Treatment of 3,4,5-trimethoxybenzaldehyde and Di-bromo-aldehyde manufacturing wastewater by the coupled Fenton pretreatment and UASB reactor with emphasis on optimization and chemicals analysis

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ABSTRACT

An integrated Fenton-UASB was investigated for the treatment of 3,4,5-trimethoxybenzaldehyde (TMBA) and Di-bromo-aldehyde manufacturing wastewater. A quadratic model for describing the individual and interactive effects of three variables independent variables (pH, concentration of H_2O_2 and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$) affecting COD abatement in Fenton pretreatment was successfully developed by the response surface methodology. The model proposed was further interfaced with the convex optimization method to optimize the variables in that convex optimization method can guarantee global optimization. A substantial increase in the BOD_5/COD ratio of the Fenton treated wastewater was observed, allowing sequent biological treatment feasible. The UASB reactor receiving treated effluent was operated continuously with an organic loading rate (OLR) from initial 3.0 g to 24.0 g COD/L/d with a stepwise reduction in hydraulic retention time (HRT) for 160 days. The degradation of organics in Fenton pretreatment and the anaerobic process was further revealed through GC-MS and FT-IR, respectively. The experimental results highlighted that the potential of integrated Fenton-UASB, providing 80.4% COD removal efficiency accompanied with 96.8% and 100% of TMBA and Di-bromo-aldehyde removal efficiency, respectively even when the applied OLR was up to 16.0 g COD/L/d.

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1. Introduction

3,4,5-Trimethoxybenzaldehyde (TMBA), a pharmaceutical intermediate, is widely used to prepare the antibacterial agent trimethoprim [1]. Trimethoprim is used solely, or in combination with sulfamethoxazole to treat a wide range of bacterial infections in humans and poultry [2]. In China today, market demand for trimethoprim has reached 1400 tons annually, and is increasing year by year. Indeed, the international demand has been expanding steadily over the last decade or more [3]. The approximately 15 thousand tons of TMBA manufacturing wastewater produced annually by the pharmaceutical industry presents a hazard to the natural water system which cannot be ignored [3], particularly it contains a large volume of Di-bromo-aldehyde (the main material

for production of TMBA). In Europe, new European Union regulations put into place in 2006 [4], require that discharge of organo-halogen compounds and substances which may form such compounds in the aquatic environment must be completely eliminated. In China, more stringent “chemical synthesis pharmaceutical industrial water pollutant discharge standards” (GB 21904-2008) were issued on August 1, 2008 [5]. Such a large volume of liquid wastes is generated during the manufacturing process highlights the need to find a sustainable treatment process to mitigate the environmental risk and ultimately comply with the effluent standards.

Generally, conventional biological treatment systems (aerobic and anaerobic) often are applied in the treatment of pharmaceutical wastewater as an initial step in removing some of the pharmaceuticals from the wastewater [6]. However, these treatment systems typically require an acclimatization period for the enrichments of microbial community. Besides, biological treatment has shown limited success due to the low biodegradability of some

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compounds [7]. As has been reported for many other types of industrial wastewater, TMBA and Di-bromo-aldehyde manufacturing wastewater is characterized by a high concentration refractory COD, a low BOD₅/COD ratio as well as toxicity [3,8]. The presence of these compounds not only resists effective breakdown, but also inhibits the activity of microorganisms, ultimately leading to the failure of biological treatment. Hence, environmentally-friendly advanced oxidation processes (AOPs) have been studied for use as a pre-treatment to complement biological treatment. The AOPs pretreatment facilitates the degradation of various initially refractory and/or toxic organic compounds to common microorganisms to readily biodegradable and less toxic intermediates [9]. Among the many existing AOPs systems, oxidation using Fenton's reagent has been the focus of much attention due to its main advantages: complete destruction of contaminants to harmless compounds, e.g. CO₂, water and inorganic salts [10]. Moreover, the process can take place at low temperature and at atmospheric pressure [11]. The Fenton reaction is a homogeneous catalytic oxidation process which utilizes a mixture of H₂O₂ and Fe²⁺ (and Fe³⁺) and causes the formation of highly reactive hydroxyl radicals that attack and destroy organic pollutants [10]. The drawback of the application of Fenton oxidation are the safety hazards associated with using H₂O₂ and that the pH must be reduced and the solution must be neutralized if followed by aerobic/anaerobic treatment [10]. Though some other AOPs (such as UV/H₂O₂, ozone [12]) do not need to adjust the pH, these options will be confronted with higher costs and have shown limit application at pilot plant scale. Over the past two decades, for practical and economic reasons, the Fenton reaction has been extensively applied in the treatment of a wide range of wastewater (predominantly in the treatment of industrial effluents) or as a pretreatment step to enhance the biodegradability of these effluents. Recent reports on the use of Fenton oxidation followed by biological treatment in treating pharmaceutical effluents have included antibiotic wastewater containing amoxicillin and cloxacillin [13], wastewater containing three nitrochlorinated herbicides (alachlor, atrazine and diuron) [14], etc. However, biological treatment in these studies treating pharmaceutical effluent was restricted to aerobic treatment. The advantages of anaerobic treatment over aerobic treatment are many: low maintenance, low operating costs, and biogas generation for energy recovery, etc [15]. Therefore, for the management of high strength toxic pharmaceutical wastewater, the coupling of Fenton and anaerobic treatment should provide a novel and sustainable strategy.

To the best of our knowledge, no literature has been published so far on the combination of Fenton pretreatment and the anaerobic treatment of TMBA and Di-bromo-aldehyde manufacturing wastewater. The molecular formulae of TMBA and Di-bromo-aldehyde are present in Fig. 1. Regarding the huge operational cost of the Fenton oxidation process for large discharges of TMBA and Di-bromo-aldehyde manufacturing wastewater generated from a pharmaceutical plant in China, a policy of minimizing the consumption of the chemicals involved is urgently required. In this work, a second-order regression equation was developed using response surface methodology (RSM) to test the hypothesis that

Fenton oxidation of TMBA and Di-bromo-aldehyde manufacturing wastewater for COD reduction can be optimized for three independent variables, viz. the concentration H₂O₂ (mg/L), the ratio of H₂O₂ to Fe²⁺ and pH. Further, concave optimization is applied to achieve optimization process condition because concave optimization can ensure a global optimization. Like genetic algorithm, convex optimization belongs to the global optimization method, which has been applied in such areas as automatic control systems, estimation and signal processing, and so on, [16]. Finally, the COD removal regularity with hydraulic retention time (HRT) reduction in a single upflow anaerobic sludge blanket reactor (UASB) treating the Fenton treated effluent wastewater under optimal Fenton oxidation condition was also evaluated. In addition, the degradation of the main organic pollutants in Fenton oxidation and the anaerobic process was revealed and compared by GC–MS and FT-IR.

2. Materials and methods

2.1. Pharmaceutical wastewater characteristics

The pharmaceutical wastewater used in this work was obtained from the 3,4,5-trimethoxybenzaldehyde (TMBA) and Di-bromo-aldehyde manufacturing department in Fukang pharmaceutical industry plant, Shangdong Province, China. The wastewater mainly consisted of TMBA and Di-bromo-aldehyde manufacturing wastewater and washing wastewater. The wastewater characteristics are summarized in Table 1. The extremely low BOD₅/COD ratio of 0.01 indicates the presence of organic compounds and/or toxic compounds with poor biodegradability. The biological toxicity of wastewater was determined using the strain of *Vibro Fischeri*. The inhibition rate was measured as 88%, indicating strong acute toxicity.

2.2. Experimental setup and procedure

2.2.1. Stage 1: Fenton oxidation process

The batch experiments were conducted using a 1 L glass reactor with 250 mL raw pharmaceutical wastewater. The temperature was 20 ± 2 °C during the reaction process. pH value was adjusted to the desired value using 3 N NaOH or 3 N H₂SO₄. After that, based on the experimental design, the required amount of iron (FeSO₄·H₂O) was added to the glass reactor, and then a known volume of hydrogen peroxide (30% w/w) was added to the mixture. In the following step, the solution was mixed with a magnetic stirrer at 200 rpm for 2 h. The samples were withdrawn and filtered through a 0.45 μm membrane syringe filter for analysis. The precipitated iron was separated from the reactor. Thereafter, the supernatant was heated for 1 h to remove excess H₂O₂ in alkaline condition. Finally, prior to the introduction of supernatant to UASB reactor, the pH of Fenton treated effluent was adjusted to 6.6–7.0.

2.2.2. Stage 2: UASB reactor

The anaerobic treatment of the Fenton-treated effluents was carried out by a cylindrical organic glass-made UASB with an

Fig. 1. Chemical structure of TMBA (Left) and Di-bromo-aldehyde (Right).

Table 1
Characteristics of TMBA and Di-bromo-aldehyde manufacturing wastewater.

	Unit	Range	Average
COD	mg/L	9600–9800	9700
BOD ₅	mg/L		2037
BOD ₅ /COD			0.01
Conductivity	μs/cm	2.1–2.3	2.2
pH		7.8–8.2	8.0
3,4,5-Trimethoxybenhyde	mg/L	498–556	527
Di-bromo-aldehyde	mg/L	186–226	206

internal diameter of 100 mm and a working zone, with a height of 0.8 m and a volume of 6 L. The UASB was inoculated with 3 L of granular sludge from a full-scale UASB reactor treating food manufacturing wastewater, Shijiazhuang City, Hebei province, China. This study was conducted at mesophilic condition at 35 ± 2 °C by water bath with water recirculation through the reactor's double jacket. The initial sludge concentration of the reactor was around 45.8 g VSS/L. Biogas was collected by a gas stockpile bottle after sequentially passing through a water lock filled with a 3 N NaOH solution and soda lime pellets to remove H₂S and CO₂, respectively. Methane production was determined daily by a wet gas-flow meter. The UASB was initially operated from an organic loading rate (OLR) of 3.0 g COD/L/d at an HRT of 2 days and a 4.0 g COD/L/d at an HRT of 1.5 days respectively for 20 days. Thereafter, to evaluate the performance of the UASB reactor and its treatment capacity, the reactor was further switched from 6.0 upto the maximum 24.0 g COD/L/d through HRT reduction in a stepwise fashion in the following 100 days. In the last stage (140–160 day), the operating OLR was returned to 16.0 g COD/L/d to investigate the recovering ability of the rector in treatment efficiency.

2.3. Experimental design and data analysis

In this work, the pH (X_1), concentration H₂O₂ (mg/L) (X_2) and ratio of H₂O₂ to Fe²⁺ (X_3) were chosen as the three independent variables with six replicates at center points and six star points, according to the central composite design (CCD). The range and levels of the variables (high and low) investigated in the work are given in Table 2. Each of the parameters was coded at five levels: $-\alpha$, -1 , 0 , $+1$, and $+\alpha$. The variables x_i was coded as X_i according to the following relationship:

$$X_i = (X_i - X_0)/\delta X_i \tag{1}$$

where x_i is the coded value of an independent variable, X_i is corresponding natural value, x_0 is the natural value of an independent variable at the center point and δx_i is the step change value.

In order to further develop an empirical model of the release process and to gain a more precise estimate of the optimum operating conditions for the factors involved, a central composite design with five coded levels was performed. The relationships among the variables are expressed mathematically in the form of quadratic polynomial equation as follows:

$$Y = \hat{a}_0 + \hat{a}_1X_1 + \hat{a}_2X_2 + \hat{a}_3X_3 + \hat{a}_{12}X_1X_2 + \hat{a}_{13}X_1X_3 + \hat{a}_{23}X_2X_3 + \hat{a}_{11}X_1^2 + \hat{a}_{22}X_2^2 + \hat{a}_{33}X_3^2 \tag{2}$$

where Y is the response variable, $\hat{a}_0$ is the intercept term, $\hat{a}_1$, $\hat{a}_2$ and $\hat{a}_3$ are linear coefficients, $\hat{a}_{12}$, $\hat{a}_{22}$ and $\hat{a}_{33}$ are quadratic coefficients, and x_1 , x_2 and x_3 are coded values of three independent variables.

Data were analyzed using Minitab 14 statistical software (USA) including analysis of variance (ANOVA) to explain the interaction between the variables and the response. The optimal result was calculated using the convex optimization method.

Table 2
Experiment ranges and levels of the independent variables.

Independent variables	Range and level				
	$-\alpha$	-1	0	$+1$	$+\alpha$
pH (X_1)	0.64	2	4	6	7.36
H ₂ O ₂ concentration, mg/L (X_2)	318	1000	2000	3000	3682
H ₂ O ₂ /Fe ²⁺	0.64	2	4	6	7.36

2.4. Analytical methods

The chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD₅), pH and volatile suspended solid (VSS) were determined according to the standard analytical procedures published by the American Public Health Association [17]. The analysis of main organic compounds in raw wastewater and Fenton-treated wastewater was performed using a 6890 N network GC–MS system (Agilent, USA) equipped with a 5973 network Mass Selective Detector and a DB-5ms capillary column with an inner diameter of 0.25 mm and a length of 30.0 m. Prior to GC–MS analysis, wastewater samples were extracted by CH₂Cl₂ into nautical, basic and acid phases (repeated three times for each phase) and then concentrated by evaporating in a water bath at 39–41 °C. The GC column was operated in a temperature programmed mode at 80 °C for 2 min, and then raised 5 °C/min to 250 °C, as in a previous paper [18]. Fourier Transform Infrared (FT-IR) spectroscopy was performed on Spectrum One, Perkin Elmer, UAS. Prior to the FT-IR analysis, the samples were dried. Then, 1 mg of the dried samples was mixed with 100 mg of spectroscopic grade potassium bromide and grinded. The samples were made in the form of pellets and scanned in the spectral range of 4000–400 cm^{−1}.

3. Results and discussion

3.1. Optimization for COD removal using Fenton's reagent

The batch mode of Fenton's oxidation process was carried out in central composite design (CCD) to illustrate the effect of three independent variables on responses and the optimal condition. Fourteen experiments were augmented with six replications conducted at the center values (zero level) to evaluate the pure error. According to the experimental design and result (see Table 3), the regression model obtained by the application of response surface methodology is given by following equation:

$$Z = 5983 + 384.22x_1 - 117.03x_2 + 155.72x_3 + 499.54x_1^2 + 374.20x_2^2 + 333.90x_3^2 + 1.13x_1x_2 - 23.37x_1x_3 + 28.87x_2x_3$$

where Z is the value of COD after Fenton pretreatment, x_1 (pH), x_2 (concentration H₂O₂) and x_3 (ratio of H₂O₂ to Fe²⁺) are the coded values of the test variables.

Table 3
Corresponding results, experimental design and levels of three independent variables based on central composite design (CCD) for COD after treatment.

Run	Independent variables (coded value)			Dependant variables COD (mg/L)
	x_1	x_2	x_3	
1	0	$-\alpha$	0	7280
2	+1	+1	-1	7378
3	0	0	0	5740
4	0	0	0	6070
5	0	0	0	5930
6	-1	-1	+1	7000
7	-1	-1	-1	6700
8	0	0	0	6117
9	+1	+1	+1	7700
10	0	$+\alpha$	0	6800
11	$+\alpha$	0	0	7900
12	-1	+1	+1	6700
13	0	0	0	6048
14	0	0	0	6000
15	-1	+1	-1	6600
16	+1	-1	-1	7789
17	$-\alpha$	0	0	6889
18	0	0	$+\alpha$	7376
19	0	0	$-\alpha$	6476
20	+1	-1	+1	7680

The student's t -value and P -value was employed to determine the significance of the regression coefficients of the three effects (see Table 4). Based on the fact that the coefficients are significant if the $\text{Prob} > |t|$ is smaller than 0.05 (95% confidence level), Table 4 implies that first-order effects, square effects of x_1 , x_2 and x_3 and interaction of x_1x_3 are significant while interaction of x_1x_2 and x_2x_3 are insignificant. The optimal pH (x_1), concentration H_2O_2 (mg/L) (x_2) and ratio of H_2O_2 to Fe^{2+} (x_3) obtained from the minimum point of the model were calculated using the convex optimization method. The traditional method in optimizing the second-order regression response surface methodology (RSM) model is to solve the partial derivative of the target function and make it to zero to obtain analytical solutions. The shortcoming of this method is that it cannot ensure the global optimality when the objective function is non-convex (or non-concave) due to the existence of local extreme points. In the present study, our paper will utilize the convex optimization method to firstly prove that the second-order regression equation is concave and then to find the solution of the objective function using Lagrange multiplier method. The problem at hand is to minimize the (1) while satisfying (2).

Let $\mathbf{X} = [x_1, x_2, x_3]^T$, original minimization problem can be equivalently expressed as

$$\begin{aligned} \min \quad & \mathbf{X}\mathbf{X}^T\mathbf{A}\mathbf{X} + \mathbf{X}^T\mathbf{B} + 5983 \\ \text{s.t.} \quad & x_1^2 \leq 1.68^2 \\ & x_2^2 \leq 1.68^2 \\ & x_3^2 \leq 1.68^2 \end{aligned} \quad (3)$$

$$\begin{aligned} \text{where, } \mathbf{A} = & \begin{bmatrix} 499.54, & 1.13/2, & -23.37/2 \\ 1.13/2, & 374.20, & 28.87/2 \\ -23.37/2, & 28.87/2, & 333.90 \end{bmatrix} \\ \mathbf{B} = & [384.22, -117.03, 155.72]^T \end{aligned} \quad (4)$$

We then find the Hessian matrix of the objective function (3) which can be calculated as

$$\frac{\partial(\mathbf{X}^T\mathbf{A}\mathbf{X} + \mathbf{X}^T\mathbf{B} + 5983)}{\partial\mathbf{X}^T\partial\mathbf{X}} = 2\mathbf{A} \quad (5)$$

Eigen-decomposition of $2\mathbf{A}$ yields eigen values 657.0319, 757.5244 and 1000.72. This Hessian matrix is definitely positive, an optimal solution does exist. We now employ the Lagrange multiplier method to solve this solution. The Lagrangian L associated with (3) is given by

$$L(\mathbf{X}, \lambda_1, \lambda_2, \lambda_3) = \mathbf{X}^T\mathbf{A}\mathbf{X} + \mathbf{X}^T\mathbf{B} + \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \lambda_3 \end{bmatrix}^T \begin{bmatrix} x_1^2 - 1.68^2 \\ x_2^2 - 1.68^2 \\ x_3^2 - 1.68^2 \end{bmatrix} + 5983 \quad (6)$$

Table 4
Regression analysis using the 2^3 factorial central composite design.

Model term	Coefficient estimate	t -Value	p -Value
Intercept	5983	79.98	0.000
x_1	384.22	7.74	0.000
x_2	-117.03	-2.36	0.040
x_3	155.72	3.14	0.011
x_1^2	499.54	10.33	0.00
x_2^2	374.2	7.74	0.00
x_3^2	333.90	6.91	0.00
x_1x_2	1.13	0.02	0.98
x_2x_3	-23.37	-0.36	0.72
x_1x_3	28.87	0.45	0.04

We use the convex optimization method to extract the global minimum value Z . Then we can obtain the minimum value $Z = 5878.4018$ and the corresponding $\mathbf{X} = [-0.3907, 0.16676, -0.25406]^T$. Thus, at the optimal condition of pH (3.2), the H_2O_2 concentration (2166.8 mg/L) and ratio of H_2O_2 to Fe^{2+} (3.5), a minimum COD value of 5878.4 mg/L can be obtained, which corresponds to a maximum removal efficiency of 39.4%. The actual experimental result under optimal condition was 39.1%. It was clear that, no significant COD reduction efficiency was achieved during the Fenton process even at the optimal condition. The COD removal efficiency varies greatly when Fenton reagent is applied to treat industrial effluent. A 45–65% COD removal efficiency was observed in a previous work in the treatment of a pharmaceutical wastewater [19]. In another earlier work, 78.3% of COD removal efficiency was found in treating dyeing industrial effluent [20]. Thus, the characteristic of hazardous components in raw wastewater should be assumed to greatly influence the extent of COD removal in Fenton's oxidation process [10].

The statistical significance of the quadratic model was evaluated by the analysis of variance (ANOVA), which revealed that this regression is statistically significant at a 95% confidence level at an F value of 28.49 and values of $\text{prob} > F$ (<0.0001) (Table 5). The predicted value of R^2 (0.963) was close to the adjusted R^2 (0.929), indicating a good agreement between the model-predicted and the experimental values. The adequacy of models was tested through lack-of-fit F -tests. The lack of fit F -statistic is not statistically significant as the P -value is greater than 0.05.

3.2. Three-dimensional (3D) response surface plot for COD removal after Fenton pretreatment

3D response surface plots as a function of two factors, with all of the other factors fixed, are helpful in understanding both the main effects and the interaction effects of these factors. When tested with pH in the range of 0.64–7.36, as shown in Fig. 2a and c), COD abatement by Fenton's oxidation varies with pH value of the solution. No significant differences in the treatment efficiency between pH 3 and 4.1 were observed though a pH of 3.2 can result in maximum COD removal efficiency. The existence of an optimal pH range can be explained by Reaction (1), which is a chain initiation reaction whereby H_2O_2 decomposes catalytically by means of Fe^{2+} to give raise to reactive HO.

When the pH is lower than 3, the Fenton's reaction (Eq. (1)) is severely affected, due to a reduction in the hydroxyl radical production [21]. Furthermore, hydrogen peroxide is stable at low pH probably because it solvates a proton to form an oxonium ion (H_3O^+). An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to substantially reduce the reactivity with ferrous ion [22]. At pH values above 4, the precipitation of iron hydroxides inhibited both the regeneration of the active specie Fe^{2+} and the formation of hydroxyl radicals [23]. Additionally, the oxidation potential of the hydroxyl radical is

Table 5
Analysis of variance (ANOVA) for the response surface quadratic model.

Source	df	Sum of squares	Mean square	F -value	$\text{Prob} > F$
Regression	9	8,629,096	958,788	28.49	0.000
Residual	10	336,497	33,648		
Lack of fit	5	244,590	48,918	3.19	0.153
Pure error	5	91,889	18,378		

$R^2 = 0.963$, adjusted $R^2 = 0.929$.

Fig. 2. Contour plot showing the effect of pH and concentration H_2O_2 (a), concentration H_2O_2 and ratio of H_2O_2 to Fe^{2+} (b) and pH and ratio of H_2O_2 to Fe^{2+} (c) on COD of Fenton-treated wastewater.

known to decrease with increasing pH. Finally, another reason for the inefficient degradation at $\text{pH} > 3$ is due to the dissociation and auto-decomposition of H_2O_2 [24].

Since the critical issue in the economy of the Fenton oxidation process is closely related to the consumption of H_2O_2 , optimal H_2O_2 is needed for scale-up applications. As can be observed from Fig. 2a and b, the H_2O_2 concentration can significantly influence the oxidation capacity of the Fenton system. Increasing the H_2O_2 concentration from 318 mg/L to around 2200 mg/L enhances COD removal efficiency because more hydroxyl radicals are generated. However, at a concentration of more than 2200 mg/L, the performance of the reaction oxidation remained almost unchanged and even slightly decreased when the concentration was further altered to over 3200 mg/L. This finding may be explained by the recombination of hydroxyl radicals and also the reaction of hydroxyl radicals with H_2O_2 , which contributes to the OH-scavenging capacity (Eqs. (2)–(4)) [25].

In the Fenton oxidation process, the Fe^{2+} acts in the decomposition of hydrogen peroxide as a catalytic agent. By optimizing the amount Fe^{2+} , the reagent cost is reduced and less additional iron sludge treatment is required. Variations of COD removal with $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ at different concentrations of H_2O_2 and pH are depicted in Fig. 2b and c. Apparently, according to Eqs. (1) and (5), the excess iron ions react with hydroxyls radical and inevitably result in a scavenging effect on hydroxyl radicals.

3.3. Biodegradability improvement after Fenton pretreatment and FT-IR spectrum analysis

Traditionally, the biodegradability of wastewater is indexed by BOD_5/COD and biological treatment is suitable only when the BOD_5/COD value of the wastewater is higher than 0.5 [26]. With a BOD_5/COD ratio of 0.01, the raw TMBA and Di-bromo-aldehyde manufacturing wastewater was clearly bio-refractory and difficult to be biodegraded. Although no remarkable removal of the raw wastewater COD was observed after Fenton-pretreatment at the optimal condition, the BOD_5/COD ratio raised dramatically to 0.68. In this study, the augmented biodegradability of TMBA and Di-bromo-aldehyde manufacturing wastewater can be attributed to the substantial degradation of bio-refractory organic compounds in the Fenton process. This can be further confirmed by the GC–MS analysis of raw and Fenton-treated wastewater. According to Fig 3, seven main compounds were identified, as summarized in Table 6. As observed in Fig. 3 and Table 6, the amount of main organic pollutants decreased sharply during the Fenton pretreatment process. Among them, 90.7% of TMBA, 100% of Di-bromo-aldehyde and 98.1% of 3,4,5-trimethoxy-benzaldehyde was decomposed. Moreover, no Br^- was found in the Fenton effluent, suggesting that Br^- was totally oxidized to bromate during the Fenton oxidation process. Since COD removal efficiency was just 39.1%, it is reasonable to conclude that the main organic compounds were mostly degraded into various intermediate organic matters without complete mineralization during this Fenton oxidation process. As yet, the pathway of 3,4,5-Trimethoxybenzaldehyde degradation in Fenton oxidation process is unclear. According to the degradation process of some benzene series (structurally similar to TMBA) in the Fenton oxidation process reported in some previous literatures [27,28], it is speculated that

Fig. 3. GC–MS chromatograms of raw wastewater, Fenton-treated and UASB treatment of TMBA and Di-bromo-aldehyde manufacturing wastewater.

Table 6

Main organic compounds identified in raw wastewater, Fenton-treated and UASB treatment by GC–MS.

No.	Retention time (min)	Chemicals	Similarity (%)	Area (10^6) (quantitative iron)		
				Raw	Fenton	UASB
1	14.90	1,2,3-Trimethoxy-5-methyl-benzene	95.1	1.38	0	0
2	16.95	3,4-Dimethoxy-benzaldehyde	93.1	1.79	0	0
3	18.10	1,2,3,4-Tetramethoxybenzene	93.2	1.4	0.18	0
4	19.50	3,4,5-Trimethoxy-benzaldehyde	99	326	18.1	10.3
5	20.5	Di-bromo-aldehyde	99	0.7	0	0
6	21.1	4-Hydroxy-3,5-dimethoxy-benzaldehyde	98	15.9	0.13	0
7	22.4	3,4,5-Trimethoxy-methylester	97.5	1.77	0.1	0

the pathway of TMBA degradation mainly consists of five steps. The first step is likely to be direct $\cdot\text{OH}$ attacks on the TMBA molecule to form 3,4,5-trihydroxyphenol. After the initial reaction, further attack on 3,4,5-trihydroxyphenol by hydroxyl radical results in the cleavage of the aromatic rings in the second step, where maleic acid is the primary product from ring cleavage [28]. After that, in the third step, when high Fe^{2+} and H_2O_2 concentrations are used, all of the intermediates are finally oxidized to formic acid and oxalic acid [28]. Finally, formic acid is completely mineralized into carbon dioxide and water whereas oxalic acid remains in the solution due to quite refractory behavior [28]. The pathway of TMBA degradation during the Fenton oxidation process needs be further confirmed by the analysis of intermediates.

FT-IR spectroscopy was used to gain a superficial understanding of the organic compounds characteristics [29]. The FT-IR spectra of raw wastewater and after Fenton oxidation are presented in Fig. 4. A broad peak in the $3400\text{--}3600\text{ cm}^{-1}$ region was observed, responding to the overlap of N–H, O–H stretching and hydrogen-bonded OH of carboxylic acids in the inter- and intra-molecular hydrogen bonding of polymeric compounds including alcohols, phenols and carboxylic acids [30]. The peak appeared at 3015 cm^{-1} is due to the presence of CH stretching mode of the $\text{HC}=\text{CH}$ groups [31]. The peaks appeared at 2965 cm^{-1} and 2250 cm^{-1} are assigned to the stretching of CH_2 group and $\text{C}=\text{N}$ in fatty nitriles, respectively [32]. The band around 2820 cm^{-1} and 1423.21 cm^{-1} is attributed to the presence of C–H stretching in aldehyde and C–N stretching respectively. The band in the range $950\text{--}1200\text{ cm}^{-1}$ is indicative of valent C–O, C–C and deformation vibrations of ring structures of origin [33]. These peaks demonstrated that aromatic and phenolic compounds are the main organic pollutants in raw wastewater. Most of the peak adsorption intensities decreased after Fenton oxidation, as shown in Fig. 4. No

peak at 2250 cm^{-1} was observed. The intensity and/or more accurately the area of the adsorption bands are directly related to the concentration of the molecules [31]. The results clearly indicate that the main aromatic pollutants were largely decomposed or transformed during the Fenton oxidation process, which was consistent with the results of the GC–MS analysis. The only exception is the peak which appeared at around 600 cm^{-1} , which implies that inorganic compounds, such as sodium sulfate in raw wastewater appear to resist the Fenton oxidation process. Further biological treatment is required for the reduction of sulfate.

3.4. UASB treatment process and GC–MS and FT-IR spectrum analysis

In order to achieve a further reduction in the residual COD in wastewater after Fenton pretreatment, a post treatment step is required. Anaerobic treatment is the preferred option due to its ability to deal with high concentration organic wastewater with lower energy inputs, sludge yield and, nutrient requirements, and also improved biogas recovery [15]. Generally, in the treatment of high strength wastewater containing refractory compounds using the UASB process, a start-up stage is necessary in order to accumulate the active bacterial biomass by introducing co-substrates such as sucrose. With prolonged operation time, the concentration of co-substrates gradually decreases while the concentration of wastewater increases correspondingly. However, Fenton process allows the subsequent biological degradation to be achieved in a short detention time [34]. In the present work, the seed inoculums were unexposed to TMBA and Di-bromo-aldehyde manufacturing wastewater prior to the trial. Even though the pre-treated wastewater was solely introduced to UASB with no initial adaptive process, as can be seen from Fig. 5a and b, COD removal rate was steadily maintained in the range of 82.1–83.8% when the UASB was operated with an OLR from initial 3.0 g to 4.0 g COD/L/d in the start-up period. In parallel, HRT varied from initial 2 to 1.5 days and the CH_4 production rate increased from 0.65 to 0.87 L/L/d (Fig. 5c). During the following 100 days of operation (41–100 days), the UASB responded to gradually elevated OLRs with applied HRT reduction. A COD removal efficiency of around 70.6% was observed even at the OLR of 16.0 g COD/L/d, corresponding to a CH_4 production rate of 3.3 L/L/d. COD removal efficiency dropped dramatically to around 61.5% when OLR was enhanced to maximum 24 g COD/L/d at a HRT of 0.25 day. Meanwhile, the CH_4 production rate slightly increased to 3.6 L/L/d. In order to prevent possible acidification, from 140 to 160 days, the reactor was operated back to 16.0 g COD/L/d by altering the HRT to 0.38 day. As can be observed from Fig. 5, the COD removal efficiency quickly recovered to nearly 70% within four days of operation, showing how stable the system was. The excellent performance of the UASB can be attributed to the depletion of main refractory compounds and the higher activity of degradable low molecular organic compounds produced by Fenton pretreatment.

Furthermore, even at an OLR up to 16.0 g COD/L/d (with HRT as short as 0.38 days), a comparison of the concentrations in the

Fig. 4. FTIR spectra of raw wastewater, Fenton oxidation treatment and Fenton + UASB treatment.

Fig. 5. Overall performance of the UASB in continuous operation: (a) influent and effluent COD variation; (b) OLR variation; (c) CH₄ gas production rate variation.

Fenton-treated effluent (Table 6 and Fig. 3) indicate that 45% of TMBA and 100% of Di-bromo-aldehyde were degraded in the reactor (Table 6 and Fig. 3). The accumulation of TMBA and Di-bromo-aldehyde-degrading microorganisms in the sludge after successive operation resulted in the effective decomposition. This is further confirmed by FT-IR spectrum analysis. Fig. 4 shows that all of the peak intensities of the combined Fenton and UASB treated wastewater were lower than those of a single Fenton treated. The peak at 2815 cm⁻¹ and 3015 cm⁻¹ almost completely disappeared. The considerable reduction of peak intensity at around 600 cm⁻¹ can be attributed to the accumulation of sulfate reduction bacteria

(SRB) in the reactor. However, UASB cannot achieve 100% removal efficiency of TMBA in Fenton effluent (see Table 6). Thus, with the aim of achieving complete TMBA removal, aerobic treatment can be used as a sequent option. For instance, in a previous lab-scale study, it was found that after Fenton pretreatment, complete degradation of p-aminophenol, paracetamol, phenol, benzoic acid, diclofenac, nitrobenzene can be observed in further aerobic process [34]. However, so far, no complete removal of diclofenac has been reported in actual municipal wastewater treatment plants. In the effluents of municipal wastewater treatment plants, the effluent maximum concentrations varied between 0.12 and 4.7 µg/L and mean concentrations between 0.002 and 2.5 µg/L [35]. The average removal efficiency varied between only 20% and 50% [35]. Thus, following the aerobic treatment, further polishing technologies (such as adsorption and membrane separation) should be extensively investigated with the intent of complete elimination of diclofenac.

In addition, it should be noted that no inhibition of methanogens was observed in this reactor overtime. The measured inhibition rate of Fenton effluent (using *Vibro Fischeri*) decreased sharply to 27%, suggesting that Fenton pretreatment reduces the toxicity of wastewater to a very low level by decomposing the toxic compounds (such as Sodium Methyl Sulfate) [8] in raw wastewater. Higher concentrations of toxicants after long term acclimation generally lead to the significant inhibition of the anaerobic process [36]. It can be further confirmed that there was no potential risk (generation of novel and more toxic chemicals) caused by the Fenton oxidation process. The final result of 80.4% COD removal efficiency with 96.8% and 100% of TMBA and Di-bromo-aldehyde removal efficiency at shorter HRT was encouraging with respect to the treatment of TMBA and Di-bromo-aldehyde manufacturing wastewater using the integrated Fenton-UASB.

4. Conclusion

A combination of the Fenton oxidation and the UASB was successfully employed to treat 3,4,5-trimethoxybenzaldehyde and Di-bromo-aldehyde manufacturing wastewater. The Fenton oxidation process was successfully modeled by the response surface methodology and further optimized by the convex optimization method. A maximum COD removal efficiency of 39.4% was achieved with an optimal pH 3.2, an H₂O₂ concentration of 2166.8 mg/L and a ratio of H₂O₂ to Fe²⁺ of 3.5. Fenton pretreatment significantly augmented the BOD₅/COD ratio of wastewater, suggesting that further biological treatment is practical. A GC-MS and FT-IR analysis revealed the substantial degradation of organic compounds. A satisfactory COD removal result and 3,4,5-trimethoxybenzaldehyde and Di-bromo-aldehyde removal efficiency was concomitant with methane production in the UASB reactor within 160 days' operation when the HRT was as short as 0.38 day.

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