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ScienceDirect
Journal of Hazardous Materials 144 (2007) 159–163
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Removal of organic pollutants from 2,2′,5,5′-tetrachlorobenzidine (TCB) industrial wastewater by micro-electrochemical oxidation and air-stripping

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Received 27 August 2005; received in revised form 30 September 2006; accepted 3 October 2006
Available online 13 October 2006

Abstract

A feasible method for treatment of the wastewater from the two-staged neutralization in 2,2′,5,5′-tetrachlorobenzidine (TCB) manufacturing processes, a refractory dye intermediate effluents, based on combined micro-electrochemical oxidation or iron-chipping filtration (ICF) and air-stripping reactor (ASR), was developed. On conditions of HRT 1 h, pH 3.0 in ICF and HRT 38 h, gas–liquid ratio 15, pH 6.0–8.65, temperature 26 °C in ASR, the overall COD, color, TCB and NH_4^+-N removal were 96.8%, 91%, 87.61% and 62%, respectively, during the treatment of TCB wastewater from the two-staged neutralization dissolved by methanol. The averaged 18.3%, 81.7% of the total degraded COD, 35.2%, 64.8% of TCB were carried out in ICF and ASR, respectively. NH_4^+-N removal was finished mainly in ASR. The experimental results indicated that the combined micro-electrochemical oxidation and air-stripping process performed good treatment of COD, color, TCB and NH_4^+-N removal in TCB wastewater from the two-staged neutralization dissolved by ethanol or acetone, came up the discharge standard in China. But the TCB wastewater from the two-staged neutralization dissolved by methanol should be deeply treated before discharged.
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Keywords: Air-stripping; Micro-electrochemical; 2,2′,5,5′-Tetrachlorobenzidine (TCB); Wastewater treatment

1. Introduction

2,2′,5,5′-Tetrachlorobenzidine (TCB), an important intermediate in the industrial manufacture of dyes and pigments, with the molecular formula $C_{12}H_8N_2Cl_4$, molecular weight 322.02, low solubility in water, is classified as a human carcinogen or a probable human carcinogen in USA [1,2]. In a four-stage synthesis of 2,2′, 5,5′-tetrachlorobenzidine (TCB), about 30 tonnes wastewater per ton products, containing high concentration of NaOH and Na_2SO_4 solution, methanol or ethanol or acetone and lots of impurities, along with a small amount of TCB products, are generated. If TCB wastewater were not treated, it would heavily pollute the environment around the plant.

To date there are much less researches in TCB wastewater treatment. Considering that containing similar toxicoids in TCB and DCB wastewater, thus the DCB wastewater treatment processes were also reviewed for TCB wastewater treatment. The current recommended technologies for treating DCB-containing industrial wastewaters mainly include biological process, wet air oxidation, incineration, and chemical or electrolytic oxidation [3]. Owning to the strong affection of the heavy salt concentration, the wastewater containing DCB cannot be effectively treated by wet air oxidation, incineration and biological process in practical plants [4–6]. In the last decade, experimental investigations related to dyestuff effluent treatment have focused on alternative treatment methods being capable of removing colored compounds in an environmentally safer and economically more feasible way [5,7].

The object of our work was to combine the micro-electrochemical oxidation and air-stripping process for treatment of TCB wastewater from the two-staged neutralization. This method not only has the advantages of both oxidation and also increases the dissolved oxygen in water [8]. COD and color

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doi:10.1016/j.jhazmat.2006.10.028

Table 1
The characteristics of TCB wastewater

Parameters	Raw wastewater					
	A[a]		B[b]		C[c]	
	Range	Average	Range	Average	Range	Average
Na_2SO_4 (mg/l)	23000	23000		–	–	–
COD_{Cr} (mg/l)	6600–14890	10073	7500–8290	7895	2045–2630	2338
BOD_5 (mg/l)	261.0–373.0	317.0	–	–	–	–
BOD_5/COD_{Cr}	0.03–0.025	0.028	–	–	–	–
NH_4^+-N (mg/l)	1042–1246	1144	–	–	–	–
TP	n.d.	n.d.	–	–	–	–
TCB (mg/l)	78–89	83.5	38–62	50	26–46	36
Chroma (DT)[a]	200–600	400	200–600	400	200–600	400
SS (mg/l)	126–288	207	–	–	–	–
pH	11.47–13.2	–	12.6–13.3	–	11.47–12.45	–

[a] Raw wastewater from the two-staged neutralization with methanol addition.
[b] Raw wastewater from the two-staged neutralization with ethanol addition.
[c] Raw wastewater from the two-staged neutralization with acetone addition; DT = dilution times.

removal efficiencies of TCB wastewater were mainly investigated in this paper.

2. Materials and methods

2.1. Raw wastewater

The TCB wastewater, containing high concentration of NaOH and Na_2SO_4 solution, along with a small amount of TCB products, was obtained from the two-staged neutralization with methanol or ethanol or acetone addition, named as the raw wastewater A–C, respectively, in this paper. The characteristics of the raw wastewater A–C are listed in Table 1. Due to its heavy salt concentration, the wastewater containing TCB cannot be effectively treated by biological process in practical plants.

2.2. Experimental methods

The experimental set-ups were mainly made up with the iron-chipping filtration (ICF) and the air-stripping reactor (ASR), demonstrated as Fig. 1. ICF was made of glass, volume 500 ml, filled by iron and carbon as padding accounting for 60% of the total volume. A 2 l beaker with a microporous diffuser was used as ASR in this study.

2.2.1. Iron-chipping filtration (ICF) operation

The iron-chipping filtration (ICF), a micro-electrochemical process used for treatment of the TCB industrial wastewater, consists of myriad slim cell batters. It has the functions of electrolysis, coagulation, electrical flocculation, and adsorption. The dyestuff molecules were firstly absorbed by the surface of carbons, then the oxygenation and reduction reaction occurred on the two poles, as follows:

anode anticathode

$$Fe–2e \rightarrow Fe^{2+} \quad E^\circ (Fe^{2+}/Fe) = -0.44\,V$$

cathode

$$2H^+ + 2e \rightarrow 2[H] \rightarrow H_2,$$

$$E^\circ (H^+/H_2) = 0.00\,V \text{ (acidic solution)}$$

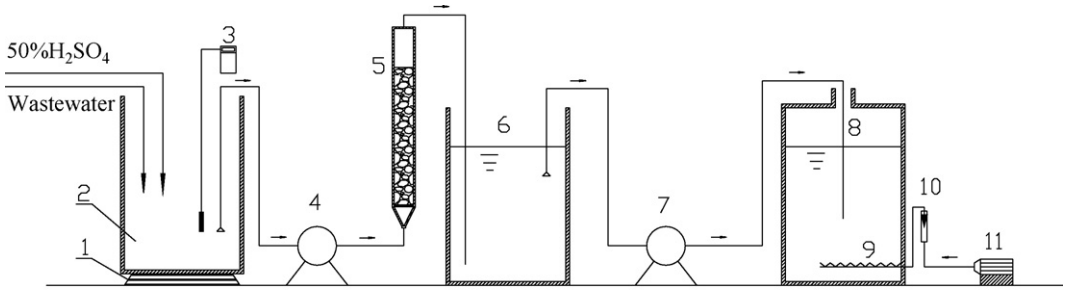
$$O_2 + 4H^+ + 4e \rightarrow 2H_2O,$$

$$E^\circ (O_2/H_2O) = 1.22\,V \text{ (acidic solution)}$$

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-,$$

$$E^\circ (O_2/H_2O) = 0.41\,V \text{ (middle or alky solution).}$$

Hydrogen free radixes caused through the electrochemical reactions would attack the organic substances, such as the unsat-



1、Magnetic stirrer；2, 6, 8、2L beaker; 3、PH meter; 4, 7、Vermicular pump;
5、ICF；9、Microporous diffuser; 10、Rotameter; 11、Air pump

Fig. 1. A schematic of the experimental set-ups.

urated dye molecules. The chromophore or chromogen of the dye molecules can be destroyed and the wastewater can be decolorized [9–11]. Meanwhile, microcell electrolysis can also translate the most nitrobenzene into benzidine, which is easily biodegraded [12].

The micro-electrolysis oxidation experiments in our lab were carried out according to the following steps: (1) take 1000 ml wastewater sample in a 2 l beaker with a stirrer; (2) drip amount of the wasted 50% H_2SO_4 solution produced during the production of TCB into the wastewater sample and turn slowly on the stirrer, aiming that the pH was adjusted to lie in the interval pH 2–5 with based on other's study [9,10]; (3) pump the wastewater sample by a vermicular pump (BT00-300 M, Baoding Lange Peristaltic Pump Company, China) into the iron-chipping filtration (ICF) acting as a micro-electrolysis reactor for HRT 1 h at the fixed flowrate. After reactions had completed, COD, color, NH_4^+-N, TCB and pH values of the sample were measured.

2.2.2. Air-stripping reactor (ASR) operation

The air-stripping experiments in this lab were performed with 1000 ml wastewater sample after micro-electrolysis oxidation in a 2 l beaker supplied with an aerator. During the experiments samples were drawn out from the beaker at different times and analyzed.

2.3. Analysis

Dissolved oxygen (DO), pH, total salt concentration, COD, BOD_5, NH_4^+-N and color in both influent and effluent were regularly analyzed. The color of wastewater was measured with the standard dilution multiple method. COD was determined with a Rex COD-571 meter (REX Instrument Factory, China). DO was measured by a JPSJ-605 dissolved oxygen analyzer (REX Instrument Factory, China), as well as the pH value was measured by a pHS-3C meter (REX Instrument Factory, China).

Table 2
Characteristics of effluent wastewater from the aeration oxidation in lab

Parameters	Effluent			Discharged standard in China
	A[a]	B[b]	C[c]	
COD_{Cr} (mg/l)	412	186	124	200
NH_4^+-N (mg/l)	434.7	–	–	–
TCB (mg/l)	12–22	12–18	10–16	–
Chroma (DT)[a]	20–50	20–60	20–60	200
pH	6.8–9.0	7.4–8.4	7.2–8.4	6.0–9.0

[a] Raw wastewater from the two-staged neutralization with methanol addition.
[b] Raw wastewater from the two-staged neutralization with ethanol addition.
[c] Raw wastewater from the two-staged neutralization with acetone addition; DT = dilution times.

The concentration of 2,2′,5,5′-tetrachlorobenzidine (TCB) in the wastewater was determined by a high performance liquid chromatography (HPLC) with an electrochemical detection (ECD) (LC-10A Model, Shimadzu, Japan).

3. Results and discussion

The averaged results in experiment were described in Tables 2 and 3. It can be learned that the overall COD, color, TCB and NH_4^+-N removal were 96.8%, 91%, 87.61% and 62%, respectively, during the treatment of TCB wastewater from the two-staged neutralization dissolved by methanol on conditions of HRT 1 h, pH 3.0 in ICF and HRT 38 h, gas–liquid ratio 15, pH 6.0–8.65, temperature 26 °C in ASR. The averaged 18.3%, 81.7% of the total degraded COD, 35.2%, 64.8% of TCB were carried out in ICF and ASR, respectively. NH_4^+-N removal was finished mainly in ASR. The experimental results indicated that the combined micro-electrochemical oxidation and air-stripping process performed good treatment of COD, color, TCB and NH_4^+-N removal for wastewaters B and C, which the effluent came up the discharge standard in China. But for wastewater

Table 3
Pollutants removal of TCB wastewater during processes

Raw wastewater A	S_0 (mg/l)	ICF		η (%)	ASR		Overall
		pH_{inf} = 3.0; HRT = 1 h			R = 15; HRT = 38 h		η (%)
		Inf. (mg/l)	Eff. (mg/l)		Eff. (mg/l)	η (%)	
COD and TCB removal of wastewater A during processes[a]							
COD	12910	12910	10928	15.4	412	96.2	96.8
TCB	83.5	83.5	60.1	28	17	71.7	87.6
Raw wastewater	COD_0 (mg/l)	ICF		η (%)	ASR		Overall
		pH_{inf} = 3.0; HRT = 1 h			R = 15; HRT = 38 h		η (%)
		Inf. (mg/l)	Eff. (mg/l)		Eff. (mg/l)	η (%)	
COD removal of wastewater B and C during processes[b]							
B	8290	8290	6253	20.6	186	97.2	97.8
C	2338	2338	1938	17.1	124	93.6	94.7

[a] S_0, original COD or TCB value in the raw wastewater; Inf., influent; Eff., effluent; ICF, iron chipping filtration; ASR, air-stripping reactor; pH_{inf}, pH of influent into ICF; R, gas–liquid ratio; η, removal efficiency; overall η, total removal efficiency in lab.
[b] COD_0, original COD value in the raw wastewater; Inf., influent; Eff., effluent; ICF, iron chipping filtration; ASR, air-stripping reactor; pH_{inf}, pH of influent into ICF; R, gas/liquid ratio; η, COD removal efficiency; overall η, total removal efficiency in our lab.

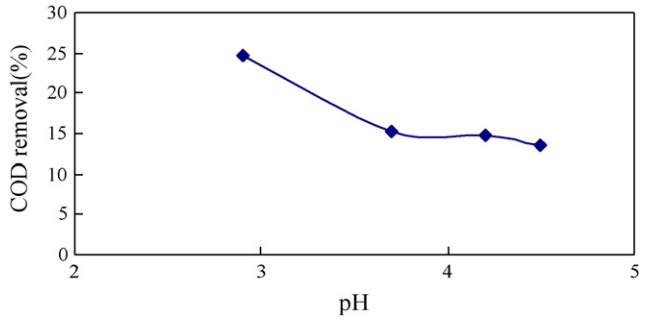


Fig. 2. Effect of pH on COD removal of raw wastewater A in ICF (conditions: $T = 26\,^{\circ}C$, HRT = 1.0 h, influent COD 14,880 mg/l).

A (dissolved by methanol), deeper treatment before discharged was needed.

3.1. Performance of the micro-electrolysis reactor or iron-chipping filtration

When HRT was 1.0 h, the effect of different pH-adjusted wastewater sample's pH on COD removal in wastewater A is shown in Fig. 2. The results indicate that the COD removal is highest at pH 2.9, decreasing sharply while the pH value increased. According to other's similar researches [5,7,9–11], the COD removal is highest under acid condition (pH 2–5). So pH 3 was chosen as the most suitable controlling value in study. The averaged COD removal 17.7% in ICF at pH 3 and HRT = 1.0 h, accounting for 18.3% of the overall COD removal efficiency, could be concluded from Table 3.

The most important role of ICF was to improve the biodegradation of the organic wastewater [11,12]. BOD_5/COD of wastewater A increased from 0.028 to 0.26, which meant an improvement of biodegradability by ICF. TCB, COD and NH_4^+-N in effluent of wastewater A in lab were still high, the discharge standards were not met. So a biological process could be used for deeply treating the effluents before discharged.

3.2. Performance of the air-stripping reactor

Experiments of degradation profile of COD under different inflow COD after micro-electrolysis in air-stripping reactor were carried in batch reactors. The results indicate that COD was degraded quickly in the first 24 h of the air-stripping reactor, decreased continually from 24 to 38 h. This figure also shows that COD was depleted very slowly in the final stage thereafter 38 h (Fig. 3). This was probably due to the fact that there are some intermediaties that are more difficult to remove.

Fig. 4 shows the relations between the variation of COD and pH in air-stripping reactor. The results indicated that, when the COD values decreased quickly in the first 24 h, the pH values increased, and there are no obvious relations between the changes of COD and pH in final stage thereafter 24 h.

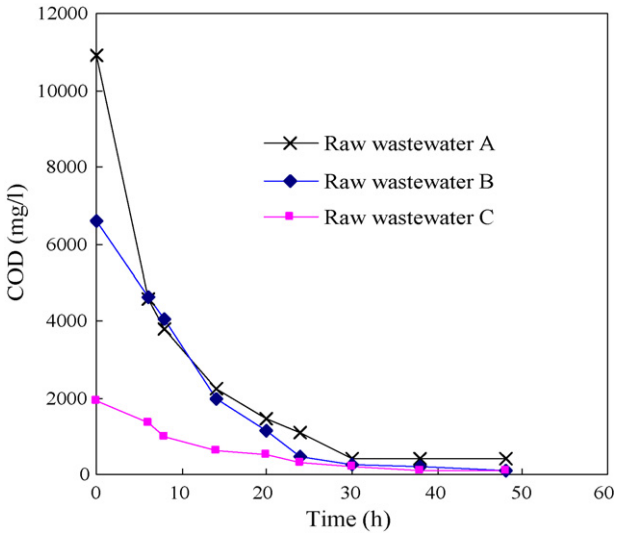


Fig. 3. COD removal curve in air-stripping reactor (conditions: $T = 26\,^{\circ}C$, $R = 15$, pH 7.44–8.46).

3.3. Effect of gas–liquid ratio (R) on COD removal

The ratio of the air flowrate to the raw wastewater, gas–liquid ratio (R), has heavily affections to ASR. Fig. 5(a) demonstrates the influence of R on COD removal in our lab. Fig. 5(b) reveals that the kinetic of the pseudo-first-order reactions with $R = 15$ is

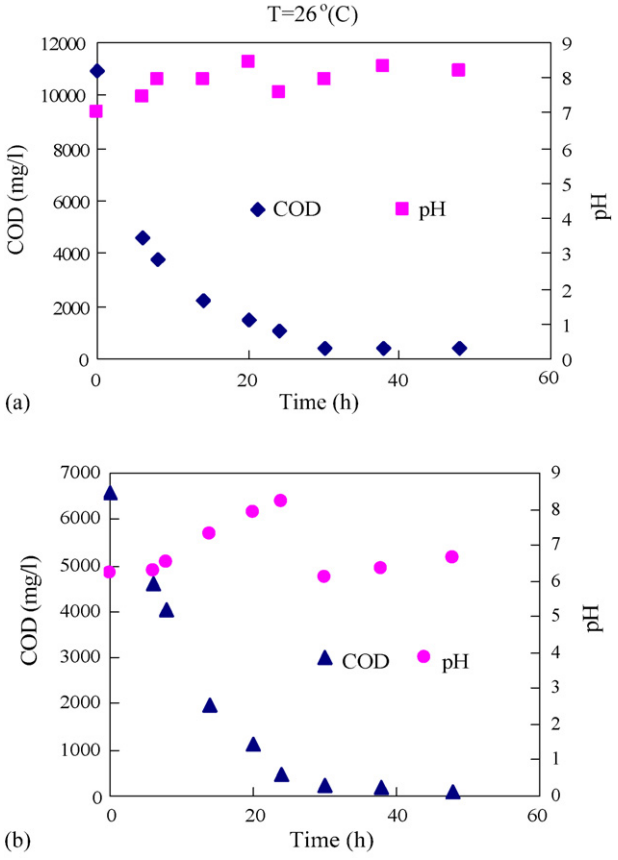


Fig. 4. COD and pH varied in air-stripping reactor (conditions: HRT = 48 h, $R = 15$, $T = 26\,^{\circ}C$). (a) Raw wastewater A, and (b) raw wastewater B.

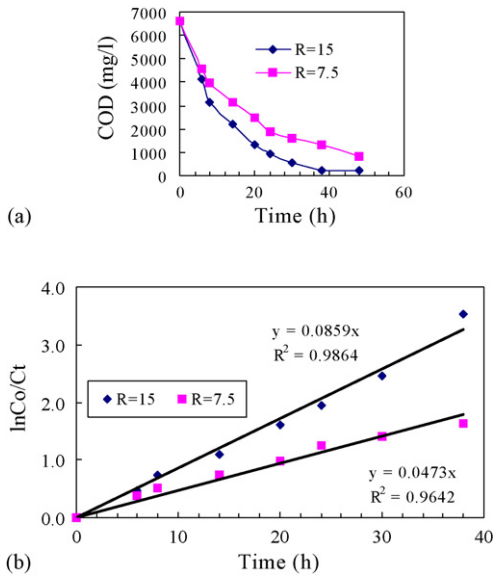


Fig. 5. Effect of R on the COD removal in air-stripping reactor (conditions: HRT = 48 h, $T = 26\,^{\circ}C$). (a) Influence of R on the COD removal efficiency in air-stripping reactor. (b) Kinetic analysis for COD removal in air-stripping reactor.

$0.086\,h^{-1}$, 83% higher than that with $R = 7.5$. The result seemly indicates that a higher air flowrate is useful for quickly removing of COD in air-stripping reactor. Therefore, COD removal is more likely by air-stripping of volatile organic compounds rather than oxidation.

4. Conclusion

The feasibility of a combination oxidation process for TCB wastewater treatment was investigated in this study. The combined process consisted of an iron-chipping filtration (a micro-electrolysis reactor) and an air-stripping reactor. The experimental results of the lab-scale setup indicated that the new method was very effective and reliable for treating TCB industrial wastewater. The treated effluents came up the discharge standard in China as the raw wastewater from the two-staged neutralization dissolved by with ethanol or acetone addition. But the TCB wastewater from the two-staged neutralization dissolved by methanol should to be deeply treated by biological process before discharged.

Acknowledgement

The authors thank Dr. Gaoke Zhang for his helps for the manuscript revision.

References

[1] International Agency for Research on Cancer (IARC), Summaries and Evaluations, vol. 27, Suppl. 7; 1987.
[2] M. Bouzige, P. Legeay, V. Pichon, M.C. Hennion, Selective on-line immunoextraction couple to liquid chromatography for the trace determination of benzidine, congeners and related azo dyes in surface water and industrial effluents, J. Chromatogr. A 846 (1999) 317–329.
[3] http://www.atsdr.cdc.gov/toxprofiles/tp108-c4.pdf.
[4] Z. Jia, C. Zhu, D. Fu, et al., Comprehensive utilization of acidic wastewater from 3,3′-dichlorobenzidine hydrochloride manufacture, J. Chem. Technol. Biotechnol. 76 (10) (2001) 1085–1090.
[5] L. Lei, D. Wang, Advanced Oxidation Technologies for Wastewater Treatment, Chemical Engineering Press, Beijing, 2001, pp. 181–183.
[6] H.R. An, Y. Qian, Biodegradation of dyeing wastewater technology with anoxic reactor, Environ. Protection Technol. Chem. Ind. 14 (4) (1994) 200–205 (Chinese).
[7] I.A. Balcioglu, I. Arslan, M.T. Sacan, Homogenous and heterogenous advanced oxidation of two commercial reactive dyes, Environ. Technol. 22 (2001) 813–822.
[8] Z. Wangpeng, Y. Zhihua, L. Wang, Application of ferrous hydrogen peroxide for treatment of DSD-acid manufacturing process wastewater, Wat. Res. 35 (8) (2001) 2087–2091.
[9] P. Zhou, D. Fu, Application and development for microelectrolysis technology, Tech. Equip. Environ. Pollut. Con. 2 (4) (2001) 18–24 (Chinese).
[10] Y. Wang, J. Yang, Research and application of micro-electrolysis technology to industrial wastewater treatment, Tech. Equip. Environ. Pollut. Con. 3 (4) (2002) 69–73 (Chinese).
[11] Y. Zhao, M. Qi, Treatment of bleaching and dyeing wastewater by microelectrolysis-SBR process, J. Environ. Sci. Shanghai 17 (9) (1998) 22–24 (Chinese).
[12] L. Huo, L. Chen, The experiment and practice on treatment of chemical pharmaceutical waste by microcell electrolysis-biochemical process, Pollut. Treat. Technol. 11 (4) (1998) 237–239 (Chinese).