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Practical remediation of 3-nitro-1,2,4-triazol-5-one wastewater

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Limiting environmental impact is a top priority for the chemical industry, and manufacturing practices need to be well controlled to avoid any potential contamination. In order to reduce waste streams during the processing of 3-nitro-1,2,4-triazol-5-one (NTO), potentially evironmental hazardous at concentrations of 1 g/l , we investigated the potential remediation and recycling of water using a wide range of commercial sorption media. We studied the effect of experimental conditions, including flow rate, initial contaminant concentration and temperature. This led to the selection of Amberlyst A26 OH in a batch process and Activated Carbon in continuous flow, as the most effective sorption methods. Using high performance liquid chromatography photodiode array detection (HPLC-PDA), NTO was quantified from solutions, before and after remediation, showing a complete removal from a 10 g/l NTO solution. Our purification method therefore appears to be suitable for the remediation of NTO-contaminated wastewater.

1. Introduction

A key target in energetic materials chemistry is the replacement of explosives whose response to accidental ignition is detonation. The energetic material 3-Nitro-1,2,4-triazol-5-one (NTO) (Figure 1) exhibits similar performance to the well-known high explosive N,N',N''-trinitro-1,3,5-triazacyclohexane (RDX, Table 1) but has greater resilience to physical insults (such as heat, impact and friction), does not readily transition to detonation during accidental ignition and therefore fulfills the required safety parameters of an Insensitive Munitions (IM) formulation. These properties have resulted in the development of several NTO-based formulations, including IMX-101, IMX-104 and PAX-48 of which, many will be subject to industrial-scale manufacture.[1–5]

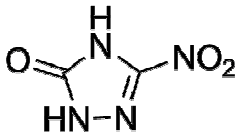


Figure 1: Structure of NTO.

However, NTO is unusual among explosives in that it is highly soluble in water (1.28 g/100 ml at 19 °C)[1] and industrial wastewater produced during the manufacture and processing of its formulations can therefore contain up to 10-15 kg of dissolved NTO in every 1000 l.[6] Recent reports on the toxicity of aqueous NTO on *Ceriodaphnia dubia*, northern leopard frog and rat, cite toxic effects when concentrations reach and exceed the range of 1 kg/1000 l, approximately one tenth of the maximum aqueous concentration.[7-9] Remediation of the effluent stream is therefore necessary to remove this potentially harmful explosive from solution and reduce the risk of environmental contamination.

Table 1. Comparative performance of NTO and RDX.

	NTO	RDX
Velocity of detonation (m/s)[3]	8510	8850
Crystal density at 20°C (g/cm^3)[10]	1.93	1.82
Decomposition temperature (°C)[10]	273	213
GAP test (number of cards)[3]	260	310
30 kg hammer drop: no-reaction height (m)[3]	>4	1
Friction sensitivity (N)[3]	0% at 353 N	133 N

Due to its high solubility, previous articles have suggested "carbon scrubbers" to be inefficient in removing NTO from aqueous solutions, opting instead for electrochemical remediation.[11,12] However, sorption technology is widely used for the treatment of water[13] and has also been explored for the removal of explosives[14] as a simple, rapid and cost-effective method for wastewater treatment. The work presented in this study illustrates that the potentially costly and environmentally hazardous contamination of wastewater with NTO may be remediated through the application of easy-to-use and cost-effective sorption media such as activated carbon (AC).

The effectiveness of sorption for the removal of NTO was explored in a continuous fixed-bed column and in a fluidised batch process using a variety of sorption media investigated. These included, AC, ion exchange resins (Amberlyst A26 (A26) in particular), and several grades of silica and alumina.

2. Materials and methods

2.1. Materials

Aqueous NTO stock solutions were prepared, from material synthesised at Cranfield University,[15] at a concentration of 1 g/100 ml (10,000 ppm) by sonication. The purity of the NTO and the concentration of the

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prepared solutions were validated by HPLC-PDA using a certified reference sample of NTO (AccuStandard).

Formic acid (Fisher, analytical reagent grade), acetonitrile (Fisher, HPLC gradient grade), activated carbon (Fluka, DARCO®, ~100 mesh), Amberlyst A26 OH (Aldrich), basic alumina (Fluka, activated, basic, Brockmann I), neutral alumina (Fluka, type WN-6, neutral, activity grade super I), Celite® S (Fluka) and silica gel (Aldrich, Davisil grade 633, 60 Å, 200-425 mesh and 40 Å, 70-230 mesh) were procured from Sigma-Aldrich. High purity water, prepared using the Millipore Milli Q plus purification system (18.2 MΩ.cm at 25 °C), was used for all experiments.

Acid-washed silica was prepared by passing 36% HCl through 60 Å silica, followed by rinsing with water and oven drying at 100 °C for 24 h until constant mass.

2.2. Experimental procedures

2.2.1. Fixed-bed column (continuous process)

The fixed-bed columns (Figure 2) were prepared in 10 ml BD Discardit™ II syringes and were driven using a KD Scientific 100 Legacy Syringe Pump.

Table 2. Experimental conditions of adsorption experiments.

Study parameters	Fixed bed column		Fluidised bed	
	Baseline condition	Variable	Baseline condition	Variable
Sorbent	AC, A26	A26, AC, BA, NA, 60 Å, 40 Å, AWS, C	A26	A26, AC, BA, NA, 60 Å, 40 Å, AWS, C
Flow rate (ml/h)	60	15, 30, 60	N/A	N/A
Volume of sorbent (ml)	1	0.5, 1, 1.5, 2, 2.5	1	0.2, 0.5, 0.6, 0.7, 0.8, 1
NTO concentration (g/100 ml)	1	0.1, 0.25, 0.5, 1	1	N/A
Temperature (°C)	20	N/A	20	10, 20, 30, 40
Stirring rate (rpm)	N/A	N/A	100	100, 200, 400

The baseline conditions, which were maintained in each experiment, were room temperature (approximately 20 °C) and that each experiment consisted of 10 ml of 1 g/100 ml aqueous NTO filtered through 1 ml of consolidated sorption medium at a constant flow rate of 60 ml/min. The variables which were investigated for their effect on the efficiency of sorption were the flow rate, the volume of sorption media and the initial NTO concentration (Table 2).

2.2.2. Fluidised bed (batch process).

The baseline conditions for the fluidised bed experiments were that a suspension of 0.4 g of sorption medium in 8 ml of 1 g/100 ml NTO stock solution was stirred at 100 rpm at room temperature (~20 °C) within a 20 ml scintillation vial equipped with a 1 cm magnetic flea. The variables investigated for their effect on the efficiency of sorption were temperature, the quantity of sorption medium, and the stirring rate (Table 2).

2.3. Media screening

As the basis for comparative assessment, 1 ml of each sorption medium per 10 ml of aqueous NTO at a concentration of 1 g/100 ml was used (Table 3).

Table 3. Quantity of medium used under baseline conditions.

	Mass of 1 ml of medium (g)
Amberlyst A26 OH (A26)	0.5
Activated carbon (AC)	0.3
Basic alumina (BA)	1.0
Neutral alumina (NA)	1.0
Silica gel (60 Å)	0.6
Silica gel (40 Å)	0.7
Acid washed silica (AWS)	0.5
Celite (C)	0.2

2.4. Analytical methods

Reversed phase HPLC-PDA analysis was performed using a Waters Alliance 2695 separation module, a Waters 996 photodiode array detector and Kinetex® 2.6 µm phenyl-hexyl 100 Å 100 x 4.6 mm column. The column was conditioned to 30 °C with a mobile phase comprising 50% acetonitrile and 50% of 0.1% formic acid/water at a flow rate of 1.5 ml/min. The injection volume was 10 µl and the run time was 1.6 min. NTO was detected at 315 nm[1] with a retention time of 0.73 min. The limit of detection (LoD) was calculated as 1.7 ppm (1.7×10^{-4} g/ 100 ml) and the

limit of quantification (LoQ) as 5.1 ppm (5.1 x 10^{-4} g/ 100 ml).

3. Results and discussion

Sorption media were selected for their recognized properties in chromatography, purification and remediation.[16-18] The efficiencies of the media under the baseline conditions were investigated and are presented in Figure 2.

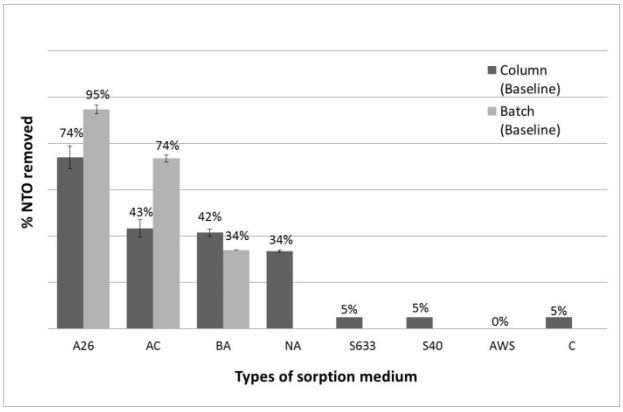


Figure 2. Efficiency of NTO removal under baseline conditions.

The two most effective sorption media studied were A26 and AC, and these were selected for more detailed analysis. The influence of different operating parameters (Table 3) on sorption efficiency was investigated.

3.1. Column/continuous process

3.1.1. Effect of flow rate.

Flow rates of 15, 30 and 60 ml/h were tested, while all other parameters remained at baseline conditions. In the A26 and the AC system, under the conditions studied, increasing the flow rate did not have an appreciable effect on NTO removal (Table 4). It is expected that increasing the flow rate would eventually lead to a reduction in contact time between the aqueous NTO and the sorption medium leading to a reduction in the percentage of NTO removed. A similar trend was reported when using AC for the adsorption of TNT.[19] This result confirmed that under the conditions used, the baseline flow rate of 60 ml/h was appropriate.

Table 4. Effect of flow rate on the removal of NTO using A26 and AC.

Flow Rate (ml/mins)	AC	A26
	% NTO Removed	% NTO Removed
60	43	74
30	43	74
15	35	69
10	57	53

3.1.2. Effect of varying the quantity of sorbent.

The quantity of the sorption medium was varied while all other parameters remained at baseline conditions.

Table 5. Effect of sorbent volume on the removal of NTO using A26 and AC.

Amount of sorbent (ml)	AC	A26
	% NTO Removed	% NTO Removed
0.5		40
1	43	74
1.5	72	83
2	90	100
2.5	100	
4		100

In both systems, the amount of NTO removed increased with the amount of sorbent as expected, reaching 100% sorption with 2.5 ml of AC and 2 ml of A26 (Table 5). From extrapolation of the data, it was estimated that 2.2 ml (6.6% w/v) of AC would be the minimum quantity required for the complete remediation of 10 ml of 1 g/100 ml NTO solution however no data was collected for this volume of the sorbent.

3.1.3. Effect of initial concentration.

Solutions of various NTO concentrations (0.1, 0.25, 0.5 and 1 g/100 ml) were purified under the column baseline conditions.

Table 6. Effect of the initial NTO concentration on its removal using A26 and AC.

Initial [NTO] (g/100 ml)	AC	A26
	% NTO Removed	% NTO Removed
1	43	74
0.5	57	86
0.25	67	100
0.1	99	98

Baseline data suggested that a volume of 1 ml of A26 would be sufficient to remediate 10 ml of the lower concentration solutions. However, a non-linear relationship was observed as only solutions below 0.25 g/100 ml were decontaminated. Similar results were obtained for AC (Table 6).

3.2. Batch process

Due to the fine particle size of AC, during the sampling in the batch process, removal of variable quantities of sorbent was unavoidable, leading to inaccuracies in the results. It was therefore decided to solely study A26 from this point onwards.

3.2.1. Effect of temperature.

The temperature of the system was varied from 10 °C to 40 °C while all other parameters were maintained at baseline levels.

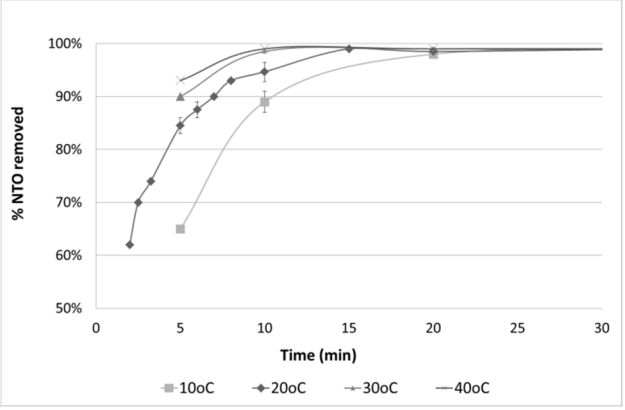


Figure 3. Effect of temperature on the removal of NTO by A26.

As anticipated, the rate of ion exchange increased at higher temperatures (Figure 3). Ion exchange is a form of chemisorption; therefore, a specific activation energy must be overcome and a higher reaction temperature is favourable.[19] Although all of the experiments achieved complete remediation of the NTO solution, the sorption process took twice as long to complete at 10 °C compared to the same reaction at 30 °C or 40 °C.

3.2.2. *Effect of varying the quantity of sorbent.*

The quantity of A26 was varied between 1% and 5% w/v while keeping all other parameters at baseline conditions.

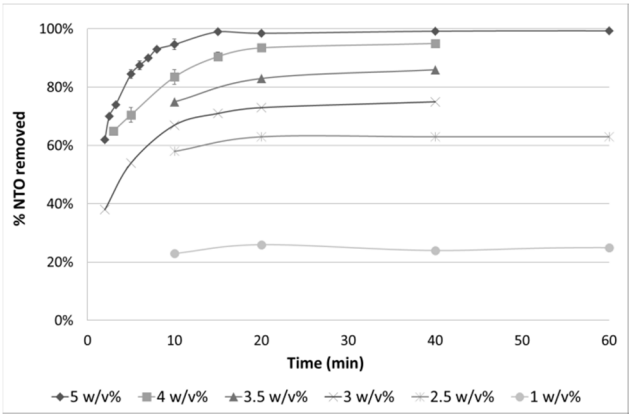


Figure 4. Effect of the quantity of adsorbent on NTO removal.

As anticipated, the amount of NTO removed increased with the amount of A26 used as this would result in an increase in the number of available ion-exchange sites (Figure 4). Additionally it was observed that all of the sorption processes were complete at 40 min. Furthermore, a linear relationship was observed between the amount of A26 and the quantity of NTO removed after 40 min (Figure 5).

Extrapolating from these data, 4.1% w/v would be the minimum amount of A26 necessary to achieve the complete remediation of a 1 g/100 ml solution of NTO.

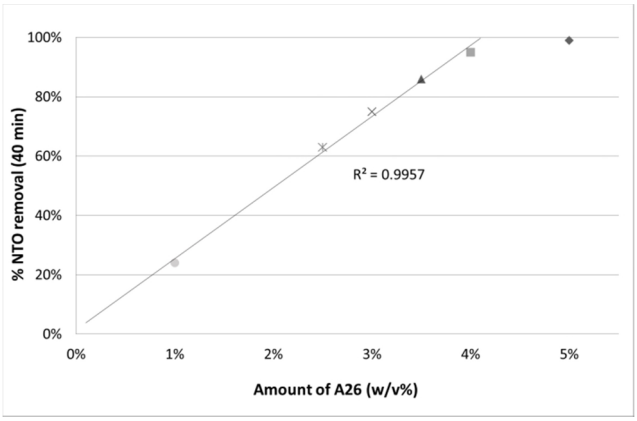


Figure 5. Amount of NTO removed versus quantity of A26 at equilibrium.

3.2.3. *Effect of the stirring rate.*

The stirring rate in the batch process was increased from 100 rpm to 200 rpm and 400 rpm while all other parameters were maintained under baseline conditions.

Table 7. Effect of different stirring rates on the removal of NTO.

Time (mins)	100 rpm	200 rpm	400 rpm
	% NTO Removed	% NTO Removed	% NTO Removed
2	62	75	70
5	85	88	89
10	95	99	98
20	99	99	99
40	99	99	99

The rate of NTO removal increased with stirring rate as shown in Table 7. Visual inspection of the fluidised batch procedure showed that a stirring rate of 200 rpm was sufficient to disperse the A26 beads throughout the aqueous suspension.

4. Conclusion

We have presented the effective use of AC and A26 for the complete remediation of heavily contaminated NTO aqueous solutions. These solutions, with initial concentrations approximately ten times that of the reported toxicity range for aqueous NTO, were purified of NTO using AC and A26 as sorption media.[7-9] While AC has been previously dismissed, it is suggested that the particle size and surface area of the grade of material used in this work is key to its effectiveness.

Remediation using column and batch processes was studied for a variety of media including AC, A26, alumina and silica. AC and A26 showed the greatest potential for NTO removal and were selected for optimisation of the process parameters. The combined data suggested that the quantity of sorbent was the most influential variable on NTO remediation in both the batch and column-based processes. In the fixed-bed columns, a flow rate of 30–60 ml/h with 2 ml (10% w/v) of A26 achieved the complete remediation of a 1 g/100 ml solution of NTO; while the

effect of flow rate was negligible when using AC and 2.5 ml (7.5% w/v) of sorbent was shown to be the minimum quantity required for the same impact. For the A26 batch process, the more efficient contact between the NTO solution and the medium allowed complete remediation to be achieved with only 4.1% w/v of resin.

Although further work will be required to translate the laboratory results presented here to an industrial scale, it is hoped that this may contribute towards an environmentally friendly manufacturing process for NTO-containing formulations. For a truly green process, we have also studied the possibility of regenerating the sorbents and re-using the NTO as well as an easy colourimetric test to evaluate the NTO concentration in aqueous solutions; these results will be presented elsewhere.[20]

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Keywords: Remediation • Wastewater • NTO • Sorption • Explosive

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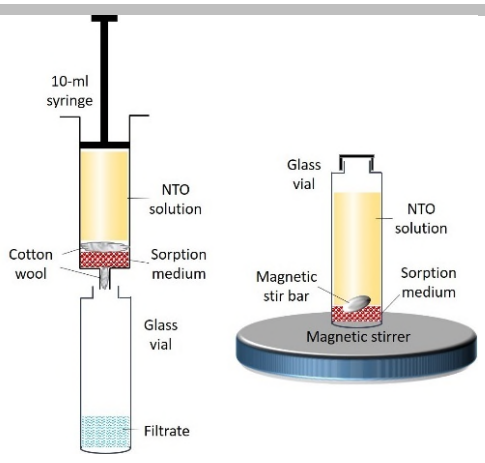
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