photo-Fenton-aerobic treatment was the most efficient of the coupled treatments, both in terms of final COD level and reagent consumption.

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