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Removal of highly toxic components from hexanitrobibenzil wastewater by vacuum distillation

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ABSTRACT

Hexanitrobibenzil (HNBB) wastewater, generated in the first process during the synthesis of hexanitrostilbene, was treated using vacuum distillation. The effect of the treatment was determined using high-performance liquid chromatography, UV–Vis spectroscopy, gas chromatography–mass spectroscopy, and other physical and chemical analytical techniques. The concentrations of all of the nitroaromatic compounds were much lower in the distillate (2.21 mg/L) than in the wastewater (165 mg/L), and the chloride ions were completely removed by distilling the wastewater, indicating that the highly toxic components were efficiently removed by the vacuum distillation process. The concentrations of 14 types of nitroaromatic compounds that were detected in the HNBB wastewater were decreased by more than 98% by distilling the wastewater, but the 2,4-dinitrotoluene concentration was only decreased by about 67%. Toxicity tests based on the luminescence inhibition of *Vibrio qinghaiensis* sp. Nov were performed on the wastewater and its distillate, and the acute toxicity was found to be decreased by more than 96% by distillation. Vacuum distillation could be a useful method for removing these toxic and refractory components from other types of wastewater that are similar to HNBB wastewater.

Keywords: Vacuum distillation; Hexanitrobibenzil wastewater; Hexanitrostilbene; GC–MS; Acute toxicity

1. Introduction

Hexanitrostilbene (HNS) is a high explosive with the properties of insensitivity to heat and impact [1,2], and so it is widely used in the fields of military, aeronautics, and astronautics. Large volumes of hexanitrobibenzil (HNBB) wastewater are generated during the first process in the two-step synthesis of HNS [3]. This wastewater is highly toxic because of its high salinity (the HNBB synthesis reaction produces sodium chloride) and it contains a complex mixture of nitroaromatic compounds. The high salinity (>5%) of the wastewater, indicated by a high chloride ion concentration, can inhibit microbial metabolism in traditional biological treatment systems [4–6]. The nitroaromatic compounds are refractory to biodegradation, so they can easily remain in the biosphere where they will contribute to environmental pollution and ecological risks because they are highly toxic and mutagenic to humans, fish, algae, and microorganisms [7–10]. Discharging HNBB wastewater

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without effectively treating it can cause serious environmental problems, so it is imperative to remove the highly toxic components from the wastewater before it is discharged.

A similar type of wastewater produced during the HNS production process has been treated using the supercritical water oxidation process [11], and the organic compounds were found to be completely oxidized after a short treatment at 560℃ and 27 MPa. The chemical oxygen demand (COD) was decreased by up to 99% (from an initial COD of 63,000 mg L^{-1}) using this process. However, the main disadvantage of the process for its practical application was its high-energy consumption. Wu et al. [12] flocculated pollutants from HNS wastewater using seven bioflocculant-producing strains of microbe that had been isolated from soil and poplar tree branches that had been contaminated with HNS wastewater. They optimized the culture and flocculation conditions, and found that the micro-organisms could decrease the color intensity in HNS wastewater by 93%, the turbidity by 51%, and the COD by 73%.

Vacuum distillation is commonly used to desalinate or remove contaminants from seawater or brackish water to produce drinking water [13–15]. Vacuum distillation has also been used to treat industrial wastewater [16–19]. The distillation process can allow components with different boiling points to be separated to facilitate follow-up treatment or to collect useful components for recycling. Connecting a vacuum decompression device to a distillation apparatus will decrease the boiling point of the liquid, decreasing the energy required for the distillation process considerably. Therefore, there is the potential for vacuum distillation to be used to treat wastewater in engineering applications. The objective of the work presented here was to evaluate the efficiency at which highly toxic components are removed from HNBB wastewater using the vacuum distillation process. The water quality was determined before and after the distillation treatment using high-performance liquid chromatography (HPLC), UV–Vis spectroscopy, gas chromatography–mass spectroscopy (GC–MS), and other physical and chemical analytical techniques. The acute toxicities of the wastewater and its distillate were also tested using bacterial bioluminescence assays [19].

2. Materials and methods

2.1. Materials

The HNBB wastewater was provided by the state-owned 525 Chemical Factory, Xiangfan, China, where HNS is produced using a two-step method. The first step is the oxidation of 2,4,6-trinitrotoluene to form HNBB using sodium hypochlorite, using an ethanol–benzene mixture as the solvent. The second step is the oxidation of the HNBB to form HNS using liquid bromine, using a pyridine–benzene mixture as the solvent. The HNBB wastewater used in our study is produced during the first step. The wastewater was dark brown, had a strong and pungent odor, and it was at pH 7.0. Ammonium ferrous sulfate (CAS No. 10045-89-3), concentrated sulfuric acid (CAS No. 7664-93-9), mercuric sulfate (CAS No. 7783-35-9), phenanthroline (CAS No. 66-71-7), phenolphthalein (CAS No. 77-09-8), potassium chromate (CAS No. 7789-00-6), potassium dichromate (CAS No. 7778-50-9), pyridine (CAS No. 110-86-1), silver nitrate (CAS No. 7761-88-8), silver sulfate (CAS No. 10294-26-5), sodium chloride (CAS No. 7647-14-5), and sodium hydroxide (CAS No. 8012-01-9) were all of analytical pure grade. Dichloromethane was of chromatographic grade. All of these reagents were purchased from the Beijing Chemical Reagent Company (Beijing, China). The luminescent bacterium *Vibrio qinghaiensis* sp. Nov was provided by Beijing Hamamatsu Photon Techniques (Beijing, China).

2.2. Experimental procedure

A 400 mL sample of HNBB wastewater was put into a 1,000 mL distillation bottle and kept in a water bath at a constant temperature of 70, 80, or 90℃. The pressure (Table 1) was adjusted to keep the wastewater sample boiling. The distillate was collected until the pressure in the rotary evaporator had decreased rapidly and no more distillate drip from the condensing system.

2.3. Water quality detection methods and instruments

The COD of a water sample was determined using the Hach method (Hach, Loveland, CO, USA). The total organic carbon (TOC) content was determined using a TOC-V CPN system (Shimadzu, Kyoto, Japan). The chloride ion concentration was determined following Chinese standard method GB 11896-89 (suitable for a concentration range of 10–500 mg L^{-1}). A type 201 pH detector (Hanna Instruments, Woonsocket, RI, USA) was used to measure the pH. The total nitroaromatic compound concentration was measured following Chinese standard method GB 4918-85.

2.4. UV–Vis spectroscopy analysis

The absorption spectra for the HNBB wastewater and its distillate, each diluted 100 times, were determined using UV1800 spectrophotometer (Shimadzu).

Table 1
Temperature and pressure parameters

Temperature (°C)	Initial pressure (MPa)	Final pressure (MPa)
70	0.058	0.088
80	0.054	0.085
90	0.050	0.081

The instrument used a deuterium lamp and had a wavelength range of 190–1,100 nm, with an accuracy of ±1 nm.

2.5. GC–MS analysis

The organic compounds in a sample were extracted with dichloromethane under acidic, neutral, and basic conditions. A GC–MS system (GC6890/MSD5973 N; Agilent Technologies, Santa Clara, CA, USA), equipped with a DB-5MS capillary column (Agilent Technologies), was used to analyze the organic components in the extracts of the HNBB wastewater and distillates. A 1 μL aliquot of an extract was injected into the GC–MS. The oven temperature program started at 40°C (held for 5 min) and increased at 2°C min^{-1} to 280°C, which was held for 10 min. The standard NIST 05 mass spectral library database was used to identify the organic compounds that were detected and to allow them to be analyzed qualitatively.

2.6. GC–flame ionization detector (FID) analysis

A GC–FID instrument (GC6890; Agilent Technologies) was used to qualitatively and quantitatively determine ethanol in the wastewater and distillate samples [20]. A 1.0 μL aliquot of a sample was injected into the GC; separation was achieved using a DB-FFAP column (30 m long, 0.25 mm i.d., 0.25 μm film thickness; Agilent Technologies), and the eluted components were measured using an FID detector. The oven temperature program started at 50°C (held for 5 min) and increased at 15°C min^{-1} to 150°C, which was held for 2 min.

2.7. Toxicity tests

A BHP9511 water toxicity analyzer (Beijing Hamamatsu Photon Techniques) was used to determine the acute toxicity of the wastewater and distillate samples by determining the luminescence inhibition ratios (LIRs) for *V. qinghaiensis* sp. Nov [19]. A higher dilution ratio at a certain LIR indicated a more toxic water sample. The LIR for *V. qinghaiensis* sp. Nov was calculated using the following equation,

$$\text{LIR}\ (\%) = ((\text{RLI}_{\text{ref}} - \text{RLI}_{\text{s}})/\text{RLI}_{\text{ref}}) \times 100$$

where RLI_{ref} and RLI_{s} are the relative luminescence intensities in the reference and actual sample systems, respectively. The dilution rate at 50% LIR was used as the evaluation criterion.

3. Results and discussion

We distilled wastewater samples at 70°C, 80°C, and 90°C, but found no significant differences between the results obtained at the different temperatures (data not shown). Therefore, we used the distillation sample obtained at 70°C in the subsequent analyses described below.

3.1. Water quality analysis

An almost transparent fraction with a volume of 358 mL was obtained from the 400 mL wastewater sample that was distilled at 70°C. The CODs, TOC contents, total concentrations of all of the nitroaromatic compounds, chloride ion concentrations, and pH values found for the wastewater and its distillate are shown in Table 2. It can be seen that the total nitroaromatic compound concentration was much lower (2.21 mg L^{-1}) in the distillate than in the wastewater (165 mg L^{-1}), indicating that these highly toxic components were efficiently excluded from the distillate. The chloride ion concentration also decreased greatly, from 4,997 mg L^{-1} in the wastewater to below 10 mg L^{-1} (the detection limit) in the distillate, indicating that vacuum distillation was also a highly efficient method of decreasing the salinity. This would allow more effective microbial growth, if the distillate was required to be further treated using a traditional biological treatment system, because a high salinity (>5%) can inhibit microbial metabolism [6]. The pH was almost the same for the wastewater and the distillate.

Table 2
Chemical oxygen demands (CODs), total organic carbon (TOC) contents, total nitroaromatic compound concentrations, chloride ion concentrations, and pH values found for the wastewater and its distillate

	COD (mg/L)	TOC (mg/L)	Total nitroaromatic compound (mg/L)	Cl^- concentration (mg/L)	pH
HNBB wastewater	74,894	21,618	165	4,997	6.9
Distillate (70˚C)	57,380	16,400	2.02	<10 (detection limit)	7.2

The COD and TOC contents were almost the same in the wastewater and distillate, which suggest that the volatile components that were transferred to the distillate may have contributed most of the COD in the HNBB wastewater.

3.2. UV–Vis spectroscopy

In the absorption spectra for the HNBB wastewater and its distillate, strong absorption in the wavelength range 190–600 nm was found for the HNBB wastewater, indicating that the wastewater contained large amounts of aromatic compounds [21]. The absorption in this wavelength range was found to be almost zero for the distillate, suggesting that most of the organic compounds containing chromophores and auxochromous groups remained in the distillation residue [19].

3.3. GC–MS analysis

The wastewater and distillate were analyzed by GC–MS to further evaluate their compositions. According to the NIST 05 mass spectral library database, most of the organic compounds in the wastewater were nitroaromatic compounds. The main components in the HNBB wastewater were identified and are shown in Table 3. Most of the organic compounds in the wastewater were identified as being nitroaromatic compounds such as 1,3,5-trinitrobenzene, 1,3,5-trinitrophenol, and 2,6-dinitrophenol, which might have been present because they were in the raw materials or because they were by-product of the HNBB synthesis process. Four kinds of nitroaromatic compounds were detected in the distillate, and they were present at very low concentrations. From abundance calculations, we determined that the concentrations of most of these nitroaromatic compounds were decreased by more than 98% by distilling the wastewater, although the 2,4-dinitrotoluene removal efficiency was only 67%. The 2,4-dinitrotoluene removal efficiency was similar to efficiencies that have been found previously [19], so 2,4-dinitrotoluene may volatilize more readily than other nitroaromatic compounds. The pyridine peak in the distillate chromatogram was rather large, so pyridine was quantified in the wastewater and distillate by HPLC. The pyridine concentrations in both the wastewater and the distillate were 23–25 $\mu L\, L^{-1}$, indicating that pyridine was removed poorly by the vacuum distillation system. This may be because pyridine is transferred to the distillate easily because of its relatively high volatility. Pyridine was not one of the raw materials or a by-product of the first process in the HNS synthesis method [3], so we concluded that the presence of pyridine in the wastewater might have been caused by the sample being contaminated in the factory.

3.4. GC–FID analysis

The GC–FID analysis results indicated that the distillate contained ethanol. The ethanol concentration (Fig. 1) was 3.43% (v/v). The dependence of the COD on the ethanol concentration was determined. The COD can be calculated using the equation $\mathrm{COD} = 1.6233 \times \mathrm{Ce} + 0.728$, where Ce is the ethanol concentration ($\mu L\, L^{-1}$). The ethanol concentration of 3.43% (V/V) could, therefore, cause a COD of about 52,960 $mg\, L^{-1}$. This could explain why the efficiency of COD removal from the wastewater by vacuum distillation was poor. The source of the ethanol in the distillate was the HNBB production process [3].

3.5. Acute toxicity test

The luminescent bacteria test has been proven to be a rapid and cost-effective method for evaluating the acute toxicity of wastewater. The test involves measuring the light output of luminescent bacteria [22,23]. In a previous study [24,25], we found that the freshwater luminescent bacterium *V. qinghaiensis* sp. Nov. was more sensitive and suitable than other bacteria, such as *P. phosphoreum*, for evaluating the acute toxicities of wastewater samples. With this in mind, we used *V. qinghaiensis* sp. Nov. to assess the acute toxicities of the HNBB wastewater and the distillate. The dilution rate required to give a specified LIR was

Table 3
Results of the gas chromatography–mass spectrometry analyses of the main organic components in the hexanitrobibenzil (HNBB) wastewater and its distillate

HNBB wastewater				Distillate (70˚C)			
Retention time (min)	Compounds	Relative percentage	m/z	Retention time (min)	Compounds	Relative percentage	m/z
4.9	Pyridine	9.50	79.1, 52.1	4.9	Pyridine	91.89	79.1, 52.1
49.1	1,3-Dinitrobenzene	0.85	168, 76, 50				
49.5	Dimethyl phthalate	1.18	163	49.4	Dimethyl phthalate	1.99	163
49.7	2,6-Dinitrotoluene	0.67	165				
52.5	2,4-Dinitrophenol	1.89	184, 154				
53.0	2,3-Dinitrotoluene	0.28	165, 135				
53.2	1-Chloro-2,4-dinitrobenzene	0.80	202, 110, 75				
54.0	2,4-Dinitrotoluene	1.14	165, 89, 63	54.0	2,4-Dinitrotoluene	1.79	165, 89, 63
57.4	2-Hydroxyl-3, 5-Dinitrotoluene	3.96	198, 181				
58.4	5-Nitro-1H-benzoriazole	5.77	194, 136, 63				
64.7	1,3,5-Trinitrobenzene	61.86	213, 75	63.4	1,3,5-Trinitrobenzene	4.14	213, 75
65.0	2,5-Dinitrophenol	4.26	209, 184, 63	64.3	2,5- Dinitrophenol	0.18	212, 184, 63
72.4	3-Nitrostyrene	0.48	149, 74				
76.0	2,6-Dinitrophenol	3.33	184				
77.2	4-Methyl-3,5-dinitro-benzoic acid	2.42	209, 181				
79.7	2,4,6-Trinitro-benzenamine	1.62	228, 90				

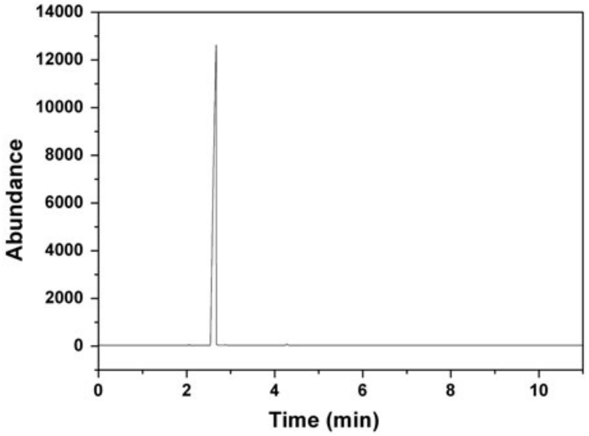

Fig. 1. Results of the GC–FID analysis of ethanol in the distillate.

used as the assessment criterion. The greater the dilution ratio at a given LIR, the more toxic was the water sample. The dilution ratio at 50% LIR was used for the HNBB wastewater and distillate toxicity tests. The dependence of the *V. qinghaiensis* sp. Nov LIR on the dilution ratio is shown in Fig. 2. The LIR of the HNBB wastewater was more than 60% even when it had been diluted by a factor of 100, indicating that the wastewater was highly toxic. However, the LIR of the distillate was close to zero when it was diluted by a factor of 100. The dilution ratios at 50% LIR for the wastewater and distillate were 160 and 2.7, respectively. We concluded that the acute toxicity of the wastewater was decreased by more than 98% by distilling it.

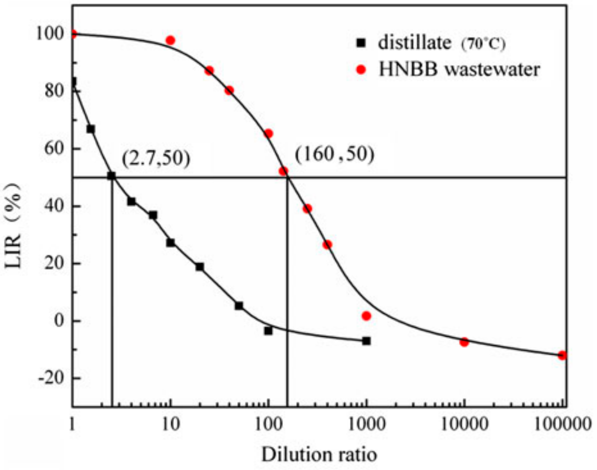

Fig. 2. Dependence of the luminescence inhibition ratio on the dilution ratio used for the hexanitrobibenzil wastewater and its distillate.

3.6. Applicability and cost of vacuum distillation

Vacuum distillation has been used to treat industrial wastewater [16–19]. In particular, it has the potential for use in engineering applications for treating wastewater from explosives production processes because the initial temperature of the wastewater generated in explosives production processes can be higher than 50°C. However, it is difficult to thoroughly treat such wastewater, which can contain high concentrations of refractory organic compounds, using only vacuum distillation. Vacuum distillation is a good pretreatment method for improving the biodegradability of wastewater; so it can be used to treat wastewater from explosives production processes before other approaches, such as biological methods, are used [26]. A method combining vacuum distillation and biological treatment would cost $0.80 to $1.00 to treat 1 tonne of wastewater from explosives production processes, which is lower than the cost of incinerating the wastewater (3–5 per tonne of wastewater) [26].

4. Conclusions

The highly toxic components in HNBB wastewater can be effectively removed by vacuum distilling the wastewater. The total nitroaromatic compound concentration decreased greatly from 165 to 2.21 mg L^{-1}, and the chloride ions were completely removed when HNBB wastewater was vacuum distilled. The concentrations of most of the nitroaromatic compounds in the wastewater were decreased by more than 98% when the wastewater was distilled, although the 2,4-dinitrotoluene concentration was only decreased by 85%. In addition, the color intensity of the wastewater was decreased greatly and the acute toxicity of the wastewater was decreased by more than 98% by distilling the wastewater. The main organic compound in the distillate was ethanol, and this was the main contributor of the COD in both the wastewater and the distillate. The distillate would be much more easily treated than the original wastewater using biological processes, because the highly toxic components of the wastewater were not present in the distillate. We therefore concluded that the vacuum distillation method was suitable for pretreating HNBB wastewater.

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