

Recovery of nitrotoluenes in wastewater by solvent extraction

Wen-Shing Chen^{a,*}, Wen-Chih Chiang^a, Chong-Chien Lai^b

^a Department of Chemical Engineering, National Yunlin University of Science & Technology, Yunlin 640, Taiwan, ROC

^b Refining & Manufacturing Research Center, Chinese Petroleum Corporation, Chia-Yi 600, Taiwan, ROC

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Abstract

Toluene extraction was utilized to recover 2,4-dinitrotoluene (DNT), 2,6-DNT, and 2,4,6-trinitrotoluene (TNT) from wastewater of toluene nitration process. The batch-wise experiments were performed to elucidate the influence of various operating variables on the extracting behavior, including extracting temperature, volume ratios of solvent versus wastewater, agitation time, acidity of wastewater, and extraction stages. It was found that recovery of total organic compounds (TOC) was significantly elevated with increasing extraction temperature. Besides, high volume ratio of toluene/wastewater (2.0) and wastewater acidified to lower pH value enhanced the recovery percentage of TOC, in which extractable tendency was as follows: 2,6-DNT > 2,4-DNT > 2,4,6-TNT. It is worth noting that the nitrotoluenes in wastewater would be almost completely recovered using three sequential stages toluene extraction at the agitation time of 12 min and pH 3.0. It is apparent that this established method is promising for the treatment of wastewater from toluene nitration processed industrially.

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1. Introduction

The toluene nitration process utilizing a mixture of sulfuric and nitric acid has been well developed due to the industrial importance of 2,4-dinitrotoluene (DNT), 2,6-DNT, and 2,4,6-trinitrotoluene (TNT), which have been widely used as intermediates in the manufacturing of tolylene diisocyanate (TDI) and explosives, respectively [1]. Prior to hydrogenation of DNT into toluenediamine, the organic product generated in the toluene dinitration process would be preliminarily washed by weakly basic aqueous solution to remove entrained nitric and sulfuric acid. Subsequently, the washed organic product was contacted with clean water to eliminate basic impurities. The two wash water streams described above constitute the bulk of the wastewater and emanate from the toluene dinitration process. Likewise, the wastewater was also generated in company with production of 2,4,6-TNT.

Owing to the severe toxicity and doubtful carcinogenicity of 2,4-DNT, 2,6-DNT, and 2,4,6-TNT, they should be abated from wastewater before its disposal to the environment

[2,3]. Consequently, the oxidative mineralization of nitroaromatic compounds of wastewater from toluene nitration process has gained much attention. According to the study of Mohanty and Wei [4], the effective mineralization of 2,4-DNT was carried out under the experimental condition of $\text{H}_2\text{O}_2:\text{Fe}^{2+}:2,4\text{-DNT}=20:2.5:1$ on the molar basis. In another publication, Ho [5] investigated the oxidation of 2,4-DNT using UV/ H_2O_2 and postulated the plausible reaction pathway, composed of dinitrobenzene and dinitrobenzaldehyde intermediates. Besides, it has been approved that 2,4-DNT was susceptible to direct photolysis at pH 12 [6]. Li et al. [7] explored the decomposition of nitroaromatic explosives by UV/Fenton's reagent, wherein oxidative degradation of nitroaromatics was significantly enhanced by photochemical regeneration of Fe^{2+} . Based on the researches by Beltrán et al. [8,9], it came to a conclusion that ozonation of 2,6-DNT was mainly developed through free radical reactions, of which reaction rate was accelerated by the presence of hydrogen peroxide or UV irradiation.

Several investigators paid attention to the mineralization of 2,4,6-TNT by a combination of H_2O_2 with UV irradiation [10–12]. Some literatures have been issued on the promoting destructive efficiency of 2,4,6-TNT using Fenton's reagent and visible light [13,14]. In addition, Oh et al. [15] investigated

* Corresponding author. Tel. +886 5 534 2601x4624; fax: +886 5 531 2071.
E-mail address: chenwen@yuntech.edu.tw (W.-S. Chen).

oxidative degradation of 2,4,6-TNT utilizing Fenton's reagent and zero-valence iron, which functioned to reduce the nitro groups of 2,4,6-TNT to amino groups, resulting in higher destructive efficiency. The photocatalytic destruction of 2,4,6-TNT in aqueous suspensions of titanium dioxide was studied under aerated condition [16]. The appreciable mineralization of 2,4,6-TNT seems to be caused by the hydroxyl radicals, generated over the semiconductor surface. In another publication, the reaction intermediates existing in TNT photocatalysis were identified as 2,4,6-trinitrobenzoic acid, 3,5-dinitroaniline, and 2,4,6-trinitrophenol [17]. Sonochemical degradation of 2,4,6-TNT with ultrasound (20–500 kHz) was carried out as a function of substrate concentration, operating temperature, and pH value [18,19]. Currently, Liou et al. [20] have investigated the oxidative degradation of 2,4-DNT and 2,4,6-TNT using Fenton's reagent with UV irradiation, of which behavior likely obeyed a pseudo first-order model.

In our previous work related to the treatment of spent acid in toluene nitration process [21–23], it has been found that high purity of 2,4-DNT crystal could be recovered from spent acid by either refrigerating or diluting method. The DNT isomers and 2,4,6-TNT may also be removed from spent acid by means of hexane or heptane extraction, wherein a little amount of water dispersed into solvent was eliminated simultaneously. Moreover, it has been verified that the total organic compounds (TOC) in spent acid could be completely mineralized by Fenton's reagent with optimal concentrations of $H_2O_2 = 7.6\text{ M}$ and $Fe^{2+} = 0.06\text{ M}$. Until now, numerous studies have put their attention to oxidative degradation of nitroaromatic compounds in wastewater, wherein the organic compounds contained were disposed in useless form, whereas the recovery manner was scarcely discussed. Therefore, this research investigated the feasibility of recovery of nitrotoluenes from wastewater by solvent extraction. Toluene was selected as the solvent due to its frequent industrial usage [24,25]. The effects of extracting temperature, volume ratios of solvent versus wastewater, agitation time, acidity of wastewater, and extraction

stages on the recovery percentage of organic compound were elucidated.

2. Experimental methods

2.1. Extraction testing

The experiments were conducted in an autoclave system under atmospheric pressure from 303 to 333 K (as shown in Fig. 1). Prior to testing, a proportionate amount of wastewater (100 ml) from dinitration or trinitration process (pH 7.0, rendered by military ammunition plant) was situated in the autoclave (Autoclave Engineers, Erie PA 16512 Model). The identical volume of toluene ($\geq 99.5\%$, Fluka) was supplied by a liquid metering pump (LDC Analytical Consta Metric 3200 Model). The extractor was made of stainless steel 316, and equipped with both heating jacket and cooling coils, connected to a circulating water bath (VWR Scientific Co. 1167 Model). One thermocouple was inserted into the extracting zone for reading and controlling the operating temperature. During the course of extraction tests, extracting temperature and stirring rate ($600 \pm 50\text{ rpm}$) were adjusted to the set points in advance. As extraction experiments were carried out at the agitation time of 6 min, the extract decanted from the extractor was analyzed by a gas chromatograph/flame ionization detector (GC/FID, Hewlett Packard 6890 SERIES) equipped with a capillary column (DB-1, $100\text{ m} \times 0.25\text{ mm}$, film thickness $0.5\text{ }\mu\text{m}$), operated from 373 to 493 K at a programming rate of 10 K min^{-1} . Furthermore, the wastewater raffinate undergone both TOC and ultraviolet–visible spectrophotometry (UV–vis) analyses to disclose the organic compounds residual and toluene content dissolved, respectively.

To find out the optimal operating conditions of extraction, six tests with various extracting temperatures (303 up to 333 K) were carried out. In another set of experiments, the influence of agitation time (6 up to 30 min) on the extracting performance was also studied. Besides, a series of tests with various volume ratios

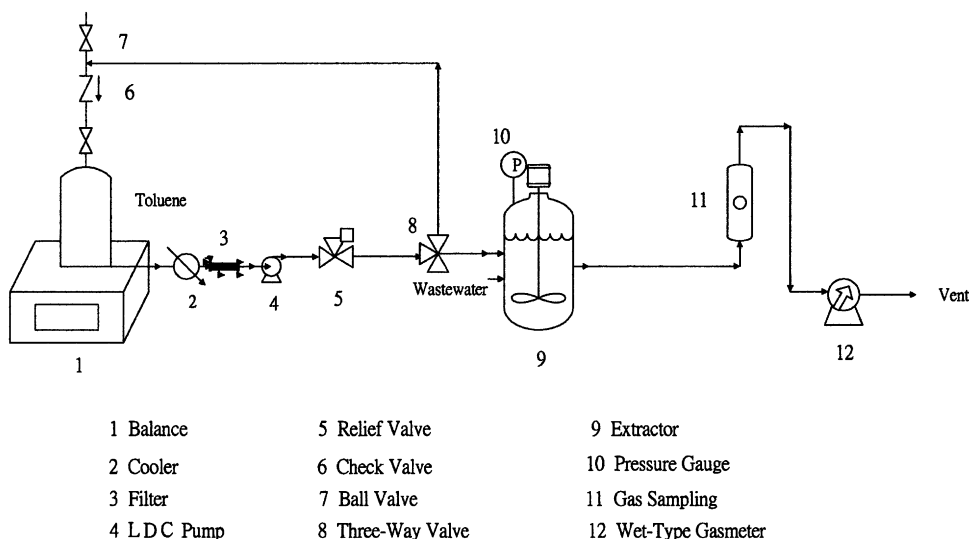


Fig. 1. Schematic diagram of the experimental apparatus used in extraction tests.

of solvent versus wastewater (1/1 up to 3/1) were performed. Furthermore, five tests with a variety of acidity of wastewater (pH 3.0 up to pH 7.0) were conducted. By the way, the multiple sequential stages extraction was undertaken to assess the feasibility of practical application of toluene extraction for disposal of wastewater. In this study, all extraction tests were performed in triplicate to ensure the reliability of experimental results.

2.2. Total organic compounds analysis

The wastewater (50 ml) that undergone extraction testing was measured using a Tekmar Dohrmann Phoenix 8000 analyzer equipped with both UV reactor and NDIR detector, wherein inorganic carbon was eliminated by phosphoric acid (85%, Fluka) and organic compounds was oxidized into carbon dioxide by sodium persulfate ($\geq 99.5\%$, Fluka). Prior to analysis, the concentration of organic compounds in wastewater was diluted to one sixth to meet the requirement of measuring range (0–200 mg/l). The results obtained were calibrated by the potassium hydrogen phthalate standard solutions.

2.3. Adjustment of pH value of wastewater

Experiments were performed on a hot plate (Heidolph MR 3001 K) at a stirring rate of 400 rpm for 10 min. The wastewater (100 ml) was situated in the jacket beaker connected to a circulating water bath (VWR Scientific Co. 1167 Model) to maintain the temperature at 300 K. By adding a proportionate amount of sulfuric acid solution (1 mol l^{-1}), the wastewater was gradually acidified to the pH values of 6.0, 5.0, 4.0, and 3.0, respectively (detected by SUNTEX SP-701 PH/mV/TEMP. Meter).

2.4. Ultraviolet–visible spectrophotometer analysis

To elucidate the toluene content dissolved in the wastewater raffinate, it was analyzed by UV–vis spectrophotometry at a wavelength of 240 nm [26]. Samples were situated in a quartz holder, scanned by a Perkin Elmer LAMBDA 850 dual beam UV–vis spectrophotometer. The data obtained were corrected by the standard solutions which were prepared from a stock methanol solution with toluene concentration range of 0–200 mg/l.

2.5. Gas chromatograph/mass spectrometer analysis (GC/MS)

The proportionate amount ($0.4 \mu\text{l}$) of wastewater was injected into a gas chromatograph/mass spectrometer (Hewlett Packard 59864B/HP 5973 MASS) equipped with a capillary column (Metal ULTRA ALLOY UA-5, $30 \text{ m} \times 0.25 \text{ mm}$, film thickness $0.25 \mu\text{m}$), operated from 313 to 573 K at a programming rate of 20 K min^{-1} . The mass spectra obtained were utilized to identify the components involved in both wastewater and extract as compared to the authentic standard compounds of database (Wiley 275.L).

3. Results and discussion

3.1. Effect of extracting temperature

Based on the analysis of GC/MS, the components of organic compounds in wastewater from toluene dinitration and trinitration processes have been identified as 2,4-DNT, 2,6-DNT, 2,3-DNT, 3,4-DNT, and 2,4,6-TNT respectively (as listed in Table 1). In addition, according to the analyses of TOC and GC/FID, the contents of TOC in wastewater from these processes mentioned were separately about 550 and 580 mg/l, wherein the detailed compositions were summarized in Table 2. With regard to the weight ratios of DNT isomers in dinitration process, that is 2,4-DNT:2,6-DNT = 77:23, it seems that the composition of DNT isomers dissolved in wastewater was closely related with that in organic product, of which composition was as follows [27]: 2,4-DNT:2,6-DNT = 77:18. In another respect, the major ingredient in wastewater of trinitration process was 2,4,6-TNT, in agreement with the report by Spalding and Albright [28]. Fig. 2 illustrates the recovery percentage of TOC from wastewater of dinitration and trinitration process by toluene extraction at different extracting temperatures. It clearly indicates that the amounts of organic compounds extracted exhibited increasing trend with increasing temperature. This phenomenon may be interpreted with enhancing solubility of organic compounds into aqueous phase with increasing temperature [29–31]. Nonetheless, the effect of enhancing solubility of organic com-

Table 1
Components involved in wastewater of dinitration and trinitration processes

Component	<i>m/z</i> (relative abundance)
2,4-DNT	39 (12.7%), 51 (13.1%), 63 (35.7%), 64 (13.1%), 78 (16.4%), 89 (60.7%), 90 (26.0%), 119 (25.6%), 165 (100%), 166 (13.8%)
2,6-DNT	51 (16.1%), 63 (35.8%), 64 (15.7%), 77 (19.7%), 78 (16.3%), 89 (40.2%), 90 (27.1%), 121 (17.6%), 148 (20.9%), 165 (100%)
2,3-DNT	30 (13.3%), 39 (12.0%), 51 (12.3%), 63 (32.7%), 64 (14.4%), 78 (16.5%), 89 (51.3%), 90 (17.7%), 119 (25.4%), 166 (100%)
3,4-DNT	30 (64.4%), 39 (32.7%), 52 (32.7%), 63 (47.2%), 66 (32.9%), 77 (29.0%), 78 (46.3%), 89 (51.1%), 94 (32.3%), 182 (100%)
2,4,6-TNT	30 (14.8%), 51 (11.0%), 62 (16.4%), 63 (31.9%), 76 (14.8%), 89 (43.1%), 134 (11.8%), 180 (13.6%), 193 (13.2%), 210 (100%)

Table 2
Compositions of total organic compounds in wastewater from dinitration and trinitration processes

Dinitration process		Trinitration process	
Component	wt%	Component	wt%
2,4-DNT	76.5	2,4-DNT	8.2
2,6-DNT	23.0	2,6-DNT	6.1
2,3-DNT	Trace	2,4,6-TNT	85.3
3,4-DNT	Trace	Unknown	0.4

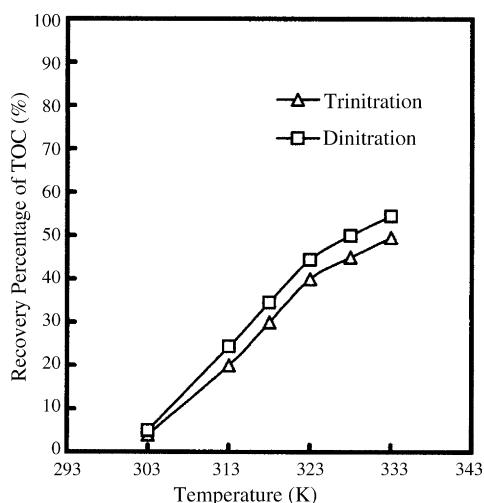


Fig. 2. Effect of the extracting temperature on the recovery percentage of organic compounds from wastewater under the condition of pH 7.0, toluene/wastewater (1/1), and agitation time of 6 min.

pounds into toluene, resulted from temperature increase, is more obvious [31]. That leads to more organic compounds extracted by toluene at high temperature. In fact, a similar trend was also observed for the treatment of wastewater from trinitration process. As compared to the data at the same temperature between dinitration and trinitration processes, the former seems better than the latter. The plausible explanation is the solubility of 2,4,6-TNT in aqueous phase being higher than those of 2,4-DNT and 2,6-DNT, as reported by Chen et al. [22]. As far as toluene extract recycled into toluene nitration process is concerned, operated between 318 and 328 K, the extracting temperature at 323 K seems more suitable to be chosen for subsequent experimental tests.

In order to find out the extractable tendency of each organic component in wastewater, the compositions of organic compounds extracted were disclosed by means of GC/FID analysis. As given in Table 3, it is to be noted that the weight percentage of 2,6-DNT in TOC extracted from wastewater of dinitration process reached nearly 39%, which was higher than that of 2,6-DNT in wastewater feedstock (23%). This reveals that 2,6-DNT was more easily extracted by toluene than by wastewater feedstock. It may be attributed to the influence of relative location of electron-withdrawing nitro groups on the solubility of DNTs in the aqueous phase. In other words, the comparative solubility of DNTs in wastewater was as follows: 2,6-DNT < 2,4-DNT [32]. As expected, an analogous result was obtained from the extracts of wastewater of trinitration process (see Table 3). It shows that the weight percentage of 2,6-DNT in TOC extracted was about 11.3 wt%, which was higher than that of 2,6-DNT in wastewater feedstock (i.e. 6.1 wt%). Additionally, the weight percentage of 2,4-DNT in TOC extracted was also higher than that of 2,4-DNT in wastewater feedstock. It is evident that 2,6-DNT was more easily extracted by toluene than by wastewater feedstock, as consistent with the previous outcome. Besides, 2,4-DNT was also more easily extracted by toluene than by wastewater feedstock, whereas the promoting effect on recovery of 2,6-DNT was more apparent. Nonetheless, 2,4,6-TNT seems to be more hardly

Table 3

Compositions of organic compounds extracted from wastewater of dinitration and trinitration processes

Operating variable	Dinitration process		Trinitration process		
	2,4-DNT	2,6-DNT	2,4-DNT	2,6-DNT	2,4,6-TNT
Temperature					
303 K	61.0	39.0	9.4	11.3	79.1
313 K	60.7	39.3	9.6	11.4	78.9
318 K	60.8	39.2	9.5	11.3	79.0
323 K	61.1	38.9	9.4	11.2	79.2
328 K	61.0	39.0	9.4	11.3	79.0
333 K	60.8	39.2	9.3	11.1	79.4
Toluene/wastewater					
(1.5/1.0)	61.0	39.0	9.5	11.0	79.4
(1.75/1.0)	61.2	38.8	9.4	11.0	79.4
(2.0/1.0)	61.5	38.5	9.5	11.2	79.2
(2.25/1.0)	61.4	38.6	9.6	11.0	79.3
(2.5/1.0)	60.4	39.6	9.6	10.9	79.4
(3.0/1.0)	60.2	39.8	9.3	11.4	79.2
Acidity					
pH 3.0	60.6	39.4	9.5	11.2	79.2
pH 4.0	61.2	38.8	9.4	11.2	79.3
pH 5.0	60.7	39.3	9.4	11.0	79.5
pH 6.0	61.1	38.9	9.6	11.4	78.9

extracted by toluene than by wastewater in consideration of the weight percentage of 2,4,6-TNT in TOC extracted, which was lower than in wastewater feedstock. As a result, the extractable priority of nitrotoluenes by toluene is in the following order: 2,6-DNT > 2,4-DNT > 2,4,6-TNT.

3.2. Effect of volume ratios of solvent versus wastewater

It has been recognized that adjustment of solvent amounts used for extraction is an important operating variable industrially. Fig. 3 demonstrates the influence of volume ratios of solvent versus wastewater on the extracting performance. Appar-

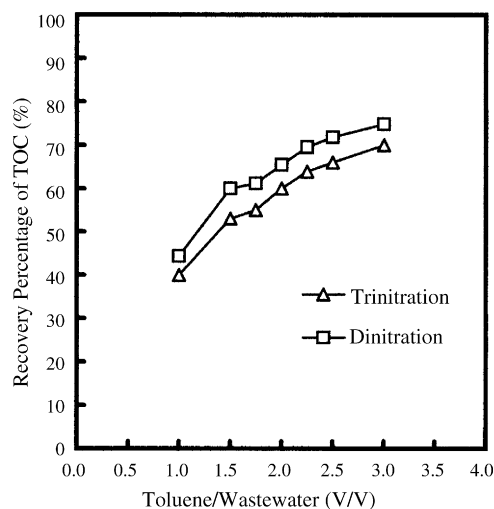


Fig. 3. Effect of the volume ratios of solvent versus wastewater on the recovery percentage of organic compounds from wastewater under the condition of pH 7.0, $T=323$ K, and agitation time of 6 min.

ently, there exists an increasing trend of recovery percentage of organic compounds with increasing volume ratios of solvent versus wastewater. The recovery percentage of organic compounds from wastewater of dinitration process in high volume ratio of solvent versus wastewater was significantly superior to that of the low one (e.g. 74% versus 44%). A similar profile was also observed in disposing of wastewater of trinitration process. Those imply that high volume ratios of solvent versus wastewater would be preferred under economic consideration. Owing to the obvious increment of recovery of TOC in the toluene/wastewater ratio of two, it was beneficially chosen for subsequent experiments. As expected, the weight percentage of 2,6-DNT in TOC extracted from wastewater of dinitration process got higher than that of 2,6-DNT in wastewater feedstock (see Table 3), corresponding to the result mentioned above. Moreover, the composition of organic compounds extracted in the case of trinitration process was similar to those described in extracting temperature-dependent testing. Consequently, it supports our previous hypothesis with regards to extractable priority of nitrotoluenes in wastewater.

3.3. Effect of agitation time

In another set of experiments, the effect of agitation time on the extracting behavior was investigated. As shown in Fig. 4, it clearly indicates that the recovery percentage of organic compounds was obviously increased with increasing agitation time from 6 to 12 min in treatment of wastewater of dinitration and trinitration processes. In contrast, the amounts of TOC extracted would be slightly changed from 12 to 30 min. It means that the equilibrium state of nitrotoluenes dissolved in either extract or raffinate may be achieved at the agitation time of 12 min with stirring rate of 600 rpm at 323 K. Longer agitation periods were avoided since they typically resulted in obvious solvent dissolution [33–35]. In fact, there is no toluene observed in wastewater raffinate within agitation time of 30 min for dinitration and trinitration processes (shown in Table 4). Nonetheless, a little amount

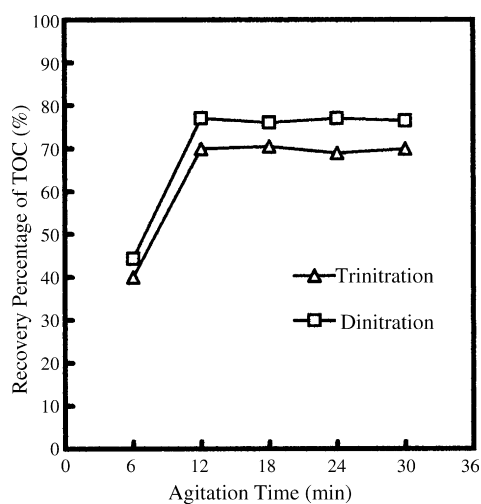


Fig. 4. Effect of the agitation time on the recovery percentage of organic compounds from wastewater under the condition of pH 7.0, toluene/wastewater (1/1), and $T = 323$ K.

Table 4

The concentration of toluene dissolved in wastewater measured by UV–vis analysis

Operating variable	Toluene (mg/l)	
	Dinitration	Trinitration
Agitation time (min)		
6	Undetected	Undetected
12	Undetected	Undetected
18	Undetected	Undetected
24	Undetected	Undetected
30	Undetected	Undetected
60	40	40
Extraction stage (12 min)		
1	Undetected	Undetected
2	Undetected	Undetected
3	Undetected	Undetected
4	40	40
Extraction stage (6 min)		
1	Undetected	Undetected
2	Undetected	Undetected
3	Undetected	Undetected
4	Undetected	Undetected

of toluene (40 mg/l) was dissolved into the wastewater at the agitation time of 60 min for the former. The recovery percentage of organic compounds was slightly decreased at the agitation time of 60 min in comparison with that of agitation time of 12 min (70% versus 77%). Likewise, 40 mg/l of toluene was detected in wastewater raffinate of trinitration process at the agitation time of 60 min, of which recovery percentage of organic compounds was lower than that at the agitation time of 12 min.

3.4. Effect of acidity of wastewater

For the purpose of enhancing recovery of nitrotoluenes from wastewater, the acidity of wastewater was adjusted by addition of sulfuric acid solution. The recovery percentage of organic compounds as a function of acidity of wastewater is demonstrated in Fig. 5. Apparently, the extracting efficiency of organic compounds from wastewater at lower pH value in dinitration process was superior to that at higher pH value. An analogous trend was also observed for wastewater of trinitration process. That may be ascribed to the solubility of nitrotoluenes in wastewater, which decreases as the pH value of wastewater decreases [36]. Therefore, one may deduce that the recovery of nitrotoluenes from wastewater would be significantly enhanced by an acidifying procedure. As far as the concentration of sulfate ions in wastewater with various acidity was concerned, there was no evident distinction between them (0–50 mg/l). According to our previous study in the laboratory, the low concentration of sulfate ions (<1000 mg/l) in wastewater would not lead to the salting-out effect, as proposed by some researchers [37–39]. As a result, the enhancing recovery of nitrotoluenes at lower pH value was independent of the salting-out effect. Furthermore, as the composition of extract was considered, the weight percentage of 2,6-DNT in TOC extracted from wastewater of dinitration process was apparently higher than that of 2,6-DNT in wastewater

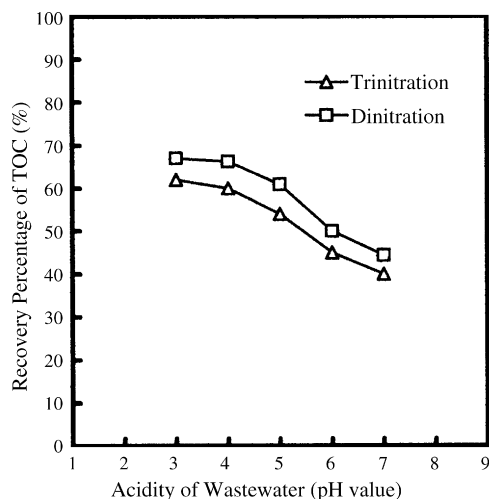


Fig. 5. Effect of the acidity of wastewater on the recovery percentage of organic compounds from wastewater under the condition of $T=323$ K, agitation time of 6 min, and toluene/wastewater (1/1).

feedstock (refer to Table 3). This fact gives another evidence on the hypothesis that 2,6-DNT was more easily extracted than 2,4-DNT by toluene. In addition, similar compositions of organic compounds extracted were obtained among wastewater with various acidities in trinitration process. The composition difference in TOC extracted between this set of extraction experiments and extracting temperature-dependent tests was very slight. Thus, it provides another proof on the inference related to extractable tendency of nitrotoluenes.

3.5. Effect of extraction stages

In order to increase the recovery percentage of organic solutes, the multiple stages extraction has always been adopted industrially. Fig. 6(a) and (b) presents the influence of multiple stages operation on the extracting performance of toluene under different conditions. The recovery percentage of nitrotoluenes from wastewater of dinitration or trinitration process was gradually increased with increasing extraction stages. It is remarkable that the value of recovery percentage reached a level as high as 99% of the TOC in wastewater at third stage for dinitration process under the condition of $T=323$ K, pH 3.0, agitation time of 12 min, and toluene/wastewater (2/1), whereas further extraction stage would fail to abate the TOC steadily. This phenomenon may be explained by the dissolution of toluene solvent into wastewater, resulted from longer contact time [34,35]. It could be verified by analyzing wastewater raffinate using UV-vis spectrophotometry, wherein the toluene concentration was ca. 40 mg/l at fourth extraction stage and no toluene detected within prior three stages (see Table 4). In another respect, the TOC in wastewater of trinitration process were almost completely recovered by toluene extraction with three stages in sequence. As expected, a little amount of toluene was also dissolved into wastewater at fourth stage, which gave rise to increasing amount of TOC in wastewater. Furthermore, the recovery percentage of organic compounds in wastewater of dinitration or trinitration process for each stage is almost equiv-

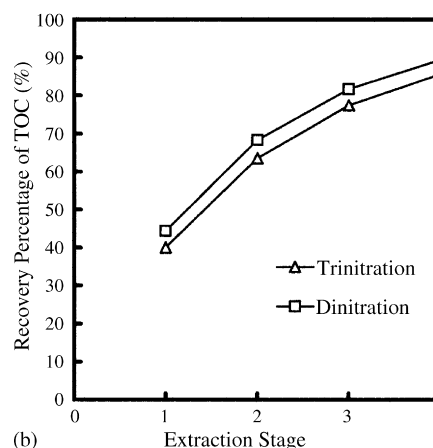
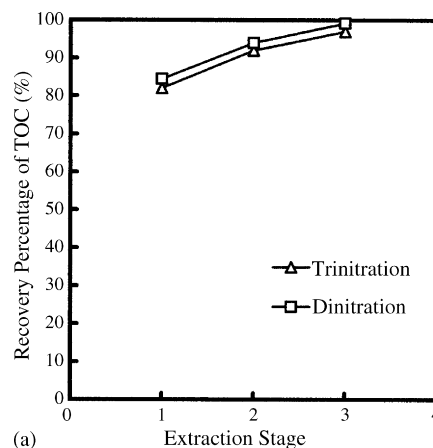


Fig. 6. Effect of the extraction stages on the recovery percentage of organic compounds from wastewater. (a) $T=323$ K, pH 3.0, agitation time of 12 min, and toluene/wastewater (2/1); (b) $T=323$ K, pH 7.0, agitation time of 6 min, and toluene/wastewater (1/1).

alent under the condition of $T=323$ K, pH 7.0, agitation time of 6 min, and toluene/wastewater (1/1). It means that the extracting tests were kinetically controlled on account of short contact time (6 min). No toluene was detected in the wastewater raffinate within four stages due to contact time shortened (24 min versus 48 min) as compared with the former. To sum up, our results suggest that the toluene extraction method established is promising for recovery of nitrotoluenes from wastewater of toluene nitration process practically.

4. Conclusion

On the basis of the above discussion, it was found that recovery of nitrotoluenes from wastewater was significantly enhanced with increasing extracting temperature. Furthermore, high volume ratio of toluene/wastewater (2.0) was more beneficial to recover nitrotoluenes, in which extractable tendency was as follows: 2,6-DNT > 2,4-DNT > 2,4,6-TNT. In addition, the recovery percentage of TOC depended strongly upon the acidity of wastewater, wherein the extracting efficiency at lower pH value was superior to that at higher pH value. It is worth noting that the nitrotoluenes of wastewater would be almost completely recovered by sequential three-stages toluene extraction at the

agitation time of 12 min and pH 3.0. This reveals that the developed toluene extraction method would be potentially applied to recover organic compounds from wastewater preliminarily.

Acknowledgement

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