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Combined Photo-Fenton and Biological Oxidation for the Treatment of Aniline Wastewater

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Abstract

The treatment efficiency of aniline wastewater by single photo-Fenton, single biological oxidation and combined photo-Fenton and biological oxidation were compared. The effect of different factors, such as pH, Fe2+ and H2O2 concentrations on degradation efficiency were investigated. Effective degradation of aniline wastewater have been observed by photo-Fenton process, but complete mineralization of aniline wastewater need to consume large numbers of H2O2, so the single photo-Fenton oxidation is uneconomical technology. The aniline wastewater is less biodegradable and very toxic to microorganisms, the removal efficiency are low by direct biological oxidation. The toxicity of the aniline wastewater was found to be reduced obviously after pretreatment by the photo-Fenton oxidation. The combined photo-Fenton and biological oxidation was an effective treatment technology for toxic aniline wastewater. Experimental results showed that 62.5% of H2O2 were saved by combined photo-Fenton and biological oxidation processes, comparing with single photo-Fenton process.

Keywords: Photo-Fenton oxidation; Biological oxidation; Combined processes; Aniline wastewater.

1. Introduction

Aniline is the prototypical aromatic amine, the largest application of aniline is for the preparation of methylene diphenyl diisocyanate. Other uses include rubber processing chemicals, herbicides, dyes and pigments. As additives to rubber, aniline derivatives such as phenylenediamine and diphenylamine, are antioxidants. Illustrative of the drugs prepared from aniline is paracetamol. The principal use of aniline in the dye industry is as a precursor to indigo, the blue of blue jeans [1]. The IARC lists aniline in Group 3 due to the limited and contradictory data available. Aniline wastewater is less biodegradable and very

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toxic to microorganisms [2]. Gheewala et al [3] reported that the productions of derivatives of aniline are difficult to be degraded and inhibit the biodegradation of other chemicals.

Biological treatment is the most common method; it has been considered the most economically feasible method for wastewater treatment. However, because the toxicity and inhibition of aromatic compounds (such as aniline) to microorganisms involved in biological treatment processes, it is obvious that the wastewater containing high concentration aromatic compounds are not appropriate for classical biological treatment [4]. Therefore, other treatments are necessary for these toxic compounds. In this sense, Advanced oxidation processes (AOPs) such as Fenton and photo-Fenton oxidation are among the most widely used technologies for the treatment of high toxicity and low biodegradable industrial effluent [5-7]. The Fenton reaction is based on hydrogen peroxide decomposition in the presence of ferrous iron to produce hydroxyl radicals [8]. Hydroxyl radicals are strong, relatively unspecific oxidants that react with most organic contaminants, including PAHs, phenols, dyes, pesticides, etc. The decomposition of hydrogen peroxide was accelerated under irradiation. The advantage of photo-Fenton oxidation is that it is able to oxidize and mineralize almost any organic molecule, yielding CO_2 and inorganic anions. However, the complete mineralization of organic pollutants by the single photo-Fenton oxidation is very expensive; the main drawback is the relatively high treatment costs compared to biological treatment, especially for the treatment of highly polluted wastewater [9].

Recently, studies on the combination of Fenton's Reagent or photo-Fenton oxidation and biological treatment have been developed [10-11]. The wastewater is first submitted to Fenton oxidation to partially degrade aromatic compounds, generating a wastewater with high biodegradable and with lesser amounts of toxic compounds that are easily assimilated by the microorganisms in the biological process. Then, the biological treatment was used for the removal of the other organic compounds. The biological treatment can be carried out in a sequencing batch reactor (SBR), which presents a great simplicity and flexibility of operation, as well as low cost when compared with other possible configurations [12]. Concerning their applicability, SBR had been successfully and widely used for domestic and industrial wastewaters biodegradation [13-14]. In this study, the treatment efficiency of aniline wastewater by combined photo-Fenton and biological oxidation processes were evaluated.

2. Materials and MethodS

2.1 Reagents

Aniline, dichromate potassium, hydrogen peroxide and $FeSO_4{\cdot}7H_2O$ were purchased from Sinopharm Chemical Reagent Co., LtdS (China). All used reagents were of analytical grade.

2.2 Synthetic Aniline Wastewaters

The synthetic aniline wastewaters were prepared for 250 mg/L. A real wastewater was not used because it revealed to be very heterogeneous, with characteristics that were changing dramatically from day to day.

2.3 Photo-Fenton Oxidation Procedure

Stock solutions of H_2O_2 (10mg/mL) and $FeSO_4{\cdot}7H_2O$ (25mg/mL as Fe^{2+}) were used as Fenton's reagents. Three of ultraviolet germicidal lamps (55 W) were used as light source, providing a UV light intensity of （270±20） $\mu W/cm^2$ into the reactor. In a plexiglass storage tank, after the addition of the desired amount of the aniline wastewater and Fe^{2+}, the pH was adjusted to the desired value with sulphuric acid or sodium hydroxide addition. Afterwards, the desired amount of H_2O_2 was added, samples were mixed rapidly, and the mixed solutions were pumped into the photo-oxidation reactor with the flow of 18 L/h by peristaltic pump. After the photo-Fenton preoxidation was finished, the aniline, COD and BOD_5 were analyzed.

2.4 Biological Oxidation

The biological treatment was carried out in an aerobic sequencing batch reactor (SBR) of 16 L equipped with an air diffuser. Air diffusers provided the oxygen necessary to keep aerobic conditions. The activated sludge used came from a municipal wastewater treatment plant and was acclimatized for two weeks. The synthetic wastewater with pH previously adjusted to 7.2±0.4 was gradually added to 4 L of acclimatized sludge to make up a final volume of 12 L. The pH value in the SBR is maintained at 7.2±0.4. Nitrogen, phosphorus, potassium and other nutrients necessary for microbial activity are added at the appropriate time. The mixtures have been kept fully aerated and the aeration proceeded for up to 12h (reaction stage). Aeration was then shut down for 1.5h, during which the sedimentation stage proceeded. After the sludge was fully settled, the supernatant was removed from the reactor and no sludge was wasted. Then a new wastewater was fed to the reactor up to the final volume of 12 L.

2.5 Coupled Photo-Fenton and Biological Oxidation System

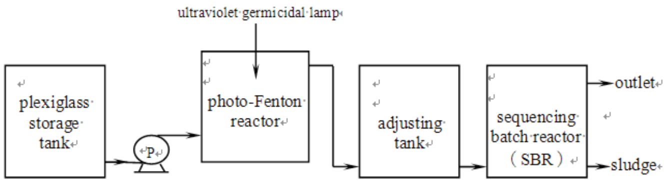

Figure 1 Diagram of the coupled photo-Fenton and biological oxidation

The coupled photo-Fenton and biological oxidation system comprises a photo-Fenton reactor, a sequencing batch reactor (SBR), plexiglass storage tank, peristaltic pumps, adjusting tank, connecting tubing and valves (shown as Fig.1). The pH of solution is pre-adjusted to 3-4, and Fe^{2+} and H_2O_2 are added into the plexiglass storage tank at the beginning of the process. The solution is continuously flowed at 18 L/h through the photo-oxidation reactor. The pH of the effluent is adjusted to 7.2±0.4 at adjusting tank after the photo-Fenton preoxidation, and the photo-Fenton pretreated solution is then piped to the SBR with the peristaltic pump. The pH value in the SBR is maintained at 7.2±0.4.

2.6 Analytical Methods

Chemical oxygen demand (COD) was determined by fast digestion-spectrophotometer method [15], the dichromate as an oxidant, the samples digested during 15 mins in a thermoreactor (5B-1, Lanzhou) and the COD directly given by the absorbance. Biochemical oxygen demand (BOD_5) was assessed by dilution and seeding method for 5 days [16], by determining oxygen consumption after 5 days of incubation in biochemistry incubators (SPX-250B-Z, Shanghai). The pH was measured by means of a pH meter (PHS-3C, Shanghai). The concentration of hydrogen peroxide was measured using the potassium permanganate method. The UV intensity was measured with a UV light radiometer (UV-A, Beijing) at 365 nm. Aniline was determined by N-(1-naphthyl) echylenediamine spectrophotometer method [17].

3. Results and discussion

3.1 Influence of the initial pH on the photo-Fenton degradation of Aniline

Previous works have demonstrated that the initial pH and iron concentration can influence considerably the photo-Fenton degradation of different compounds [9, 18]. The effect of initial pH on the photo-Fenton degradation of 250 mg/L aniline wastewater was studied in the presence of 300 mg/L H_2O_2 and the molar ratios of H_2O_2:Fe^{2+} is 20:1, reaction times are 30mins. The result showed in Figure 2.

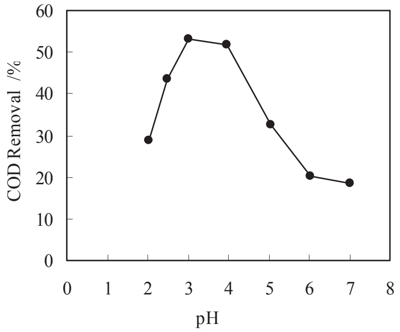

Figure 2. Effect of initial pH on the removal of COD

Apparently, the initial pH have significantly influence on the degradation of aniline by photo-Fenton oxidation. The best removal of COD was obtained at pH 3–4. It showed a decreased catalytic activity while the initial pH is more than 4, because the formation of iron hydroxide precipitation and lossed its catalytic activity. Simultaneously, the H^+ reacted as a scavenging effect of hydroxyl radicals when the initial pH is low (H^+ concentration is high). So, the optimum pH range is 3–4 for photo-Fenton oxidation.

3.2 Influence of the iron concentration on the photo-Fenton degradation of Aniline

The effect of iron concentration on the degradation of 250 mg/L aniline wastewater was studied in the presence of 300 mg/L H_2O_2 and the initial pH 3.5, reaction times are 30mins. Nine Fe^{2+} concentrations were studied, and the result showed in Figure 3.

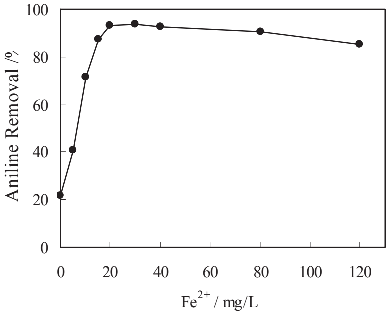

Figure 3. Effect of iron concentration on the removal of aniline

As shown in figure 3, aniline removal efficiency increased obviously with the increasing of iron concentration while $c(Fe^{2+}) \leq 30$mg/L. The aniline removal increased 53.3%, from 40.5% to 93.8%, when the Fe^{2+} concentration increased from 5 to 30 mg/L (Figure 3). However, the further augment on the Fe^{2+} concentration decreased the removal efficiency, decreased slightly 8.4%, from 93.8% to 85.4%, when the Fe^{2+} concentration increased from 30 to 120 mg/L (Figure 3). The positive sign means that the increase on the Fe^{2+} concentration increases the production rate of the hydroxyl radicals which leads to a higher removal efficiency. Nevertheless, an excess of Fe^{2+} in the solution may cause unproductive consumption of hydroxyl radicals, decreasing the degradation efficiency. In this study, the optimum Fe^{2+} concentration is 15 to 40 mg/L, accordingly the molar ratios of H_2O_2:Fe^{2+} is 30:1 to 10:1.

3.3 *Effect of H2O2 on aniline and COD removal*

Figure 4 illustrates the effect of H_2O_2 concentration on aniline and COD removals for pH is 3.5, molar ratios of H_2O_2:Fe^{2+} is 20:1 and reaction times are 30mins. The initial aniline and COD of the wastewater are 250mg/L and 599mg/L, respectively.

It can be seen from Figure 4, the aniline and COD removals depend considerably on the H_2O_2 concentration. The aniline and COD removals increased with increasing H_2O_2 concentration. More than 96% aniline removal was obtained under 400 mg/L H_2O_2 and more than 93% COD removal was obtained under 1200 mg/L H_2O_2. Apparently, high concentration of H_2O_2 may result in unproductive consumption of hydroxyl radicals and in ineffective oxidation, as observed in Figure 4. Watts et al. [19] also describes high concentration of H_2O_2 generates non-hydroxyl radical species, such as perhydroxyl radical (HO_2•), superoxide radical anion (•O_2^-), and hydroperoxide anion (HO_2^-). Perhydroxyl radical is a relatively weak oxidant; superoxide is a weak reductant and nucleophile.

As shown in figure 4, effective degradation of aniline wastewater was observed by photo-Fenton process, but complete COD removals need to consume large numbers of H_2O_2（>1200mg/L), so the single photo-Fenton oxidation is uneconomical technology.

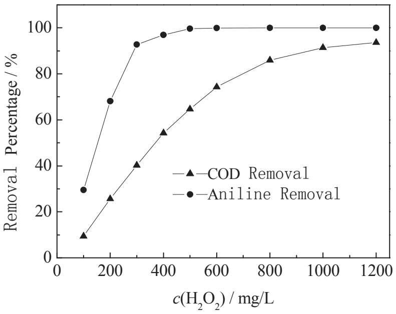

Figure 4. Effect of H2O2 concentration on aniline and COD removals

3.4 *Biological Oxidation for aniline wastewater*

The BOD_5/COD ratio of 250 mg/L Aniline wastewater is only 0.21, this means aniline wastewater is less biodegradable. The COD removal is only 52.5% using direct SBR biological treatment for 24h.

3.5 Effect of photo-Fenton preoxidation on biodegradability of aniline wastewaters

Several factors of photo-Fenton preoxidation are chosen as follow: pH is 3.5, molar ratios of H_2O_2:Fe^{2+} is 20:1, and reaction times are 30mins. The biodegradability test of aniline wastewaters was carried out by the BOD_5/COD ratio. The changes in of BOD_5/COD ratio with H_2O_2 dosage during the photo-Fenton preoxidation are shown in Figure 5.

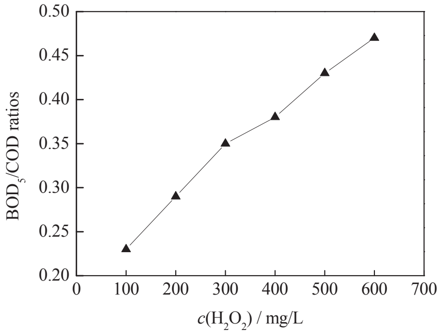

Figure 5. Changes in BOD5/COD ratios of aniline wastewater with H2O2 dosage in photo-Fenton preoxidation

As shown in Figure 5, it is evident that the photo-Fenton preoxidation is effective to enhance the biodegradability of aniline wastewater, the BOD_5/COD ratios increase with the increase of H_2O_2 dosage during the photo-Fenton preoxidation. Under the condition of H_2O_2 concentration of 500 mg/L, the BOD_5/COD ratio increases from 0.21 to 0.43, which means that the wastewater is transformed from difficultly biodegradable into easily biodegradable, the biodegradability is improved remarkably. The experiment results showed that photo-Fenton oxidation can be used as an effective pretreatment for biological treatment.

3.6 Coupled Photo-Fenton and Biological Oxidation

In this study, several factors of photo-Fenton preoxidation are chosen as follow: pH is 3.5, molar ratios of H_2O_2:Fe^{2+} is 20:1, and reaction time is 30min.

Table 1 COD and aniline removal by combined photo-Fenton and biological oxidation treatment

H_2O_2 dosage in photo-Fenton preoxidation(mg/L)	Overall Removal of COD(%)	Overall Removal of aniline (%)
400	87.9	99.88
450	93.1	99.91
500	94.8	99.98

As shown in table 1, more than 94% removal of aniline and COD were obtained by combined photo-Fenton and biological oxidation processes. The maximum efficiency was obtained with similar removal rate by the single photo-Fenton under 1200 mg/L H_2O_2 (Figure 4) and by the combined photo-Fenton and biological oxidation under 450 mg/L H_2O_2 (Table 1). Experimental results showed that 62.5% of H_2O_2

were saved by combined photo-Fenton and biological oxidation processes, comparing with single photo-Fenton process. Therefore, taking into account the environmental impact and costs, the combined photo-Fenton and biological treatment as an effective treatment technology for toxic aniline wastewater.

4. Conclusions

1) Initial pH and iron concentration can influence considerably the photo-Fenton degradation of aniline. The optimum pH and Fe^{2+} concentration is 3 to 4 and 15 to 40 mg/L, respectively.

2) Effective degradation of aniline was observed by photo-Fenton process, but complete mineralization of 250 mg/L aniline wastewater need to consume large numbers of H_2O_2. So the photo-Fenton oxidation is uneconomical technology.

3) The aniline wastewater is less biodegradable. The photo-Fenton preoxidation is effective to enhance the biodegradability of aniline wastewater.

4) The combined photo-Fenton and biological oxidation was an effective treatment technology for toxic aniline wastewater. More than 94% removal of aniline and COD were obtained by combined photo-Fenton and biological oxidation processes.

5. Acknowledgment

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