

# Recovery of nitrotoluenes from wastewater by solvent extraction enhanced with salting-out effect

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## Abstract

Toluene extraction enhanced by salting-out effect was employed to recover dinitrotoluene isomers and 2,4,6-trinitrotoluene (2,4,6-TNT) from wastewater of toluene nitration processes (e.g. dinitration or trinitration). The batchwise experiments were conducted to elucidate the influence of various operating variables on the extracting performance, including concentrations and species of inorganic salts, such as NaCl, KCl, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub>, acidity of wastewater, volume ratios of solvent versus wastewater and extraction stages in existence of inorganic salts. It was found that recovery of total organic compounds (TOC) was significantly elevated with increasing concentrations of salts, whose promoting effects were in the following order: NaCl > Na<sub>2</sub>SO<sub>4</sub> > K<sub>2</sub>SO<sub>4</sub> > MgSO<sub>4</sub> > KCl on the weight basis of wastewater. Besides, high volume ratio of toluene/wastewater (ca. 2.0) was more suitable for recovery of TOC from wastewater with or without addition of NaCl, of which extractable priority was as follows: 2,6-DNT > 2,4-DNT > 2,4,6-TNT. It is remarkable that TOC in wastewater would be almost completely recovered by sequential four stages toluene extraction, promoted continuously by salting-out effect.

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**Keywords:** Dinitrotoluene; Trinitrotoluene; Toluene extraction; Salting-out effect

## 1. Introduction

Toluene nitration processes, such as dinitration and trinitration using mixed sulfuric and nitric acids have been well developed due to the industrial importance of dinitrotoluenes and trinitrotoluene, which have been always used as intermediates of tolylene diisocyanate (TDI) and explosives, respectively [1]. According to the purifying procedure of nitration process, the organic product generated should be preliminarily washed by alkaline aqueous solution to remove entrained sulfuric and nitric acids. Subsequently, the organic product washed was contacted with clean water to eliminate alkaline contaminants. The two wash water streams mentioned constitute the bulk of the wastewater and emanate from the toluene nitration process. Due to the toxicity and possible carcinogenicity of different dinitro- and trinitrotoluene derivatives [2,3], they should be abated from wastewater before its release to the environment.

Until now, the oxidative elimination of nitroaromatic compounds from wastewater by means of advanced oxidation process has gained much attention. Based on the study of Mohanty and Wei [4], 2,4-DNT was completely destructed utilizing Fenton's reagent. The oxidative degradation of 2,4-DNT and 2,4,6-TNT by way of UV/H<sub>2</sub>O<sub>2</sub> has also been reported [5–7]. Besides, some investigators [8,9] focused their interests on the mineralization of nitroaromatic explosives by UV/Fenton's reagent, wherein photochemical regeneration of Fe<sup>2+</sup> significantly accelerated the destructive efficiency of Fenton oxidation. In another publication, much effort has been issued on the method of visible light/Fenton's reagent [10,11]. According to the reports by Beltrán et al. [12,13], the effective mineralization of 2,6-DNT was carried out using UV/O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>. Currently, sonochemical degradation of 2,4,6-TNT with ultrasound (20–500 kHz) was also investigated as a function of substrate concentration, operating temperature and pH value [14,15].

In our previous studies [16–18], it has been found that high purity of 2,4-DNT (≥98.5 wt.%) could be recovered from spent acid by either refrigerating or diluting method. Subsequently, the multiple stages hexane extraction was successfully applied for

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partial recovery of dinitrotoluenes and 2,4,6-TNT. Eventually, the total organic compounds residual in spent acid could be completely mineralized by Fenton oxidation. Up to the present, many studies have dealt with oxidative degradation of nitroaromatic compounds in wastewater, whereas the recovery treatments were scarcely discussed. Consequently, this research investigated the role played by inorganic salts, referred as salting-out, on recovery of dinitrotoluenes and 2,4,6-TNT from wastewater of toluene nitration process by solvent extraction, which has been explored previously [19]. The salting-out effect has been proposed that inorganic ions are favorably hydrated in aqueous solution and interact unfavorably with hydrophobic solutes [20,21]. Thus, it leads to a reduction in solubility of hydrophobic solutes in aqueous solution. During the extraction tests, toluene was chosen as the solvent due to its common usage industrially and being recycled into toluene nitration process [22]. The effects of concentrations and species of inorganic salts, acidity of wastewater, volume ratios of solvent versus wastewater and extraction stages, in the presence of inorganic salts, on the recovery percentage of nitrotoluenes were elucidated simultaneously.

## 2. Experimental methods

### 2.1. Extraction testing

The experiments were performed in an autoclave system as shown in Fig. 1 under atmospheric pressure at 333 K. Prior to testing, proportionate amounts of wastewater (100 ml) from dinitration or trinitration process (pH 7.0, rendered by military ammunition plant) and inorganic salts, such as NaCl, KCl,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{MgSO}_4$  ( $\geq 99.5\%$ , Fluka) were situated in the autoclave (Autoclave Engineers, Erie PA 16512 Model) and dissolved well. The identical amount (volume basis) of toluene ( $\geq 99.5\%$ , Fluka) was supplied by a liquid metering pump (LDC Analytical Consta Metric 3200 Model). The extractor (300 ml) was 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 temperature. At the beginning of extraction tests, the operating variables, e.g. extracting temperature and stirring rate ( $600 \pm 50$  rpm), were adjusted to the set points in advance. After extraction tests with agitation time of

7 min, the extract decanted from an extractor was analyzed by a gas chromatograph/flame ionization detector to disclose the compositions. Besides, the wastewater raffinate was undergone both total organic compounds and ultraviolet visible spectrophotometry analyses to evaluate the residual organic compounds and toluene contents dissolved, respectively.

To elucidate the influence of concentrations of inorganic salts on extracting behavior, four tests with various concentrations of each salt (0.5–10 wt.%) were carried out, wherein concentrations of salts were based on the weight of wastewater. In another set of experiments, the effect of acidity of wastewater (pH 4.0–7.0) accompanied with different concentration of NaCl on the extracting performance was also explored. Besides, a series of tests at various volume ratios of solvent versus wastewater (1/1 up to 3/1) with or without NaCl added were performed. Furthermore, the multiple stages extraction in existence of NaCl, operated as mentioned previously with equal volume of toluene versus wastewater, was undertaken successively to assess the feasibility of applying toluene extraction for treatment of wastewater practically. In this study, the extraction experiments were conducted in triplicate to check the reliability of testing results.

### 2.2. Total organic compounds analysis (TOC)

The wastewater raffinate (50 ml) obtained from extraction testing was analyzed using a Tekmar Dohrmann Phoenix 8000 instrument, equipped with both UV reactor and NDIR detector, wherein sodium persulfate ( $\geq 99.5\%$ , Fluka) served as an oxidizing agent. Prior to analysis, the concentration of organic compounds in wastewater was diluted to one fourth to meet the requirement of measuring limits ( $0\text{--}200 \text{ mg l}^{-1}$ ). The results obtained were corrected by the potassium hydrogen phthalate standard solutions.

### 2.3. Ultraviolet visible spectrophotometer analysis (UV-vis)

To find out the toluene content dissolved, the wastewater raffinate was analyzed by UV-vis spectrophotometry at a wavelength of 240 nm [23]. Samples were situated in a quartz holder, scanned by a dual beam UV-vis spectrophotometer (Perkin-Elmer LAMBDA 850 Model). The standard solutions were

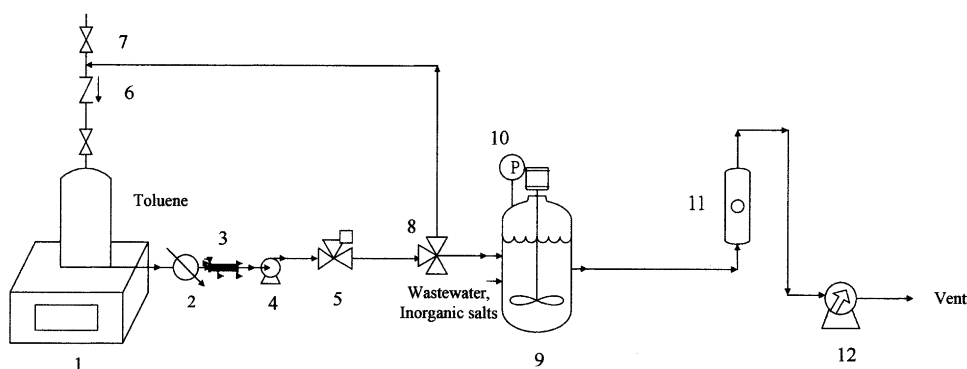


Fig. 1. Schematic diagram of the wastewater extraction system. (1) balance; (2) cooler; (3) filter; (4) LDC pump; (5) relief valve; (6) check valve; (7) ball valve; (8) three-way valve; (9) extractor; (10) pressure gauge; (11) gas sampling; (12) wet-type gasmeter.

Table 1  
Components in wastewater of dinitration or trinitration process identified by GC/MS analysis

Component	Retention time (min)	Mass/charge ratios of different relative abundance (%)
2,6-DNT	13.05	51(16.0), 63(35.7), 77(19.6), 78(16.1), 89(40.0), 90(27.1), 121(17.5), 148(20.9), 165(100)
2,3-DNT	13.29	30(13.3), 51(12.2), 63(32.6), 64(14.3), 78(16.5), 89(51.3), 90(17.6), 119(25.3), 166(100)
2,4-DNT	13.70	51(13.1), 63(35.6), 64(13.1), 78(16.3), 89(60.7), 90(26.0), 119(25.5), 165(100), 166(13.7)
3,4-DNT	13.97	30(64.3), 39(32.6), 52(32.7), 63(47.2), 66(33.0), 78(46.3), 89(51.0), 94(32.2), 182(100)
2,4,6-TNT	14.61	30(14.7), 62(16.3), 63(31.9), 76(14.8), 89(43.0), 134(11.7), 180(13.5), 193(13.2), 210(100)
2,4,5-TNT	14.90	14(7.0), 28(14.4), 30(100), 39(11.3), 44(6.4), 51(15.5), 63(12.5), 181(6.9), 210(35.7)

Values in the parentheses are in percent.

prepared from a stock methanol solution with toluene concentrations of 0–200 mg l<sup>-1</sup>.

#### 2.4. Adjustment of pH value of wastewater

Experiments were undertaken in a hot plat (Heidolph MR 3001 K) with magnetic agitation (400 rpm). The wastewater (100 ml) was situated in the jacket beaker equipped with a circulating water bath (VWR Scientific Co. 1167 Model) to maintain the temperature at 303 K. On addition of proper amount of sulfuric acid solution (0.1 mol l<sup>-1</sup>), the wastewater with volume nearly unchanged was gradually acidified to the pH values of 6.0, 5.0 and 4.0, respectively (detected by SUNTEX SP-701 PH/mV/TEMP. Meter).

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

To identify the components involved in wastewater feedstock and toluene extract, respectively, the samples obtained were initially analyzed by a gas chromatograph/mass spectrometer (Hewlett Packard 59864B/HP 5973 MASS) equipped with a capillary column (Metal Ultra Alloy UA-5, 30 m × 0.25 mm, film thickness 0.25 μm), wherein helium was used as carrier gas in a flow rate of 1 ml min<sup>-1</sup> and operated from 313 K to 573 K at a programming rate of 20 K min<sup>-1</sup>.

#### 2.6. Gas chromatograph/flame ionization detector analysis (GC/FID)

After the GC/MS analysis being carried out, the toluene extract, obtained from extraction tests with various concentrations and species of inorganic salts, and wastewater feedstock were analyzed by a gas chromatograph (Hewlett Packard 6890 SERIES) equipped with a flame ionization detector and installed a capillary column (DB-1, 100 m × 0.25 mm, film thickness 0.5 μm), wherein helium was utilized as carrier gas in a flow rate of 1 ml min<sup>-1</sup> and operated from 373 K to 493 K at a programming rate of 10 K min<sup>-1</sup>.

### 3. Results and discussion

#### 3.1. Effect of concentrations and species of salts

According to the analysis of GC/MS, the components of TOC in wastewater from toluene dinitration or trinitration process

have been identified as 2,4-DNT, 2,6-DNT, 2,3-DNT, 3,4-DNT, 2,4,6-TNT and 2,4,5-TNT (as listed in Table 1). Besides, on the basis of analyses of TOC and GC/FID, the concentrations of total organic compounds in wastewater from those processes mentioned were about 570 mg l<sup>-1</sup> and 600 mg l<sup>-1</sup>, respectively, wherein the detailed compositions were summarized in Table 2. As far as the dinitration process is concerned, i.e. 2,4-DNT:2,6-DNT = 75:24, it appears that dinitrotoluenes dissolved in wastewater were closely related with those in organic product, of which compositions were as follows [24]: 2,4-DNT:2,6-DNT = 77:18. Nonetheless, some dinitrotoluenes were also presented in wastewater from trinitration process, corresponding to the report by Spalding and Albright [25]. Fig. 2 illustrates the recovery percentage of TOC from wastewater of dinitration process by toluene extraction at various concentrations of salts, such as NaCl, KCl, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub>. It clearly indicates that the amounts of organic compounds extracted exhibited increasing trend with increasing concentrations of salts, including NaCl, KCl, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub>. This phenomenon may be interpreted with the salting-out effect, resulted from the existence of inorganic ions in wastewater, as suggested by several investigators [20,21], who have shown that the principal effect of inorganic salts upon organic solute solubility is the formation of hydrated shells around the ions, which reduce effectively available amounts of free water to dissolve organic solutes. In addition, with regard to recovery percentage of TOC at the same molar concentration of salts, it appears that the enhancing effects of salts were as follows: Na<sub>2</sub>SO<sub>4</sub> > K<sub>2</sub>SO<sub>4</sub> > MgSO<sub>4</sub> > NaCl > KCl, that was consistent with the arrangement of Setschenow constants of salts [23]. Thus, it reveals that the salting-out effect which depends strongly upon both Setschenow constant and concentrations of inorganic salts existed was in the following order: NaCl > Na<sub>2</sub>SO<sub>4</sub> > K<sub>2</sub>SO<sub>4</sub> > MgSO<sub>4</sub> > KCl on the weight basis of wastewater.

Table 2  
Compositions of TOC in wastewater from dinitration or trinitration process, respectively

Dinitration process		Trinitration process	
Component	(wt.%)	Component	(wt.%)
2,4-DNT	75.2	2,4-DNT	8.0
2,6-DNT	24.2	2,6-DNT	6.3
2,3-DNT	0.3	2,4,6-TNT	85.4
3,4-DNT	0.3	2,4,5-TNT	0.3

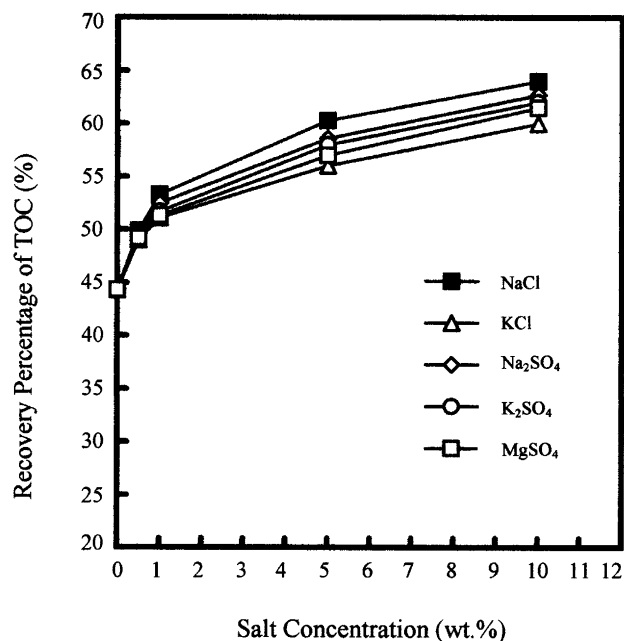


Fig. 2. Effect of the salt concentrations and species on the recovery percentage of organic compounds from wastewater of dinitration process under the condition of toluene/wastewater (1/1), pH 7.0 and 323 K.

Likewise, a similar increasing trend with recovery percentage of TOC versus concentrations of salts was observed for each salt in disposing of wastewater from trinitration process (see Fig. 3). It may be also ascribed to the salting-out effect, as mentioned in our previous paragraph. In other words, that provides another piece of evidence for above hypothesis. As expected, an identical arrangement of inorganic salts was obtained from consideration of promoting effect at the same molar concentration, in agreement with that reported for dinitration process. The result supports previous inference that salting-out effect caused by inorganic salts was as follows:  $\text{NaCl} > \text{Na}_2\text{SO}_4 > \text{K}_2\text{SO}_4 > \text{MgSO}_4 > \text{KCl}$  on the weight basis of wastewater.

In order to make clear the extractable tendency of each organic component in wastewater from dinitration process, the compositions of organic compounds extracted were disclosed by means of GC/FID analysis. As listed in Table 3, it is worth noting that the weight percentage of 2,6-DNT of TOC extracted from wastewater of dinitration process with or without addi-

tion of NaCl exceeded 30.2 wt.%, which was higher than that of 2,6-DNT in wastewater feedstock (24.2 wt.%). That implies 2,6-DNT was more easily extracted by toluene than that by wastewater. Similar outcomes were obtained for the other salts, such as KCl,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{MgSO}_4$ , of which weight percentages of 2,6-DNT of TOC extracted were about 30–38 wt.%. The phenomenon may be attributed to the influence of relative location of electron-withdrawing nitro groups on the solubility of dinitrotoluenes in the aqueous phase [26], that is, the solubility of dinitrotoluenes in wastewater was as follows: 2,6-DNT < 2,4-DNT. According to the hypothesis of salting-out effect, as described previously, the amount of free water for dissolving organic solutes would be significantly reduced on account of inorganic salts. In contrast, the affinity of free water for organic solutes would not vary with the salts. That may be verified by the weight percentage of 2,6-DNT of TOC residual in wastewater for all tests, of which values (ca. 13.6 wt.%) makes no difference between them.

Additionally, an analogous result was observed for the extracts from wastewater of trinitration process (see Table 4).

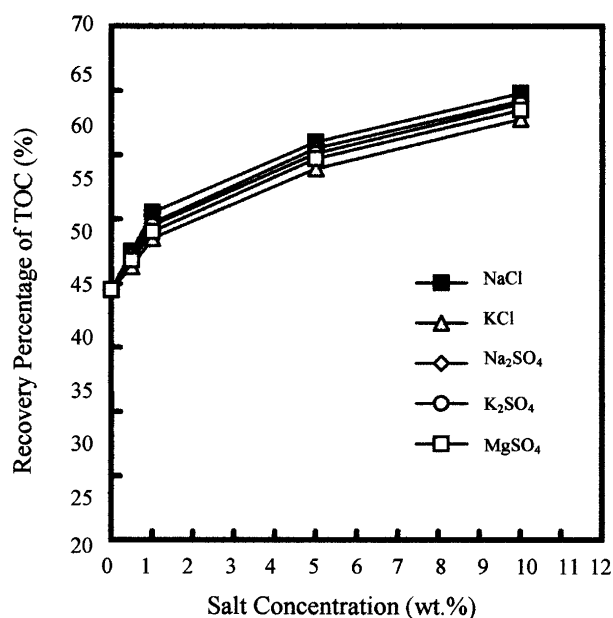


Fig. 3. Effect of the salt concentrations and species on the recovery percentage of organic compounds from wastewater of trinitration process under the condition of toluene/wastewater (1/1), pH 7.0 and 333 K.

Table 3

Product distributions of organic compounds extracted and residual in wastewater of dinitration process at various concentrations of salts

Salt (wt.%)	NaCl		KCl		$\text{Na}_2\text{SO}_4$		$\text{K}_2\text{SO}_4$		$\text{MgSO}_4$	
	2,6-DNT (E)	2,6-DNT (R)	2,6-DNT (E)	2,6-DNT (R)	2,6-DNT (E)	2,6-DNT (R)	2,6-DNT (E)	2,6-DNT (R)	2,6-DNT (E)	2,6-DNT (R)
0.0	37.5	13.6	37.5	13.6	37.5	13.6	37.5	13.6	37.5	13.6
0.5	35.1	13.4	35.0	13.5	35.5	13.5	35.0	13.5	35.0	13.6
1.0	33.8	13.4	33.7	13.4	33.9	13.6	34.2	13.5	34.0	13.6
5.0	31.1	13.5	31.5	13.5	31.6	13.6	32.2	13.6	31.8	13.5
10.0	30.2	13.6	30.4	13.6	30.5	13.5	30.8	13.6	30.8	13.5

2,4-DNT (E) was the other product balanced with 2,6-DNT (E) on the weight basis in extract (not shown). 2,4-DNT (R) was the other product balanced with 2,6-DNT (R) on the weight basis in raffinate (not shown).

Table 4

Product distributions of organic compounds extracted and residual in wastewater of trinitration process at various concentrations of salts

Salt (wt.%)	NaCl		KCl		Na <sub>2</sub> SO <sub>4</sub>		K <sub>2</sub> SO <sub>4</sub>		MgSO <sub>4</sub>	
	2,4-DNT (E)	2,6-DNT (E)	2,4-DNT (E)	2,6-DNT (E)	2,4-DNT (E)	2,6-DNT (E)	2,4-DNT (E)	2,6-DNT (E)	2,4-DNT (E)	2,6-DNT (E)
0.0	9.5	10.5	9.5	10.5	9.5	10.5	9.5	10.5	9.5	10.5
0.5	9.3	10.6	9.7	10.8	9.9	10.9	9.5	11.0	9.6	10.5
1.0	9.8	11.3	9.5	10.6	9.8	11.0	9.6	10.5	10.0	11.2
5.0	10.0	11.0	9.6	10.7	9.7	11.2	9.8	11.1	10.2	11.0
10.0	9.6	10.8	10.0	11.2	9.8	11.0	9.6	10.7	9.8	10.8

Salt (wt.%)	NaCl		KCl		Na <sub>2</sub> SO <sub>4</sub>		K <sub>2</sub> SO <sub>4</sub>		MgSO <sub>4</sub>	
	2,4-DNT (R)	2,6-DNT (R)	2,4-DNT (R)	2,6-DNT (R)	2,4-DNT (R)	2,6-DNT (R)	2,4-DNT (R)	2,6-DNT (R)	2,4-DNT (R)	2,6-DNT (R)
0.0	6.9	1.7	6.9	1.7	6.9	1.7	6.9	1.7	6.9	1.7
0.5	7.0	1.7	7.1	1.8	7.0	1.8	6.9	1.7	6.9	1.7
1.0	7.1	1.8	7.1	1.8	7.1	1.7	7.0	1.7	6.9	1.8
5.0	7.1	1.7	7.0	1.7	7.1	1.8	7.0	1.8	7.1	1.8
10.0	7.0	1.8	7.0	1.7	7.1	1.8	7.1	1.7	7.1	1.8

2,4,6-TNT (E) was the other product balanced with 2,4-DNT (E) and 2,6-DNT (E) on the weight basis in extract (not shown). 2,4,6-TNT (R) was the other product balanced with 2,4-DNT (R) and 2,6-DNT (R) on the weight basis in raffinate (not shown).

It clearly indicates that the weight percentage of 2,6-DNT of TOC extracted was about 10.8 wt.%, which was higher than that of 2,6-DNT in wastewater feedstock (6.3 wt.%) and independent of species of inorganic salts. It supports that 2,6-DNT was more easily extracted by toluene than that by wastewater as mentioned. Moreover, the weight percentage of 2,4-DNT of TOC extracted (9.7 wt.%) was also slightly higher than that of 2,4-DNT in wastewater feedstock (8.0 wt.%). It means that 2,4-DNT was more easily extracted by toluene than that by wastewater. Nonetheless, the enhancing effect on recovery of 2,6-DNT was more apparent, as consistent with the result shown in Table 3. As taking the weight percentage of 2,4,6-TNT of TOC extracted (79.6 wt.%) into consideration, which was lower than that in wastewater feedstock (85.4 wt.%), it reveals that 2,4,6-TNT was more hardly extracted by toluene than that by wastewater. Consequently, the extractable priority of organic compounds from wastewater in existence of inorganic salts by toluene is in the following order: 2,6-DNT > 2,4-DNT > 2,4,6-TNT. With respect to the compositions of TOC residual in wastewater for various concentrations of inorganic salts, no obvious differences were found between them. It provides another evidence on the proposal that the affinity of free water for organic solutes was not affected by inorganic salts.

### 3.2. Effect of acidity of wastewater

For the sake of enhancing recovery of nitrotoluenes from wastewater of trinitration process, the acidity of wastewater was adjusted by addition of sulfuric acid solution. Effects of acidity of wastewater on the recovery percentage of organic compounds and salting-out are demonstrated in Fig. 4. Obviously, without addition of inorganic salts, the extracting efficiency of organic compounds from wastewater with lower pH value was superior to that with higher pH value. It may be attributed to the solubility of 2,4,6-TNT in wastewater, which decreases as

pH value decreases [27,28]. As far as the addition of NaCl is concerned, the amounts of organic compounds extracted were significantly increased with increasing concentrations of NaCl at a range of pH 4.0–7.0, similar to the trend as mentioned in above paragraph. With regard to the increment of recovery percentage of TOC between 10 wt.% NaCl and 0 wt.% NaCl, as a function of pH value, it is apparent that one at high pH value was larger than that at low pH value (i.e.  $\Delta\text{TOC}_{\text{pH } 7.0}$  versus  $\Delta\text{TOC}_{\text{pH } 4.0} = 15\%:10\%$ ). That suggests the salting-out effect depends strongly upon the acidity of wastewater. This phenomenon may be explained by higher solubility of 2,4,6-TNT in

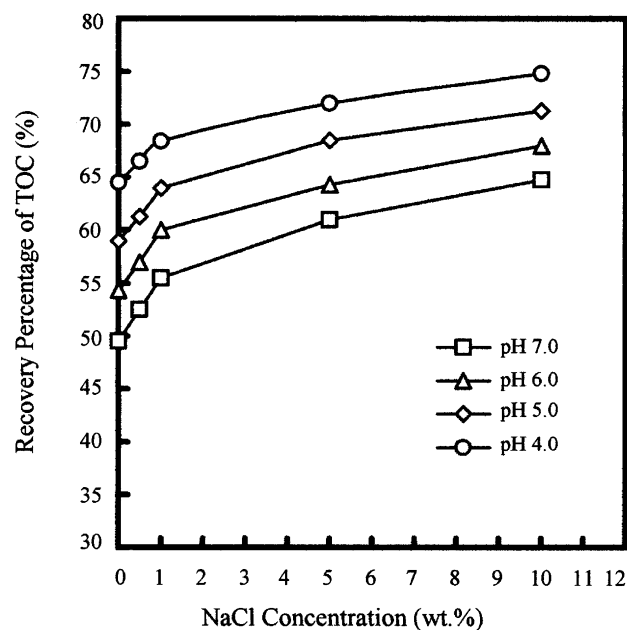
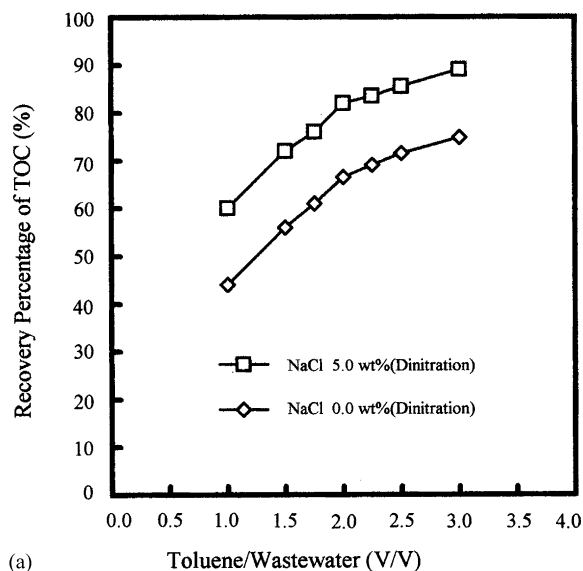
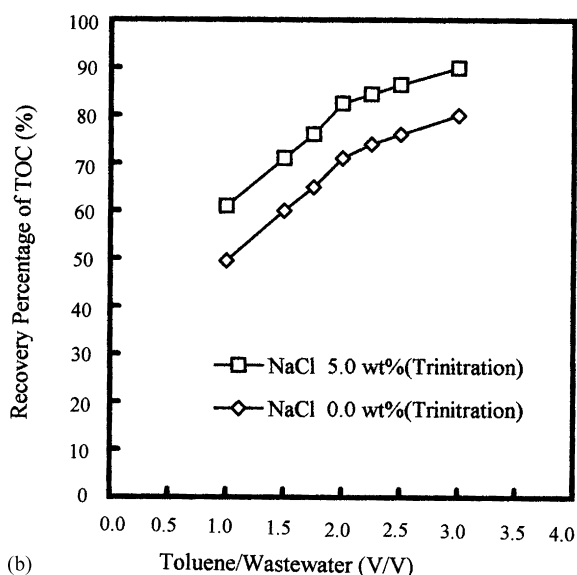


Fig. 4. Effect of the NaCl concentrations on the recovery percentage of organic compounds from wastewater of trinitration process in the range of pH 4.0–7.0 under the condition of toluene/wastewater (1/1) and 333 K.





(a)



(b)

Fig. 5. Effect of the volume ratios of solvent versus wastewater on the recovery percentage of organic compounds from wastewater of toluene nitration process. (a) Dinitration process under the condition of pH 7.0 and 323 K; and (b) trinitration process under the condition of pH 7.0 and 333 K.

the aqueous phase at pH 7.0, wherein the amount of free water was more than those at lower pH values. As a result, the former was more seriously affected by salting-out effect, leading to decreasing amount of free water.

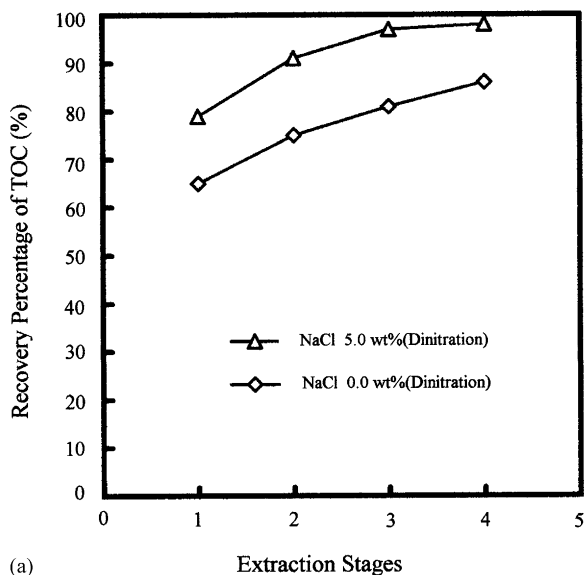
### 3.3. Effect of volume ratios of solvent versus wastewater

It has been well known that the adjustment of solvent amounts used is an important operating variable industrially. Fig. 5 presents the influence of volume ratios of toluene versus wastewater on the extracting performance with or without addition of 5.0 wt.% NaCl. Apparently, the recovery percentage of organic compounds increases with increasing volume ratios of toluene versus wastewater. Besides, the recovery percentage

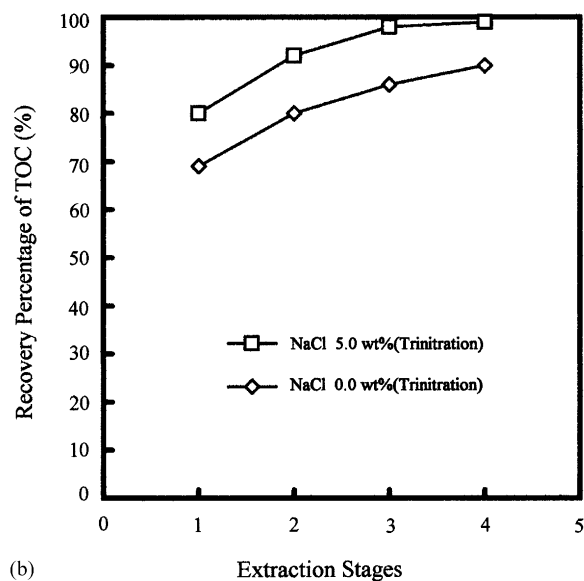
of organic compounds from wastewater of dinitration process at high volume ratio of toluene versus wastewater was significantly superior to that at low one in the presence of 5.0 wt.% NaCl (i.e. 90% versus 60%). An identical trend was also observed in dealing with wastewater from trinitration process (see Fig. 5(b)). Those imply that high volume ratio of toluene versus wastewater would be preferred from economic consideration. Due to more obvious increment of recovery of TOC under the condition of toluene/wastewater (ca. 2.0), it was beneficially chosen for all subsequent experiments. As the results in existence of NaCl were compared with those without NaCl for either dinitration or trinitration process, it clearly points out that the increment of recovery percentage of TOC enhanced by salting-out effect was independent of volume ratios of toluene versus wastewater. The plausible explanation is that the solubility of organic solutes in wastewater was significantly reduced by salting-out effect, induced from 5.0 wt.% NaCl, on the other hand, the solubility of toluene solvent in wastewater was also decreased on account of presence of NaCl [29,30]. Owing to same concentration of NaCl added for various ratios of toluene versus wastewater, the salting-out effect remains constant for a series of extraction tests.

### 3.4. Effect of extraction stages

For the purpose of increasing the recovery percentage of organic solutes, the multiple stages extraction has been always adopted practically. Fig. 6 illustrates the influence of multiple stages operation on the extracting behavior of toluene. The recovery percentage of TOC from wastewater of dinitration or trinitration process was gradually increased with increasing the extraction stages in the presence of NaCl or not. Due to the existence of NaCl in wastewater, recovery of organic compounds was continuously promoted by salting-out effect in the sequential extraction tests. As a consequence, the recovery percentage of TOC from wastewater accompanied with 5.0 wt.% NaCl was significantly higher than that without NaCl. It is noteworthy that the value of recovery percentage reached a level as high as 98% of the TOC at fourth stage in treating wastewater from dinitration process (see Fig. 6(a)). Nonetheless, the amounts of organic compounds extracted in the absence of NaCl reached only 86% of the TOC at fourth stage, and further extraction stage would not elevate the recovery percentage of TOC. The later phenomenon observed may be interpreted by the dissolution of toluene solvent into wastewater, caused by longer contact time [31,32]. It could be verified by wastewater raffinate analysis using UV-vis spectrophotometry [23], wherein the toluene concentration in wastewater from dinitration process was ca.  $40 \text{ mg l}^{-1}$  at fifth extraction stage and no toluene detected within prior four stages. On the contrary, the solubility of toluene in aqueous phase has significantly diminished because of presence of NaCl [29,33]. That suggests toluene solvent was scarcely dissolved into wastewater, corresponding to our result, wherein there was not any toluene detected. Therefore, the dinitrotoluenes in wastewater of dinitration process could be completely recovered using toluene extraction method enhanced by salting-out effect. As expected, a similar extracting behavior on multiple stages extraction was obtained for recovery



(a)



(b)

Fig. 6. Effect of the extraction stages on the recovery percentage of organic compounds from wastewater of toluene nitration process. (a) Dinitration process under the condition of toluene/wastewater (2/1) and 323 K; and (b) trinitration process under the condition of toluene/wastewater (2/1) and 333 K.

of TOC from wastewater of trinitration process in the presence of NaCl (shown in Fig. 6(b)). That approves of above hypothesis as described.

#### 4. Conclusion

Based on the above discussion, it was found that recovery of organic compounds from wastewater of toluene nitration process was significantly enhanced by addition of inorganic salts, which have the following priority:  $\text{NaCl} > \text{Na}_2\text{SO}_4 > \text{K}_2\text{SO}_4 > \text{MgSO}_4 > \text{KCl}$  on the weight basis of wastewater. That may be attributed to the salting-out effect, which depends strongly upon the acidity of wastewater. Further, high volume ratio of toluene/wastewater (ca. 2.0) was

more suitable for recovery of TOC from wastewater with NaCl existed, of which extractable priority was as follows:  $2,6\text{-DNT} > 2,4\text{-DNT} > 2,4,6\text{-TNT}$ . It is remarkable that TOC of wastewater would be nearly recovered by successive four stages toluene extraction in the presence of NaCl, leading to salting-out effect continuously. That implies the toluene extraction method accompanied with suitable inorganic salts would be potentially applied to recover nitroaromatics from wastewater stream of toluene nitration process.

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