



Combined humic acid adsorption and enhanced Fenton processes for the treatment of naphthalene dye intermediate wastewater

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ARTICLE INFO

Article history:

Received 21 July 2011

Received in revised form

27 September 2011

Accepted 10 October 2011

Available online 15 October 2011

Keywords:

Naphthalene dye intermediate

1,2,4-Acid

Multi-staged Fenton

Inner circulation

ABSTRACT

In this work, an humic acid adsorption with an enhanced Fenton oxidation was employed to treat the real effluent originating from the 1-diazo-2-naphthol-4-sulfonic acid (1,2,4-Acid) production plant. In a first step, humic acid with $MgSO_4$ was selected as adsorbent and precipitant for physicochemical pre-treatment, the synergetic effect had led to 39% of COD removal and 89% of colour removal. A multi-staged Fenton oxidation process with inner circulation was introduced subsequently. The TOC, COD, 1,2,4-Acid, NH_4^+-N , SS and colour were reduced from 3024 mg/L, 12,780 mg/L, 9103 mg/L, 110 mg/L, 240 mg/L and 25,600 (multiple) to 46 mg/L, 210 mg/L, 21 mg/L, 16 mg/L, 3 mg/L and 25 through the combined process, respectively. Hydrogen peroxide consumed per kg COD had saved up to 36% when two-staged Fenton process with inner circulation (flow-back to influent ratio: 3) was applied. Influence of H_2O_2 concentration, flow-back to influent ratio and staged Fenton mode were investigated in detail in order to find out the optimal operating parameters. The kinetics of 1,2,4-Acid degradation by two-staged Fenton process was investigated. The evolution of the main intermediates during the degradation process was conducted using the LC-(ESI)-TOF-MS technique, and the results showed a staged degradation pathway from the ring opening of naphthalene compounds to the formation of benzene compounds and carboxyl acids. The combined process had been proved effective in both technical and economic aspects.

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1. Introduction

Naphthalene series dye intermediate is an important industrial chemical and is used extensively in dye and pharmacy industries [1]. The real naphthalene dye wastewaters containing 1-diazo-2-naphthol-4-sulfonic acid (1,2,4-Acid) which are characterized by darker colour, higher strength of organic load and toxicity, and are generally recalcitrant to biological treatment [2], are of most difficulty to treat. 1,2,4-Acid is an important dyestuff intermediate and used as diazo component for synthesizing a whole range of textile and leather dyes [3]. The common characteristic of real naphthalene dye intermediate wastewater is featured by strong acidity (H_2SO_4 11–15%) and high concentration of chemical oxygen demand (8000–14,000 mg/L), as well as low ratio of BOD_5/COD (<0.1). China, as a large country to manufacture naphthalene series dye intermediate in the world, annually produces large amount of wastewaters, roughly 58–60% of which is discharged into the environment without proper treatment, causing serious environmental pollution toward soils and water bodies [2].

Recently Hu et al. reported [4] that the 1,2,4-Acid dye could be treated by solvent extraction to recover the dyes, however, this physical method simply transferred the pollutants from one phase to another rather than destroying them and the regeneration of solvent might be economically infeasible.

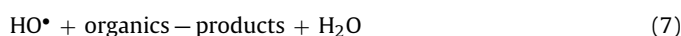
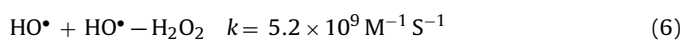
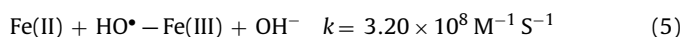
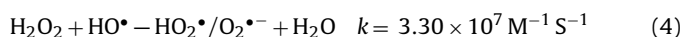
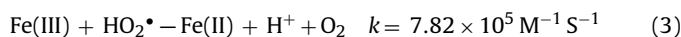
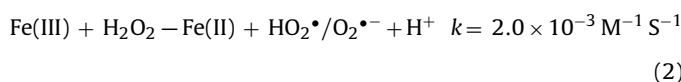
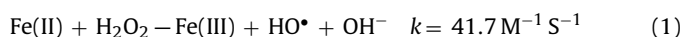
Due to the complexity of naphthalene dye intermediates wastewaters, any single treatment method would be inadequate, and to date, limited data have been published on its treatment methods. In order to meet the permitted value for production of a higher quality of the treated effluent for further reuse, it is urgent to develop a cost-effective process for the reduction of its COD_{Cr} , NH_4^+-N and colour. Generally, adsorption is a very simple and widespread method to eliminate pollutants from wastewater [5]. The use of activated carbon as an adsorbent has been well established and widely used in the wastewater treatment process [6]. However, its high cost and complicated regeneration process have led to search for alternative low-cost adsorbents such as natural clays and biological waste products, etc. Humic acids (HA) is a kind of soil organic matter (SOM), and has been identified as a key sorption medium for organic compounds in soils [7]. It is widely accepted that the presence of HA in soil is of paramount importance for the uptake of organic substance [8]. Researches on HA sorption for organic matters were intensively focused on soil pollutants elimination, its application on wastewater treatment,

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however, has rarely been reported elsewhere. From our previous study, the application of HA for the removal of pollutants from oil production wastewater was successfully demonstrated [9].

Much work has been done to probe the roles of various functionalities in HA, but the research on the importance of aromatic adsorption by HA is still lacking. From previous studies, the applications of HA for the adsorption of atrazine had been examined in detail [10], demonstrating a superior adsorbability of humic acid for the uptake of organic matters. It was proposed that the molecules of HA may form a supramolecular structure held together by non-covalent forces in water, such as Van de Waals forces, π - π and CH- π bond. The organic matters in HA possesses rubbery and glassy domains and most previous studies concluded that the amorphous domains had higher sorption for organic compounds [11]. On the other hand, magnesium sulfate was a cheap and accessible adsorbent that could be easily precipitated from an aqueous solution by adjusting the pH to alkaline region. Therefore, the present work was an attempt to use the synergetic effect of HA and MgSO_4 , as a method for the pretreatment of high concentration of naphthalene dye intermediate wastewater.

Advanced oxidation processes (AOPs) have specific advantages against to conventional methods. AOPs can be applied to wide range of organics and waste streams. Among AOPs, Fenton process is cost effective, easy to apply and effective to eliminate bio-refractory organic compounds [12]. One of the advantages of Fenton's reagent is that no energy input is necessary to activate hydrogen peroxide. Therefore, this method offers a cost effective source of hydroxyl radicals, using easy-to-handle reagents. The Fenton's reaction generally occurs in acidic medium between pH 2 and 4 [13,14] and involves the steps shown in Eqs. (1)–(7) [15–17].



In recent years, many researchers have been paying growing attention to the degradation of low concentration contaminants of dyes, especially that of RhB [18,19]. Nevertheless, Fenton was hardly involved in the remediation of high concentration organic wastewaters due to high Fenton reagents consumption and extremely low H_2O_2 oxidation efficiency.

Diverse efforts such as introducing UV light irradiation [20] or adding hydroquinone/quinine analogues [21] have been made to utilize the Fenton reaction in a better way, however, considering both economic and technical reasons, these methods seem to be infeasible in real wastewater treatment plants.

In contrast, the application of HA & MgSO_4 as a pretreatment method coupled with an enhanced Fenton process with more practical meaning has not been reported in the literature. In this study, the Fenton was applied using an inner circulation system. Inner circulation system was creatively designed and served as recycling the treated water back to influent distribution system prior to Fenton process. This was aimed to reduce the initial organic load, avoiding the side reaction from Eq. (4) due to the dilution effect (parent organics were diluted thus decreasing the H_2O_2 concentration per unit volume). Real naphthalene dye intermediate wastewater was

applied in this study. Bench-scale investigations were conducted to investigate the performance of this combined treatment system and to find out the optimum operation parameters for the removal of the key pollutants. LC-(ESI)-TOF-MS analysis was used to identify the pollutants and intermediate generated in the process. The purpose of the study is to establish a novel process that could treat the wastewater to meet the third criteria of Chinese discharge standard (GB8978-1996).

2. Materials and methods

2.1. Chemicals and supplies

All chemicals which are analytical grade or higher were purchased from Shanghai reagent company. The HA was extracted from peat soil and its extraction along with purification was described according to Wang and Xing [22]. The samples of real naphthalene series dye wastewater were obtained from the naphthalene dye production plant, Sanfeng Chemicals Co. LTD, located in southeast of China, Zhejiang province which is one of the world's largest companies to manufacture 6-nitro-1,2-diazooxy-4-naphthalene sulfonate and Acid Chrome Black T.

2.2. Analytical control

The wastewater was characterized for COD, pH, NH_4^+ -N, total solids, total suspended solids and colour using standard methods [23]. Chroma colour is determined by dilution method, i.e. the coloured sample (V_1) is diluted by distilled water (at least V_2) to the extent similar to achromic distilled water. Then the original sample's chroma value is $(V_1 + V_2)/V_1$ (times) [4]. For COD measurement, the samples were left overnight to remove the residual hydrogen peroxide that might remain in the sample solutions [24].

Total organic carbon (TOC) was measured by an Elemental liquid TOC analyzer. Main pollutants in the influent of real naphthalene dye intermediate wastewater were detected by means of liquid chromatography-(electrospray ionization)-time of flight-mass spectrometry (LC-(ESI)-TOF-MS) analysis. Solid-phase extraction (SPE) with oasis HLB cartridges from waters was employed for samples preconcentration prior to the analysis. Separation was made using reversed phase liquid chromatography (flow rate 0.5 mL/min, injection volume 20 μL) in a HPLC (Agilent series 1100) equipped with a 150 mm \times 4.6 mm C-18 analytical column of 5 μm particle size. The column temperature was 25 $^\circ\text{C}$. Degradation intermediates absorbed on the ferric sludge during each process was characterized by FT-IR spectrum (FTIR-8700, Shimadzu, Japan).

All the experiments were repeated three times, and the results in tables are the average of at least three measurements with an accuracy of $\pm 5\%$.

2.3. Characteristics of wastewater

The real wastewater used was drawn from the effluent of the sedimentation channel below the washing tower, and its characteristics are presented in Table 1, together with the limit of national third discharge standard (GB8978-1996). Under basic conditions the raw wastewater exhibited a strong dark colour.

2.4. Combined treatment process

The bench-scale setup consists of an adsorption reactor with HA as the pretreatment followed by enhanced Fenton oxidation reactor. In the adsorption process: (1) HA was proposed to be used as adsorbent (1500 mg/L); (2) a desired dose of MgSO_4 (5000 mg/L) was added as precipitant to the wastewater; (3) the stirrer was turned on for rapid mixing stage of 10 min at 60 rpm; (4) the stirrer

Table 1
Characteristic of influent from the production naphthalene series dye plant.

Parameter	Value	Discharge limit ^a
1,2,4-Acid (mg/L)	9103	NA
Colour (multiple)	25,600	100
SS (mg/L)	240	400
COD _{Cr} (mg/L)	12,000	500
NH ₄ ⁺ -N	110	100
Sulfate (mg/L)	11,030	NA
Cl ⁻¹ (mg/L)	300	NA
Conductivity (mS/cm)	4400	NA
pH	0.1	6–9

^a According to Third Criterion of National Wastewater Discharge Standard (GB8978-1996).

speed was reset for a slow mixing stage of 15 min at 20 rpm; and (5) the ensuring natural setting lasted 1 h. The supernatant was withdrawn for subsequent analysis.

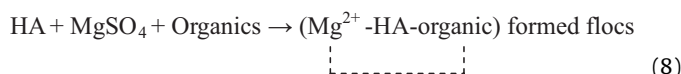
The Fenton processes were carried out in the following sequential steps: (1) effluents after pretreatment (200 mL) were put in a beaker (1 L); (2) volume of influents was diluted with the effluent (COD equals to 210 mg/L approximately) which was treated by Fenton process and was unable to be further degraded (the total volume of diluted solutions is 200 × dilution ratio); (3) pH was adjusted to 2.5–3 with raw wastewater due to its high concentration of sulfate acid; (4) a calculated amount of catalytic ferrous sulfate was added as the source of Fe²⁺ in this experiment. Then, H₂O₂ was added into the reactor to start the reaction; and (5) at selected time intervals, 3 mL of reaction mixture was taken and immediately injected into 0.1 N NaOH to increase the pH to 10 to terminate the reaction [24]. Samples were filtered through 0.45 μm membrane filters to remove the precipitates formed. Filtered samples were then analyzed for various parameters. The combined treatment was operated under the optimal conditions for all the processes. The overall efficiency of the combined treatment was evaluated. The diagram of the bench-scale experiment setup of

the combined physicochemical pretreatment and enhanced Fenton process was illustrated in Fig. 1.

3. Results and discussion

3.1. Physicochemical pretreatment

Comparative results using HA adsorption, MgSO₄ precipitation and combined HA and MgSO₄ adsorption were listed in Table 2. It had been found that the removal efficiency of both COD and NH₄⁺-N in combined system (39% and 62%) was superior than that obtained in single HA adsorption (16% and 40%) and MgSO₄ precipitation (28% and 19%). It is probably because that Mg²⁺ is capable of developing chelate-type bridges between different chemical groups of HA, shrinking the molecules and forming flocs to adsorb organics to coagulate [25]. It can be also seen from Table 2 that HA & MgSO₄ combined process had the great advantages of reducing chromaticity from 25,600 to 2700 times. The proposed mechanism was shown in Eq. (8):



To examine the influence of pH change, experimental test at various pH points were performed and the result can be seen in Fig. 2. The pH of the combined system was adjusted with 0.1 M H₂SO₄ or 0.1 M NaOH. Analysis show that zeta potential of HA decreases with increasing pH, the influence of pH on HA and MgSO₄ synergistic effect is considerable. Performance of HA adsorption on COD removal in lower pH was greater than in higher pH, however, this was somewhat different when MgSO₄ was added. In combined process, COD removal efficiency increased when increasing the solution pH, the highest COD removal 39% was achieved when solution pH was adjusted to 12, while the lowest removal 21% was obtained when pH was 5. This might be explained that organics in naphthalene wastewater like 1,2,4-Acid would be protonated at low pH values, and this protonation favors increased sorption by HA via ionic interactions when conducted in single HA adsorption process. On the contrary, HA would be in its colloids state at the high pH range, as the results of deprotonation, the HA molecule was expected to yield more favorable interaction with Mg²⁺ to form

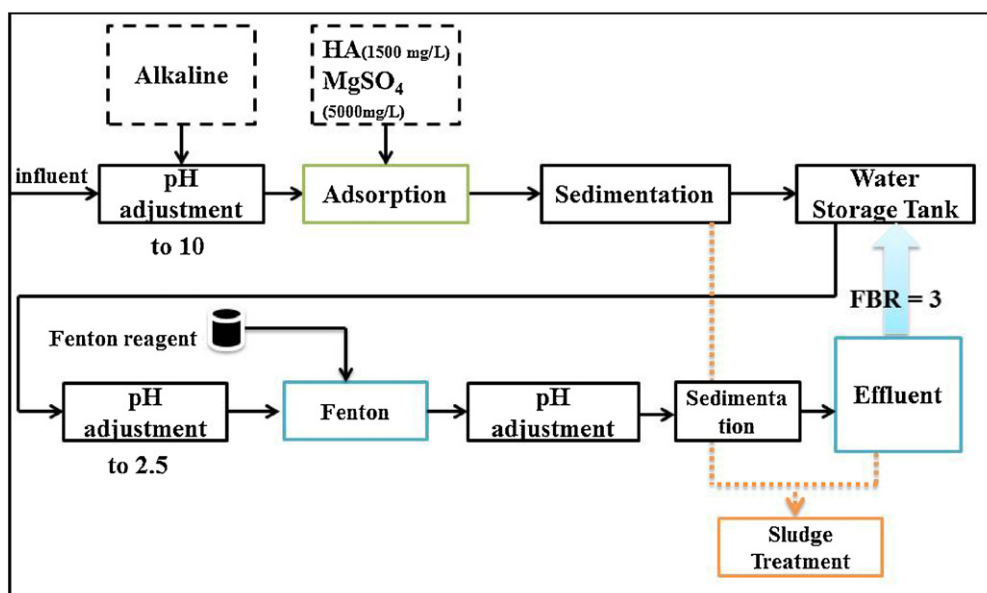
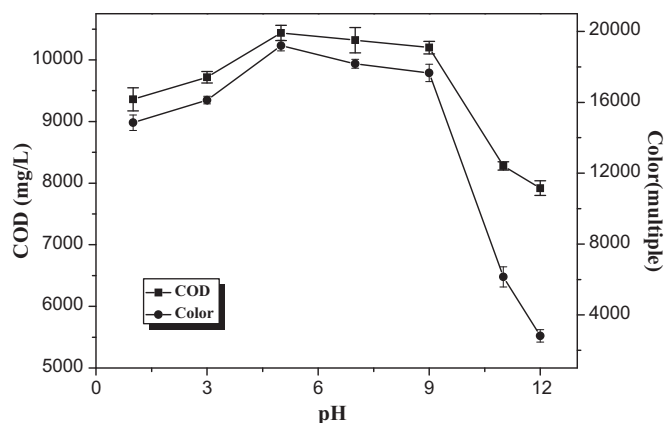


Fig. 1. Flow diagram of the combined physicochemical pretreatment and enhanced Fenton process of naphthalene dye intermediate wastewater.

Table 2Comparative results of HA, MgSO₄ and HA & MgSO₄ combined treatment process on COD, SS, colour and NH₄⁺-N removal.

	Raw wastewater	HA adsorption ^a	MgSO ₄ pretreatment ^b	HA & MgSO ₄ ^c
COD (mg/L)	12,000	10,108	8630	7319
COD removal (%)	–	15.8	28.1	39.0
1,2,4-Acid (mg/L)	9013	8810	6732	5315
SS (mg/L)	240	21	27	17
Colour (times)	25,600	14,300	18,500	2700
NH ₄ ⁺ -N (mg/L)	110	66.5	89.1	48.5

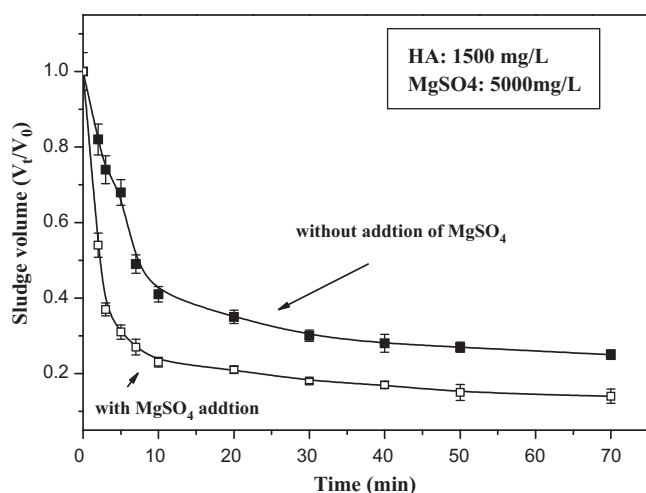
pH = 12; time = 60 min.

^a Dosage of HA 1500 mg/L.^b Dosage of MgSO₄ 5000 mg/L.^c HA 1500 mg/L + MgSO₄ 5000 mg/L.**Fig. 2.** Effect of solution pH on COD and colour variation in HA & MgSO₄ combined process. (HA 1000 mg/L + MgSO₄ 5000 mg/L; time = 60 min; total volume = 500 mL.)

Mg²⁺–HA–Mg(OH)₂ flocs. As a result, dye molecules might be partly adsorbed by both HA and Mg(OH)₂ chelated flocs.

The settling velocity of precipitate with or without addition of Mg²⁺ was also investigated and the result was shown in Fig. 3. Magnesium salt existed partly as colloidal particles in the alkaline environment, possibly by a “sweep-floc” mechanism.

Aggregates formed as a result of [Mg₂(H₂O)₆]²⁺ might have led to a faster settling velocity through reducing electrostatic repulsion between the particles [26–28]. It can be seen from Fig. 3, as MgSO₄ was added, precipitate volume was rapidly decreased in one hour's settling time, less sludge production was observed, and the sludge volume with the addition of MgSO₄ had improved by 44%.

**Fig. 3.** Comparison of settling velocity of precipitate with and without the addition of magnesium sulfate from combined process (total volume = 500 mL).

Produced sludge was shipped out for further disposal by biological land treatment.

3.2. Fenton process

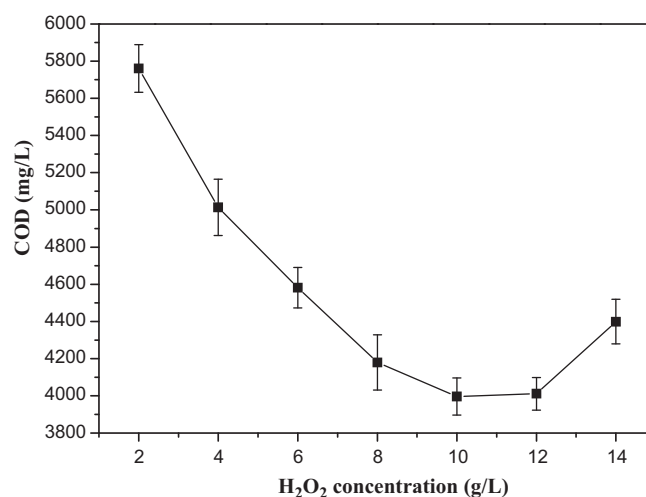
Fenton was selected as a subsequent treatment method in this study due to its capacity for the efficient removal of various azo dye compounds [29,30].

3.2.1. Effect of hydrogen peroxide concentration

Hydrogen peroxide is an active oxidizing agent in the Fenton reaction. It has been reported that the degradation efficiency of the organics increases with an increase in the concentration of hydrogen peroxide [24]. It plays role of the precursor in generating the hydroxyl radicals when reacting with ferrous ion as shown in Eq. (1). In addition, hydrogen peroxide can also react with Fe³⁺ to form a redox cycle to regenerating Fe²⁺ as illustrated in Eq. (2). However, increases in the starting concentrations of H₂O₂ do not always correspond to higher oxidation rate or even faster oxidation of the target substrate. In the presence of excess amount of hydrogen peroxide, chemical oxidation of organics can be inhibited by the formation of large amount of oxygen bubbles instead of hydroxyl radicals (Eq. (9)).



The effect of initial concentration of hydrogen peroxide by Fenton process is shown in Fig. 4. The result indicated that increasing the initial H₂O₂ concentration from 2 to 10 g/L can enhance the COD removal efficiency. When an initial H₂O₂ concentration of 2 g/L was

**Fig. 4.** Effect of H₂O₂ concentration on COD variation of wastewater by Fenton oxidation. (Reaction conditions: initial COD = 7319 mg/L; ferrous sulfate = 3.27 g/L; initial pH = 2.5; temperature = 26 ± 3 °C; treat volume = 200 mL without any dilution.)

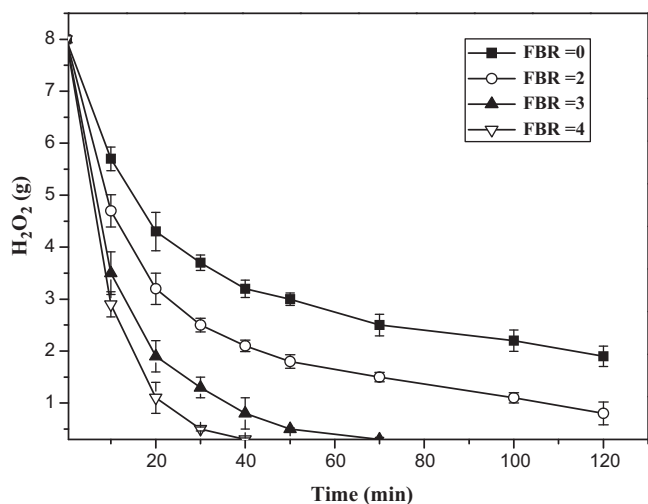


Fig. 5. Changes of H_2O_2 concentration as a function of time with various FBR. (Reaction conditions: initial pH = 2.5; temperature = $26 \pm 3^\circ\text{C}$.)

added, 21% of COD removal efficiency was achieved. Increasing the H_2O_2 concentration up to 8 g/L could meet 43% of COD removal efficiency. This was because that the presence of increasing H_2O_2 could promote the production of more hydroxyl radical with ferrous ion, as illustrated in Eq. (1).

The decreased COD removal efficiency was observed at 12 g/L of concentration. The COD removal efficiency was decreased when concentration of H_2O_2 was higher than 12 g/L. This was probably due to the competition between intermediates and organics for hydroxyl radicals. The higher concentration of H_2O_2 might have favored the side reactions that scavenged the HO^\bullet to form hydroperoyl radicals via Eq. (4), and this has a rate constant of about $(1.2\text{--}4.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [31].

3.2.2. Effect of flow-back to influent ratio (FBR)

Fenton's treatment of real industrial wastewater (especially with high organic concentrations) is always preferred as a pre-treatment method prior to the biodegradation process due to the nature of inhibitory effect of the raw wastewater [32,33]. In order to use the Fenton process in a more efficient way, in this part, methods of inner circulation which functioned as pumping the treated effluents ($\text{COD} < 210 \text{ mg/L}$) back to regulating tank, were applied to minimize the organic load of real naphthalene dye wastewater. The influence of flow-back to influent ratios was evaluated. Ratios ($V_{\text{treated water}}:V_{\text{raw}}$) were adjusted from 1 to 4 corresponding to the initial COD value from 3659 to 1463 mg/L, respectively. Amount of oxidant applied was half of the stoichiometric amount of H_2O_2 necessary to oxidize substrate to CO_2 and H_2O . Fe^{2+} was adjusted proportion to the molar ratio of $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ equal to 20:1.

Results from Table 3 indicated that solutions without dilution exhibited a poor COD removal efficiency (43% after 120 min treatment), compared with the results when FBR was 3 (a higher COD removal efficiency 62%). From Table 3, it can be seen that increasing the FBR will decrease the H_2O_2 consumed per kg COD. As FBR increased from 2 to 5, H_2O_2 consumed per kg COD decreased from 2.2 to 1.7 kg/kg COD. This was attributed to the decrease of the side reaction which can leave more hydrogen peroxide to produce hydroxyl radicals.

Fig. 5 shows the changes in total hydrogen peroxide concentration as a function of time with various FBR. Results indicated that the consumption of hydrogen peroxide depends on the FBR applied in each experiment. When FBR increased, the hydrogen peroxide is more quickly consumed, and the corresponding higher COD removal efficiency was obtained. Solutions without any circulation

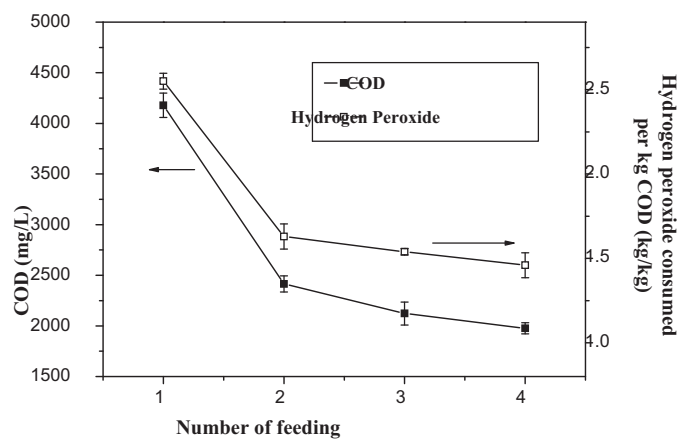
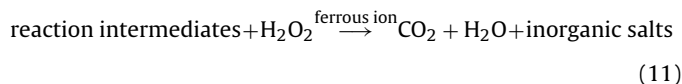
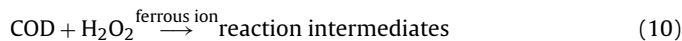


Fig. 6. Effect of Fenton reagent feeding mode on COD variation and H_2O_2 consumption. (Reaction conditions: $\text{COD} = 7319 \text{ mg/L}$; total H_2O_2 fed = 8 g/L; total $\text{FeSO}_4 = 3.3 \text{ g/L}$; initial pH = 2.5; temperature = $26 \pm 3^\circ\text{C}$; treated volume = 200 mL without any dilution.)

showed a steady decrease of hydrogen peroxide, and a mass of oxygen bubbles was observed during the reaction. In the solutions without any dilution, the per unit volume concentration of hydrogen peroxide was 8 g/L, four times more than solutions with BFR equaling to 4 (Table 3). In this case, simultaneously produced excessive hydroxyl radicals might be scavenged by themselves or be exhausted by H_2O_2 through Eqs. (4) and (6). High concentrations of ferrous ion can also react with simultaneously accumulated hydroxyl radicals, as described by Eq. (5) with a reaction rate constant of $3.20 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and the rate constant has a value of several orders of magnitude higher than that Eq. (1). The rate constant of the reduction of $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ through Eq. (2) is only $2.00 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. High concentrations of residual H_2O_2 remained in the solution would probably decompose to water and oxygen or be exhausted by other side reactions [34].

3.2.3. Effect of staged Fenton mode

Most investigations were focusing on one-staged feeding mode but fewer reported the continuous process of Fenton oxidation [35]. Zazo et al. [36] had demonstrated the pathway of phenol oxidation by Fenton's reagent by the following reactions:



In most cases these two reactions occurred simultaneously and resulted in the direct competition for hydroxyl radicals in both a system, however, the degradation rate for Eq. (2) was much slower than Eq. (1), and the Fenton reaction could not reach deep mineralization of target pollutants due to the interaction of degradation intermediate with ferric ions. Moreover, when a significant amount of Fenton reagent comparing with substrate was available, H_2O_2 , Fe^{2+} and organics competed to react with HO^\bullet , thus also reduced the degradation efficiency. Based on which mentioned above, the multi-staged Fenton reagent feeding mode (both ferrous ion and hydrogen peroxide were divided equally and were added followed the Fenton-Neutralization-Sedimentation-...-Fenton-...-Sedimentation process) was applied and the results can be seen in Fig. 6.

It can be seen from Fig. 6 when Fenton reaction was operated twice with half amount of total Fenton reagent applied in each process, better COD removal (67%) was obtained than with single

Table 3

Effect of flow-back to influent ratio on COD removal efficiency and amount of hydrogen peroxide consumed per kg COD.

FBR	Initial COD (mg/L)	Total H ₂ O ₂ (g)	H ₂ O ₂ (g/L)	COD removal efficiency (%)	H ₂ O ₂ consumed per kg COD (kg/kg COD)
Without circulation	7319	8	8	43	2.6
2	3660	8	4	50	2.2
3	2440	8	2.7	56	1.9
4	1830	8	2	62	1.8
5	1464	8	1.6	63	1.7

Reaction conditions: initial pH = 2.5; temperature = 26 ± 3 °C.

feeding (43%). The H₂O₂ consumed per kg COD was also decreased from 2.6 to 1.6 kg/kg COD with two-staged Fenton reaction. This means that more hydroxyl radicals could be produced and used to oxidize organics with staged Fenton process which was consistent with the results reported by Yoo et al. [35].

3.2.4. Performance of the staged-Fenton process with inner circulation system

A bench-scale experiment integrating the staged Fenton process with inner circulation method was utilized to investigate the effectiveness of enhanced Fenton process on the performance of COD reduction. This treatment facility received wastewater from the physiochemical pretreatment plant, with the initial COD about 7300 mg/L. The bench test setup consisted of a two-staged Fenton reaction tank configured with a reflux pump, the flow-back to influent ratio was adjusted to 3 on the grounds of economic reasons, COD of the recycled water was about 210 mg/L and the COD of the wastewater after 3 times dilution was calculated as follows:

$$\text{COD}_{(\text{wastewater after 3 times dilution with circulated water})} = \frac{\text{initial COD} + \text{COD}_{\text{circulated effluent}} \times \text{FBR}}{\text{total volume}} = 1987 \text{ mg/L} \quad (12)$$

The experiments had been in continuous operation for six rounds and the results of COD variation with the function of time are shown in Fig. 7, in which average effluent COD from secondary Fenton reactor constantly remained at 212 mg/L, increased by 22% and 27%, respectively when only two-staged Fenton or circulated Fenton (FBR=4) process was applied. The H₂O₂ consumption per kg COD was also saved up to 31% and 36% compared with the results

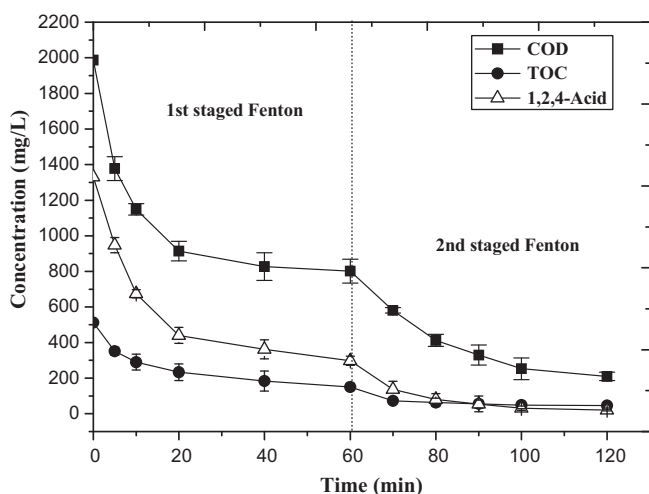


Fig. 7. Concentrations of COD, TOC and 1,2,4-Acid variation in the process of two-staged Fenton reaction with inner circulation systems. (Conditions: wastewater from HA & MgSO₄ pretreatment with initial COD of 7300 mg/L was diluted using the recycled effluent with COD of 210 mg/L, FBR = 3; total H₂O₂ fed = 8 g/L; total FeSO₄ = 3.3 g/L; initial pH = 2.5; temperature = 26 ± 3 °C; Fenton reagents were divided equally in the 1st and 2nd staged Fenton reactor.)

obtained from only two staged or circulated Fenton process. TOC is a primary index to evaluate the organic mineralization that contained in wastewater. Fig. 7 also shows TOC elimination with the function of time. As can be seen, a high mineralization degree was obtained after two-staged Fenton reactions (84% total TOC elimination), with 20% and 64% of TOC reduction after the 1st staged and 2nd staged Fenton reaction, respectively. The sharp decrease of COD and TOC was observed at the beginning of the 2nd staged Fenton process, indicating a strong sorption effect of degraded organic intermediates on ferric sludge. It is commonly accepted that most of these small molecular intermediates (SMI) are recalcitrant to HO• radicals [37], and can hardly be removed by Fenton oxidation. However, they can be easily removed by the process of ferric ion precipitation due to the strong affinity of SMI to Fe³⁺ ions which was further verified by IR investigations of the formed ferric sludge.

In addition, the process was further proved by the IR spectrum analysis and the results can be seen in Fig. 8. A strong adsorption was observed around 553 cm⁻¹ (curve a) and 561 cm⁻¹ (curve b) in the FT-IR spectrum of ferric sludge indicating Fe-O stretching groups of ferric hydroxide, whereas stretching vibration of C=O (1658 cm⁻¹), symmetric stretching vibration of COO⁻ (1396 cm⁻¹) were found after the 1st staged Fenton reaction which was believed to be the functional groups of aromatic ring opening by-product like polycarboxylate. A further degradation was also observed in the 2nd staged Fenton reaction, as characteristic peaks of naphthalene basically disappeared, only leaving some groups of stretching group of C=O (1660 cm⁻¹) and carboxylate ions (1430 cm⁻¹) which were proposed to belong to functional groups of low molecular acids.

The physicochemical adsorption and precipitation in its optimal conditions had led to the high removal efficiency of colour, NH₄-N⁺ and COD which directly reduced the cost of subsequent Fenton process. Enhanced Fenton process significantly decreased

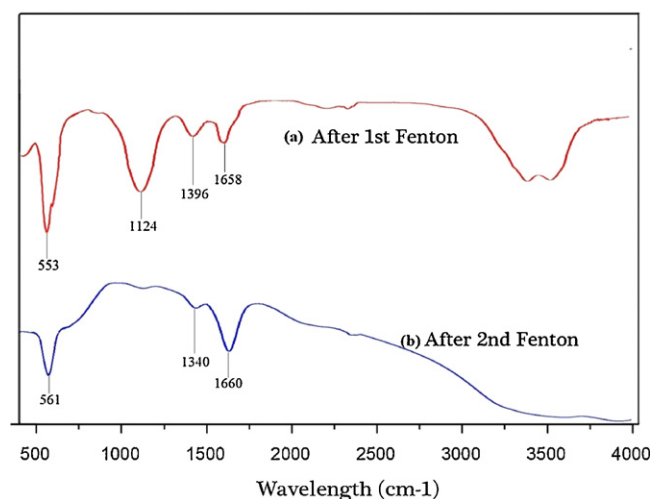


Fig. 8. FT-IR spectrum of ferric sludge collected after the 1st and 2nd staged Fenton reaction.

Table 4
Zero-, first- and second-order reaction kinetics for the degradation of 1,2,4-Acid by staged Fenton process.

Kinetics	1st staged Fenton reaction		2nd staged Fenton reaction	
	k ($M^{-1} s^{-1}$)	R^2	k ($M^{-1} s^{-1}$)	R^2
First-order	5.0×10^{-4}	0.0681	6.8×10^{-4}	0.9460
Second-order	10.7×10^{-3}	0.9404	3.5×10^{-3}	0.9897

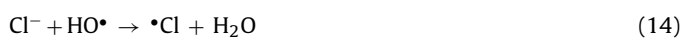
the concentration of COD and colour. The effluent concentration of COD, SS, colour and $NH_4^+ - N$ from the combined process were: 210 mg/L, 3 mg/L, 25 (multiple) and 16 mg/L.

3.2.5. Kinetic study

In most cases (especially Fenton's degradation of a model pollutant), the first order's kinetic fitted well with their degradation rate. However, it is based on the assumption that at a certain time, the concentration of reactive HO^\bullet radical will not vary with reaction time [38]:

$$\frac{d[HO^\bullet]}{dt} = 0 \quad (13)$$

Masomboon et al. used 10 min degradation rate to simulate their pollutant degradation kinetics in order to minimize the error of degradation rate of the intermediate involved in the following stage of the Fenton reaction [39]. Because hydroxyl radical's formation is faster at the initial stage of the Fenton reaction and gradually decreases with the prolonged reaction time [21]. Moreover, real wastewater always has high concentration of inorganic ions, such as chloride or phosphate. The chloride ion acts as a scavenger, consuming hydroxyl radicals [40]:



Thus, hydroxyl radicals can hardly be assumed to be constant due to a series of side reactions that would consume HO^\bullet . For the reaction kinetic, depending on the experimental conditions, the Fenton reaction might follow the first or second order kinetics in different conditions. Sun et al. compared the kinetics of Fenton's degradation of an azo dye Orange G in aqueous solution and found that the second order's kinetic model fitted well with their data [41]. The reaction between the hydroxyl radical and an organic compound was also regarded as a second-order reaction by Wang et al. they assumed that the kinetics for 2,4-D by anodic Fenton's degradation with hydroxyl radicals can be well described as [42]:

$$-\frac{d[D]}{dt} = k[HO^\bullet][D] \quad (16)$$

Real effluent from the dye manufacturing plant was complex in this study, and the degraded intermediates may immediately interact with ferric ions during the reaction. Based on what mentioned above, the degradation rate of 60 min Fenton reaction in this study should be evaluated using the first- or second-order kinetics. Moreover, it should be noted that the hydrogen peroxide concentration used in the two separated stage was half of the total amount of H_2O_2 applied. It means that the produced hydroxyl radical is insufficient for the total removal of the organics in any single staged Fenton reactor and thus the second order kinetic model might be more reasonable to explain the degradation rate in this study.

In the present study, first- and second-order reaction kinetics were used to study the removal kinetic of parent pollutant 1,2,4-Acid by two-staged Fenton oxidation process. Kinetics in two-staged process was calculated respectively in order to investigate the degradation rate of parent compound in two separated process. The individual expression was presented below (Eqs. (17)–(18)):

First-order reaction kinetics:

$$\frac{dc}{dt} = -k_1 C \quad (17)$$

Second-order reaction kinetics:

$$\frac{dc}{dt} = -k_2 C^2 \quad (18)$$

where C is the concentration of 1,2,4-Acid; k_1 and k_2 represent the apparent kinetic rate constants of first- and second-order reaction kinetics, respectively; t is the reaction time. Regression analysis based on the first- and second-order reaction kinetics for the degradation of 1,2,4-Acid in staged Fenton oxidation process was conducted and the results are shown in Table 4. Comparing the regression coefficients (R^2) obtained from Table 4, it can be seen that R^2 based on the second-order reaction kinetics was 0.9404 and 0.9897 in the first stage and second stage of the enhanced Fenton process respectively which were obviously better than that based on the first order reaction kinetics. The results indicated that the degradation kinetics of 1,2,4-Acid may probably followed the second-order kinetics. As can be seen, the initial rate (<60 min) of degradation by Fenton process of 1,2,4-Acid was 10.7×10^{-3} and 3.5×10^{-3} , respectively. The little higher reaction constant in the first staged Fenton process is probably because the small molecular organic acids accumulated in the 2nd staged Fenton process competed for hydroxyl radicals with 1,2,4-Acid and the concentration of 1,2,4-Acid has greatly been reduced in the 1st staged Fenton reaction. The degradation of aromatic compounds often leads to the formation of intermediates such as glyoxylic, maleic, oxalic, acetic and formic acids [34]. Oxalic acid, the major intermediate of aromatic compound degradation, can complex with ferric ions [39], hindering the reduction effect of Fe^{2+} through Eqs. (3), all of which would lead to the decrease of the 2nd staged Fenton degradation rate.

3.3. Identification of intermediates

Main intermediates of wastewater containing 1,2,4-Acid treated by enhanced Fenton reaction (two-staged with inner circulation) was identified in this part of study. The LC-(ESI)-TOF-MS was applied to detect the intermediates that might have generated during the staged Fenton's reaction. Several stable intermediates such as 1,2-bisnaphthol, and *o*-phthalic acid were found in the 1st staged Fenton reaction. Some short-chain organic acids were also detected such as formic acid at 0.49 min and oxalic acid at 2.44 min. The total ion chromatography of the wastewater samples after each stage's treatment was shown in Fig. 9. The accurate mass data of the molecular ions were processed through the software MassLynx which provided the elemental formula and the mass errors. The errors obtained were between 0.7 and 4.4 ppm (root mean square (RMS) value 2.02) and 0.2–1.2 mDa (RMS = 0.72) which is within the limits of the widely accepted accuracy threshold of 5 ppm. Traces shown in Fig. 8(a) correspond to $[M-H]^-$ extracted with a mass window of 20 mDa for 1,2,4-Acid (m/z 247.981), and Naphthalen-2 (m/z 143.553), the naphthalene was believed to be the raw materials used for the synthesize naphthalene dye compounds.

In the staged-Fenton oxidation, the main oxidizing species is the hydroxyl radical. It is known that HO^\bullet radicals are nonselective and

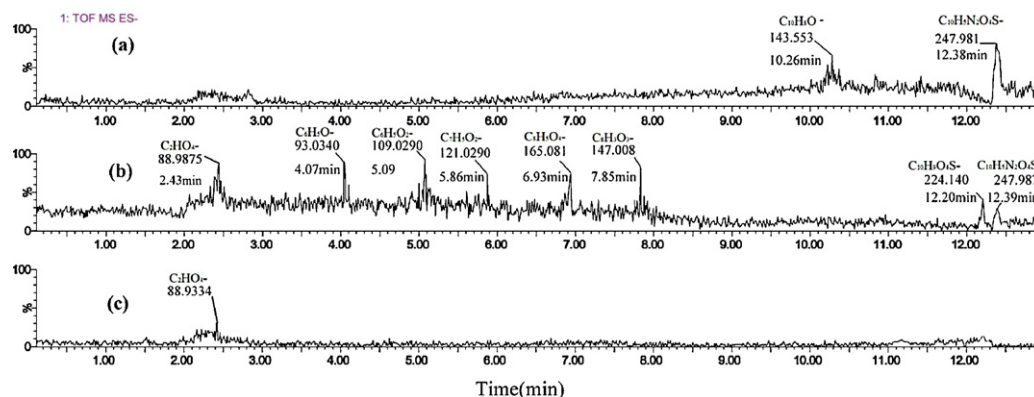


Fig. 9. UPLC-TOF total ion chromatogram of the wastewater post each treatment unit. (a, raw wastewater; b, post 1st staged Fenton; and c, post 2nd staged Fenton.)

strong electrophilic oxidizing species. The degradation process can be initiated either by the attack of HO[•] on 1,2,4-Acid that yields cleaving of –N=N– bond or by the direct hydroxylation of 1,2,4-Acid to give 1,2-dihydronaphthalene. 1,2-Dihydronaphthalene is further attacked by HO[•] generating smaller aromatic intermediates such as phthalic acid and aliphatic acid [43]. These acids are transformed into oxalic acid. The ultimate carboxylic acid, oxalic acid, is very slowly converted into CO₂ by hydroxyl radicals since it forms very stable Fe³⁺-oxalate complexes under the Fenton process.

Therefore, it could easily be detected after the 2nd staged Fenton process. It can be established that 1,2,4-Acid is degraded to 1,2-dihydronaphthalene and probably other nitrogen-free organic derivatives. The proposed mechanism of staged Fenton was also illustrated as shown in Fig. 10. The ring opening of aromatic intermediates leads to the formation of organic acids. In this case, smaller aromatic intermediates such as phthalic acid and phthalimide and aliphatic acids (such as fumaric, succinic, maleic and malonic acids) were found post the 1st staged Fenton reaction, whereas the

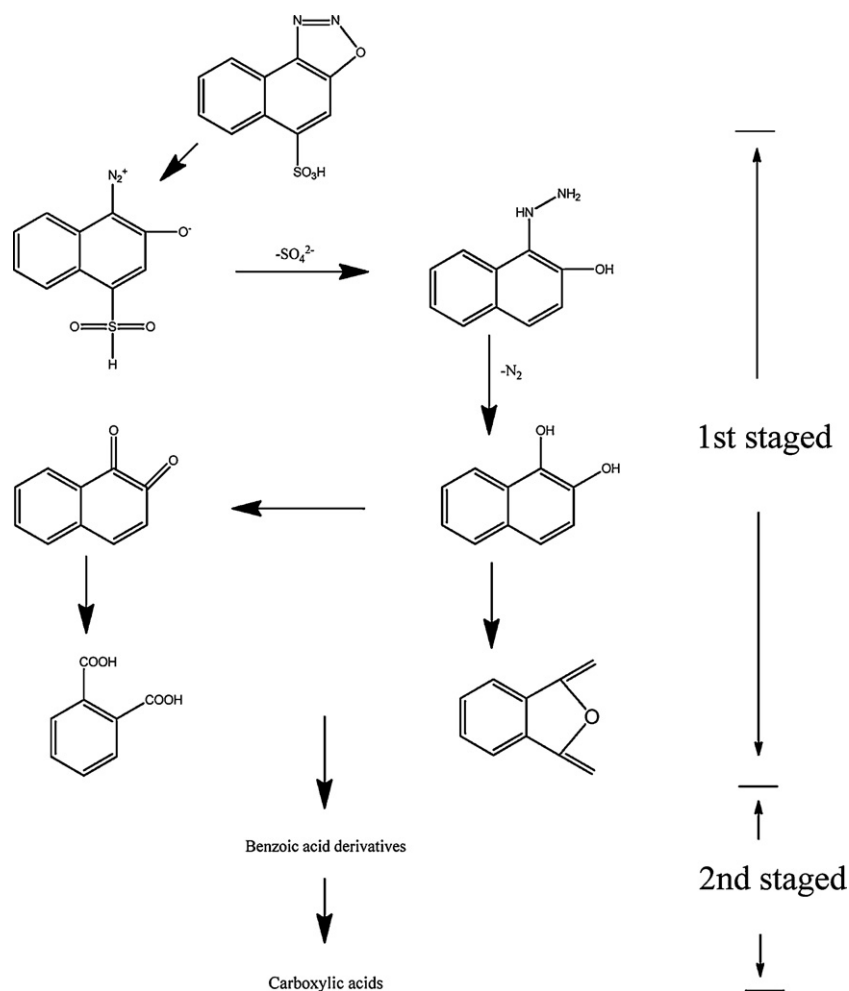


Fig. 10. Proposed degradation pathway of 1,2,4-Acid by two staged Fenton process.

low molecular weight compounds like oxalic and formic acids were extensively found at the end of 2nd staged Fenton process.

4. Conclusions

A coupled physicochemical with enhanced Fenton process has been proved to be a suitable treatment for dealing with naphthalene dye intermediate wastewater. In the first step, HA adsorption at pH ≥ 12 reduced an initial COD of 12,000 mg/L and colour of 25,600 (multiple) to 7310 mg/L and 2700 (multiple). A two-staged Fenton process with inner circulation system was introduced successfully as a subsequent treatment method. By using this enhanced technology, the remaining COD, TOC and 1,2,4-Acid decreased significantly to 210 mg/L, 46 mg/L and 21 mg/L. The hydrogen peroxide consumed could be reduced by 36% at most. The evolution intermediates of naphthalene dye intermediate wastewater through the staged Fenton was detected using a LC-(ESI)-TOF-MS technique, and the data indicated the degradation process could be initiated by the attack of HO \cdot on 1,2,4-Acid. Some benzene serial compounds were found after the 1st staged Fenton reaction, and they were continually degraded to low molecular weight acids in the 2nd Fenton stage. Based on the results obtained from bench scale test, it seems that this combined treatment method offers an attractive alternative in dealing with the high-concentration naphthalene industrial wastewater.

Acknowledgement

We thank the Shanghai Scientific Committee for financial support (Project NO. 10dz120010b).

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