

TOXIC ORGANIC WASTEWATER TREATMENT THROUGH SOLID PHASE TRANSFORMATION WITH RE-USE POTENTIAL

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Summary

A novel treatment of wastewater generated in the production of dinitrobenzene was examined. The method involves solid phase transformation of the wastewater by slaking with lime, followed by removal of the organics contained in the lime in a muffle furnace. The regenerated lime may be re-used, e.g., for the neutralization of acidic wastewaters resulting from the manufacture of *m*-aminophenol. A flowsheet for the integrated treatment of dinitrobenzene and *m*-aminophenol plant wastewaters is proposed.

Introduction

Chemical industries and adverse environmental impact have become almost synonymous. Notwithstanding the quantity of wastes generated by these industries, the discharge of toxic and non-biodegradable compounds in the wastes poses problems in conventional waste treatment plants in meeting environmental quality standards stipulated by the regulatory agencies. The wastewater generated in the manufacture of dinitrobenzene (DNB), a basic organic chemical which finds applications in dyes, explosives, etc., falls into this category and has been posing serious problems of treatment and disposal.

The wastewater which arises from the purification of the crude DNB has a fairly high organic content, measured as total organic carbon (TOC) and chemical oxygen demand (COD), consisting of nitro-aromatic and nitro-phenolic compounds which are highly toxic to aquatic life.

This wastewater does not exert any biological oxygen demand and is not amenable to biological degradation even after a large dilution with domestic sewage. Addition of nitro groups tends to make aromatic compounds less amenable to biodegradation and more toxic [1–3]. It has also been reported that even low concentrations of nitro compounds not only upset the biological life in the receiving stream but are also toxic to the micro-organisms in sewage treatment plants [1]. These observations preclude the possibility of biological treatment of this wastewater, while its toxic nature makes it imperative to consider alternative methods of treatment. Physico-chemical

methods such as activated carbon adsorption, and concentration and incineration were studied in the laboratory. An indigenous powdered activated carbon could considerably remove the organics (60% COD removal). But, for complete detoxification, a multistage carbon adsorption is required. The high doses of carbon required, the difficulty of regeneration of powdered carbon and the capital and running costs raise questions about the cost-effectiveness of this method of treatment. Concentration, followed by incineration, is usually regarded as a practical alternative for small volumes of toxic wastes, such as trinitrotoluene wastes [4]. However, in view of the energy consumption and the complex air pollution control equipment required, as well as the further treatment required for the condensates from the evaporation process, this option would prove to be expensive. Hence, a cost-effective method for the treatment of DNB wastewater needs to be evolved.

Solidification as a treatment technique for liquid wastes has been attempted as in the conversion of liquid molasses from distilleries into a solid product that will remain dry for transport and effective utilisation. Treating with limestone and admixture with plant materials have been tried [5, 6]. Bhaskaren et al. [7] utilised lime addition based on the principle that the water in the waste is used for lime slaking which is accompanied by abstraction of water and much evolution of heat. Along with this, the sugars combined with lime to form sparingly soluble and stable calcium compounds.

Solidification or encapsulation has also been used as a final step in the treatment of wastewaters containing radioactive materials [8, 9]. Various methods of solidification [10–12] have been used, such as (i) absorption of radioactive materials on natural clays followed by calcination, (ii) admixturing radioactive species with fluxing agents like borex, silica and lime to either encapsulate them in a glass matrix or to form glass-type materials, and (iii) injection of sludge from chemical precipitation into hot bitumen to form a dry solid.

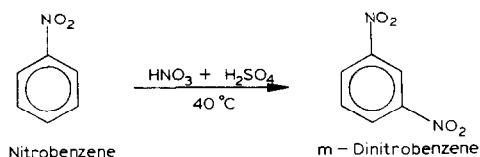
Approaches such as binding up the toxic constituents in stable compounds or coating the toxicants with inert impermeable materials have been considered for toxic and hazardous wastes which cannot be changed or destroyed by physical or chemical means [13]. Current techniques involve coating grains or blocks of waste with impermeable matter, a heated thermoplastic material such as bitumen, paraffin, polyethylene or sulphur (micro- and macro-encapsulation) and embedding wastes in organic or silicate polymer matrix.

Based on these approaches, a treatment technique has been attempted in the laboratory for DNB wastewater wherein commercial lime is slaked with DNB wastewater and the product is recalcined to recover the lime.

Process of manufacture, sources and characteristics of wastewater

Meta-dinitrobenzene (*m*-DNB) is produced by nitration of nitrobenzene with a nitration acid mixture. The reaction takes 7–8 hours at 40°C and the

spent acid is separated and recycled. The crude product contains small amounts of *o*- and *p*-isomers of DNB which are removed by consecutive washes with (i) 10% caustic solution, (ii) 15% sodium sulphite solution, and (iii) water. Each washing operation is carried out in batches and the wash waters are discharged into a holding tank. In our experiments they were collected individually and were flow composited.



Samples were collected on different days and analysed for conventional parameters as per Standard Methods [14]. Characteristics of the wastewater are given in Table 1. The total volume is about 4 m³/1000 kg product. The waste is highly alkaline (pH 9.2–12.5) with average alkalinity of 12,910 and 14,352 mg/l (as CaCO₃) at pH 8.3 and 3.7, respectively. The computation of individual alkalinity [14] indicates that nearly 80% of total alkalinity is contributed by hydroxide and the rest is due to carbonate. The COD ranges from 32,620 to 80,982 mg/l with an average of 53,243 mg/l while TOC ranges from 10,620 to 34,050 mg/l (average 20,413 mg/l). The TOC is expected to be contributed by *o*- and *p*-isomers of nitrophenols and nitrobenzene sulphonic acids which are formed during the washing operations besides some DNB. The water pollution and toxic effects of the organic constituents of the wastewater [15] are presented in Table 2. The wastewater also contains high concentrations of inorganics such as nitrites and sulphates as sodium salts. The wastewater does not exert BOD even with large dilution, due to the inhibitory action of the organics present. Acclimatisation studies to develop adopted bacterial cultures did not prove successful.

TABLE 1

Characteristics of wastewater from dinitrobenzene plant (all values except pH and flow are in mg/l)

Parameters	Minimum	Maximum	Average	Standard deviation (SD)
Flow (m ³ /tonne DNB)	—	—	4	—
pH	9.2	12.5	—	—
Alkalinity (as CaCO ₃)				
(i) pH 8.3	4,338	21,917	12,910	4,041
(ii) pH 3.7	9,212	23,085	14,352	6,356
Total solids	84,484	193,605	128,450	35,816
Total volatile solids	34,620	118,844	63,300	23,522
COD	32,620	80,982	53,243	17,447
TOC	10,620	34,050	20,413	6,923

TABLE 2

Water pollutional and toxic effects of organics present in DNB wastewater

Compound	Water pollution factors	Toxic effects
<i>o</i> -Dinitrobenzene	Biodegradation: decomposition by soil microflora: period > 64 days.	—
<i>m</i> -Dinitrobenzene	Biodegradation: decomposition by soil microflora in > 64 days.	Bacteria: inhibition of cell multiplication starts at 5 mg/l.
<i>p</i> -Dinitrobenzene	Biodegradation: decomposition by soil microflora in > 64 days.	—
Nitrobenzene	BOD ₅ : Nil, ThOD: 1.95 Impact on biodegradation processes: inhibition of degradation of glucose by <i>Pseudomonas fluorescens</i> at 30 mg/l. Inhibition of degradation of glucose by <i>E. coli</i> at 600 mg/l. Biodegradation: decomposition by soil microflora in > 64 days.	Bacteria: <i>E. coli</i> : LD ₀ : 600 mg/l. Algae: LD ₀ : 40 mg/l. Fish: Vairon (F): distilled water: TLM (6 h): 20–24 mg/l; hard water: TLM (6 h): 90–100 mg/l.
<i>o</i> -Nitrophenol	Biodegradation: decomposition by soil microflora in > 64 days. Impact on biodegradation processes: inhibition of degradation of glucose at 20 mg/l.	Bacteria: <i>E. coli</i> : LD ₀ : 1000 mg/l. Algae: LD ₀ : 36 mg/l. Fish: Bluegill: TLM (24–48 h): 67–46.3 mg/l.
<i>p</i> -Nitrophenol	Biodegradation: decomposition by soil microflora in 16 days. Impact on biodegradation processes: inhibition of degradation of glucose by <i>Pseudomonas</i> at 20 mg/l. Inhibition of degradation of glucose by <i>E. coli</i> at 100 mg/l.	Bacteria: <i>E. coli</i> : LD ₀ : 100 mg/l. Algae: inhibition of cell multiplication starts at 56 mg/l. Fish: Vairon (F): TLM 6 h: distilled water 4–6 mg/l; hard water: 30–33 mg/l.
<i>o</i> -Nitrobenzene sulphonic acid	Biodegradation: decomposition by soil microflora in > 64 days.	—
<i>p</i> -Nitrobenzene sulphonic acid	Biodegradation: decomposition by soil microflora in > 64 days.	—

ThOD: Theoretical oxygen demand.

TLM: Median threshold limit.

LD: Lethal dose.

Experimental

The experimental programme was divided into three parts. In the first, the slaking experiments, the mode of mixing the lime and wastewater was

studied and the addition ratio of lime to waste was optimised. In the next, the removal of organics contained in the lime was studied and the optimum temperature for muffling determined. Finally, the re-use potential of the regenerated lime was investigated.

The slaking experiments were carried out in porcelain dishes with commercial lime which was powdered and calcined at 800°C prior to use. The CaO content of the lime, as measured by the sucrose method [16], was about 60%. The residual moisture content of the slaked lime was determined by drying in an oven at 105°C.

The regeneration experiments were conducted in a laboratory muffle furnace at different temperatures. A suitable sample of the regenerated lime was selected by the quartering and coning method, extracted with a known volume of distilled water, and the COD of the extract was estimated and the values were expressed as COD per gram of the sample.

In the re-use experiments, a 5% slurry of the regenerated lime was prepared in distilled water and titrated against standard hydrochloric acid and an acidic wastewater from the factory using a Beckman pH meter. Control experiments were carried out by slaking lime with distilled water and adopting all other procedures as above, to evaluate the quality of the final product for re-use studies.

Results and discussion

The objective of the slaking experiments was to optimize the proportion of wastewater and the lime to be mixed, as well as to study the mode of mixing. The results are presented in Table 3. In optimising the ratio of lime to wastewater, ease of handling or the spadability of the slaked lime was the main consideration. It was observed that a 1:1 ratio was the optimum (Expt. 1, Table 3). This ratio was further confirmed in experiment 2 by doubling the quantities. To study the effect of mode of mixing additional experiments were conducted in which lime powder was added to the wastewater at the optimum ratio. The results shown in Table 3 (Expt. 3) indicate that more water is removed during slaking when lime is added to the wastewater than vice versa. This could be due to the better utilization of the heat generated during slaking. When lime is added to the wastewater, the heat generated with each incremental addition is transferred to the wastewater, thereby raising its temperature progressively and evaporating more of water. On the other hand, when the wastewater is added to the lime powder, the heat generated is partly lost since the heat dissipation in the solids is poor. Having optimized the ratio and mode of mixing, slaking was tried with different samples of DNB wastewater and the results (Exp. 4) were found to be consistent. However, the moisture contents of these samples were higher since the mixing was incomplete.

The next step in the treatment scheme was to remove the organics contained in the slaked lime. This is important, as otherwise the organics may

TABLE 3

Optimization of DNB wastewater:lime ratio and mode of mixing

Expt. no.	Mixing ratio (wastewater:lime)	Mode of mixing ^a	Water removed during slaking (% of total wt.)	Moisture con- tent in slaked lime (%)
1	2:1	A	11.0	49.3
	1.5:1		10.0	43.7
	1:1		13.0	29.7
2	1:1	A	11.2	23.9
	1:1		10.0	25.5
3	1:1	B	15.8	14.2
	1:1		15.6	17.5
4	1:1 with different DNB samples	B	9.1—13.0	26.3—29.3 ^b

^a A — wastewater added to lime; B — lime added to wastewater.

^b Incomplete mixing.

be leached out through various mechanisms if the slaked lime is disposed of to land, or the organics may be transferred to treated effluent if the lime is used for neutralization. The slaked lime mass was muffled at different temperatures to determine the optimum temperature for destroying the organic impurities present. The organics remaining in the lime after muffling were extracted with water and the COD contributed by the organics was estimated. The percentage COD removal was calculated with respect to the COD contributed by the wastewater added in the slaking process. The results, presented in Table 4, indicate that practically all the organics are destroyed by muffling at 300°C. It is to be remembered that in a muffle furnace the heat transfer to the lime mass will be poor. If the slaked lime is regenerated in a

TABLE 4

Optimum temperature for muffling of slaked lime

Muffling temp. (°C)	COD remaining after muffling (mg COD/g slaked product)	COD removal (%)
105 ^a	21.6	35.7
200	8.4	75.0
300	0.32	99.1
400	0.24	99.3
500	0.24	99.3

^a Oven-dried sample.

kiln, with better heat transfer, then the organics may be removed with less energy input.

It is possible that some organics may be removed and destroyed during slaking since high temperatures (400–450°C), which cannot be properly controlled, are reached. A measure of this removal may be indicated by the COD removal obtained with the oven-dried sample (100°C) which is about 35.7%. This naturally raises concern about the possible air pollution effects during slaking and the slaker unit should, therefore, be carefully designed. Since the pH during slaking is very high, it is unlikely that Ca or Na salts of nitrophenolics present in the waste would be volatilised.

The real benefit of this scheme of treatment lies in the re-use potential of the regenerated lime. This aspect was investigated by using the regenerated lime to neutralize standard acid and an acidic wastewater. The neutralization capacity of the regenerated lime was compared to that of original lime and results are given in Table 5. It is seen that the neutralization capacity (expressed as milliliter acid per gram of lime) of the regenerated lime is less than that of the original lime. This may be due to two reasons.

- (i) In the process of slaking, the CaO in lime is converted to Ca(OH)₂, thereby increasing the weight of the product. Hence, 1 g of the product will have less neutralization capacity than 1 g of the original lime.
- (ii) In the above process of slaking and muffling, the organics will be converted to CO₂ which reacts with Ca(OH)₂ to form CaCO₃, thereby reducing the neutralization capacity of the lime to a certain degree.

TABLE 5

Neutralization capacity of lime

Description	Amount of 1 N HCl required to neutralise 10% lime slurry to pH 3.7 (ml/g lime)	MAP acid waste required to neutralise 10% lime slurry to pH 7.0 (ml/g lime)
Original lime	35.1	7.8
Regenerated lime	25.0	5.84

However, the DNB wastewater is highly alkaline and this alkalinity may compensate to some extent for the reduction of the neutralization capacity of the regenerated lime. Since the weight of the regenerated lime is about 1.4 times that of the original lime, the total neutralization potential of the regenerated lime is greater than the equivalent quantity of original lime.

The acidic wastewater with which the re-usability of the regenerated lime was studied is generated in the manufacture of *meta*-aminophenol (MAP) from the same industry. (It is highly acidic and is biodegradable. However, it has to be neutralised prior to biological treatment. About 2 tonne/d of fresh lime is required for this purpose.) Some other acidic wastewaters are

also released from the same industry and about 4–5 tonne/d of fresh lime is used for neutralization of all the acidic wastewaters. DNB wastewater treatment by the present method generates about 5–7 tonne/d of re-usable lime which can easily substitute the fresh lime requirement, thereby resulting in a considerable savings on treatment for the industry, aside from saving the cost of treatment and disposal of DNB wastewater itself.

A schematic flowsheet for the integrated treatment of DNB and MAP plant wastewaters as described above is shown in Fig. 1. The treatment scheme was studied with additional batches of DNB wastewater (5 sets of samples) and the results indicated that the treatment scheme is consistent. The volume of MAP acid waste required to neutralize 1 g of regenerated lime ranged around 5.83 ± 0.28 ml.

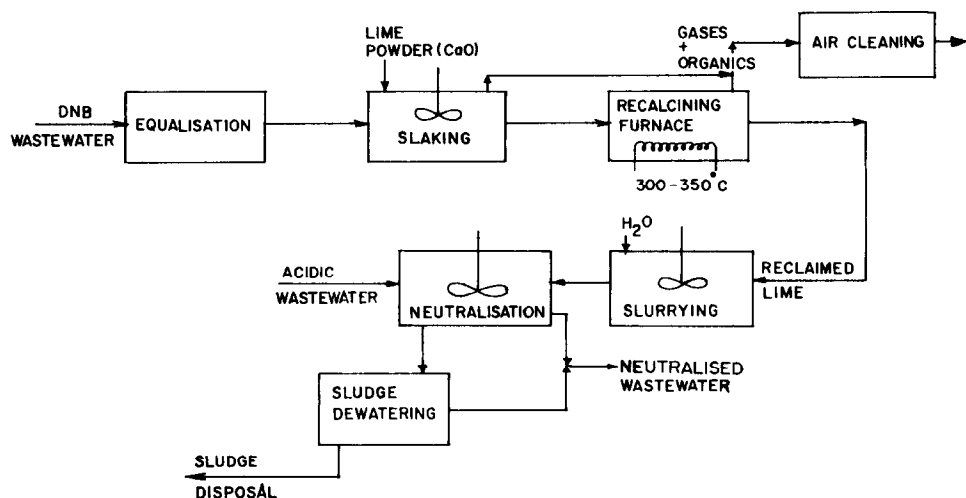


Fig. 1. Schematic flow sheet for treatment of DNB wastewater with lime.

Conclusion

The present studies show that solid phase transformation could offer an effective method of treatment of DNB wastewater. The basic advantages of this method of treatment would be lower requirements of energy and material. The results of the laboratory studies need to be confirmed by pilot plant studies with special reference to probable air pollution during slaking and muffling. However, due to the alkaline nature of the material, air pollutants like SO_x and NO_x may not arise as they would be fixed by lime during muffling. It should be possible to apply this method to the treatment of other difficult-to-degrade and toxic wastewaters having a small volume.

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