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ABATEMENT OF NITROBODIES IN AQUEOUS EFFLUENTS FROM TNT PRODUCTION AND FINISHING PLANTS

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In the manufacturing of TNT, there are three waste water streams that must be processed in order to comply with federal and local government regulations. These are: (1) "red" water which is produced by the sellite (sodium sulfite) treatment; (2) "pink" water which is produced when the partially purified TNT is washed following the sellite treatment; and (3) wash waters from the TNT finishing process. While all these polluted streams are being investigated at the U. S. Army Natick Laboratories, this paper will cover results obtained with wash waters from TNT finishing processes.

The finishing plant is the final step in the TNT manufacturing process; consequently, the principal pollutant of these wash waters is α TNT. These waters when leaving the finishing plant are acidic (pH 3-4) and colorless. As this effluent flows to the equalization basin, it may be exposed to sunlight, and it acquires a "pink-amber" color. From the equalization basin the effluent flows into a neutralization tank where Na_2CO_3 is added until a pH 6 is achieved. This treated stream is directed into a settling tank, and from there it flows into a second neutralization tank where additional Na_2CO_3 is added to adjust the pH to 7.0. The neutralized stream containing nitrobodies is then directed into a second settling tank and the overflow of this tank is diluted approximately 8-fold with clean process water to reduce the concentration of nitrobodies and color producing compounds, and then it is discharged into waterways or rivers. This treatment scheme is shown in Figure 1.

The concentration of α TNT and/or color producing compounds dis-

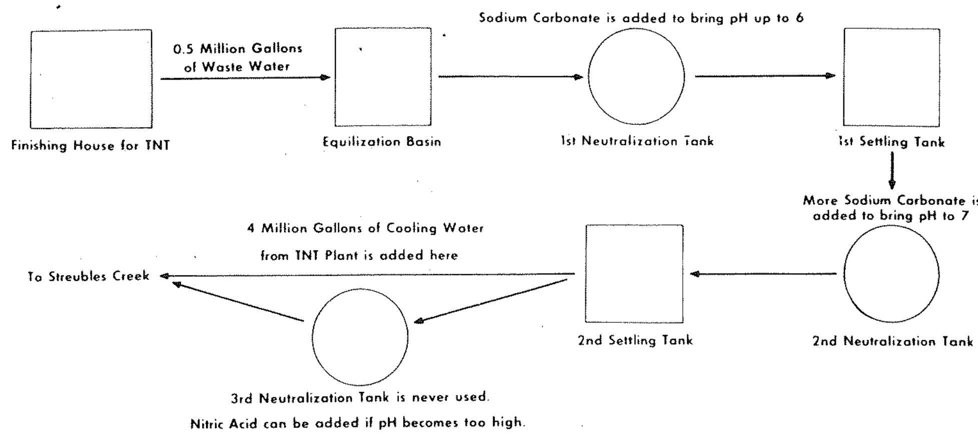

Fig. 1 TNT FINISHING PLANT WASH WATER TREATMENT PROCESS

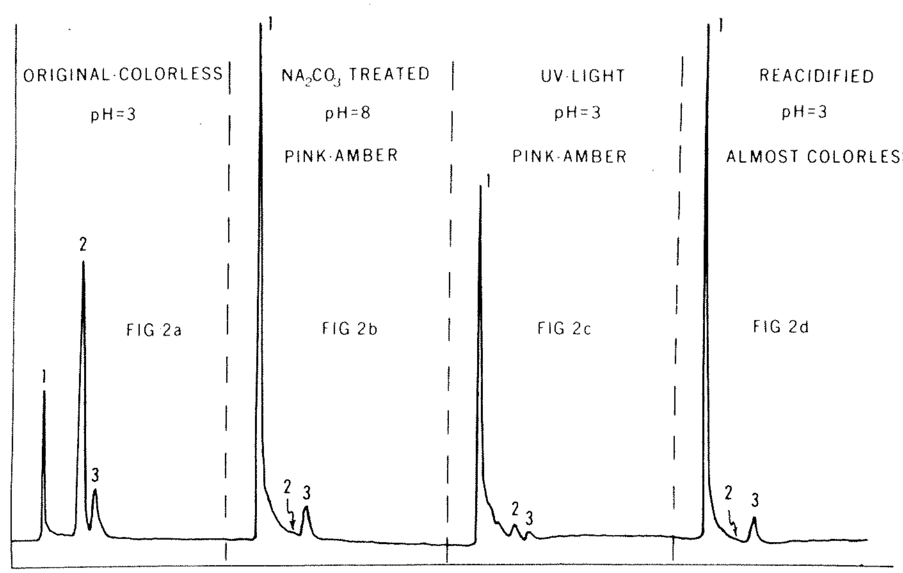

FIG 2 TNT-FINISHING PLANT WASH WATER CHROMATOGRAM

charged into waterways must be limited to less than 2.5 ppm. It has been found that α TNT at concentration of 2.5 ppm is toxic to fish and other aquatic life.

To overcome both the red discoloration imparted by this "pink" water to the receiving river and reduce the concentration of the nitrobodies discharged, to levels below those found toxic to living organisms, two approaches are being investigated at the U. S. Army Natick Labs. These are: (1) direct absorption on polymeric resins and (2) biodegradation processes. This paper is limited to results obtained with a resin adsorbent that is a copolymer of styrene and divinylbenzene. This material is a commercial product produced by the Rohm and Haas Co., and is sold under the trade name of Amberlite XAD-2. It is supplied in the form of white insoluble beads, and is designed for use in columns or in batch operations for the adsorption of water soluble organic substances. The manufacturer of the resin claims that the adsorption on this resin is dependent largely on Van der Waals' forces, consequently, both the adsorption and regeneration of the resin can be controlled by changing the hydrophobic/hydrophilic balance of the molecules adsorbed.

Initially this resin was considered as a potential media to concentrate the nitrobodies in the "pink" water for analytical purposes. However, results of preliminary experiments proved so promising that it was decided to investigate XAD-2 as a potential adsorbent bed to clean the total effluent stream from the α TNT finishing process.

The colorless wash water after leaving the α TNT finishing plant is neutralized, usually with Na_2CO_3, and turns a "pink-amber" color. This color can result also from exposure to sunlight (UV) prior to pH adjustment with Na_2CO_3. The color producing compounds that are formed when the acidity of the waste stream is shifted from a low pH (3-4) to a pH (6-7), have been postulated to be "Meisenheimer complexes" that are formed through reactions of the α TNT.

Figure 2 is a series of high speed liquid chromatograms made for the separation of the various constituents present in the polluted wash water effluent from the α TNT finishing house of an actual ammunition plant.

Chromatogram 2a was obtained from a sample of wash water leaving the α TNT finishing house prior to any treatment. This water sample was acidic (pH-3) and colorless. Chromatogram 2b was obtained from a sample of the same wash water after adjusting its pH to 8. This water sample turned to a "pink-amber" color when treated with Na_2CO_3. Chromatogram 2c was obtained from a sample of the same wash water, however, the "pink-amber" color for this sample was produced by exposure to UV light while its acidity was maintained constant to that of the original sample (pH-3). Chromatogram 2d was obtained with the same sample used to obtain chromatogram 2b except that the sample had been reacidified to the original acidity (pH-3) and the "pink-amber" color removed. It should be noted that while the sample reverted to its original color, the chromatogram shows that the color-causing compound did not change back to α TNT. In other words, the chemical change is irreversible. Peak 2 on these chromatograms represents α TNT in the waste stream. Peaks 1 and 3 represent other polluting constituents that, as yet, have not been identified at the Natick Laboratories. These data confirm that the "pink-amber" color is produced by structural and chemical changes of α TNT in the waste stream, and that the change is not reversible by altering the pH. It has been reported by other researchers that these color producing constituents when adsorbed on activated carbon, have a tendency to reduce its adsorbing effectiveness. Consequently, it is desirable to remove all pollutants from the effluent stream prior to any color formation.

Chromatograms 2a and 2c in Figure 2 indicate that nearly all the α TNT in the original sample undergoes reaction to form color producing constituents. This is confirmed by the data shown in Figure 3. The data shown in Figure 3 were obtained with an aqueous solution of pure α TNT containing 100 ppm of α TNT. Figure 3a shows the concentration of α TNT present in solution, and Figure 3b shows that nearly all the α TNT has been converted into color producing compounds when the original colorless solution was made alkaline with Na_2CO_3. Integration of the peaks shown in Figure 3a and 3b shows that 95% of the α TNT present in the original solution has been transformed into other compounds.

To check the feasibility of using XAD-2 for the elimination or abatement of nitrobodies in acid wash waters leaving the TNT finishing house of a typical ammunition production plant, samples of colorless wash waters from the TNT finishing house of an actual munition plant were passed through an XAD-2 packed column and the eluant analyzed for pollutants by high speed liquid chromatography. The acidic eluant was found clear of α TNT, and upon neutralization did not develop the characteristic "pink-amber" color that is normally produced, when α TNT is present in the solution.

Activated carbon has been used extensively for the adsorption of organic compounds including TNT present in waste water streams. Filtrasorb-400 which is one form of activated carbon is now being used to remove α TNT and RDX in wash waters from munitions loading and packing (LP) operations. At one loading and packing site, two columns packed with Filtrasorb-400 are operated in series, and the effluent of the first column is monitored to determine when the packed bed must be replaced. The effluent is normally analyzed for α TNT by a colormetric technique. The standard operating procedure is that when the effluent from the first packed bed shows a concentration of 2 ppm, the column is repacked with new carbon and the used carbon is incinerated. No attempt is being made for its regeneration.

Since XAD-2 was found to be easily regenerated, studies were conducted to compare the adsorption effectiveness and regeneration characteristics of XAD-2 and Filtrasorb-400 after both have been used to adsorb pollutants present in "pink" water from α TNT finishing plants.

Two one centimeter diameter glass columns were set up holding equal volumes of XAD-2 and Filtrasorb-400. Wash waters obtained from an actual ammunition plant TNT finishing operation were passed through both columns, and the eluants from both columns were analyzed for eluted α TNT. The concentration of α TNT in the wash waters used was 34 ppm. The flow rate through both columns was maintained at 250 ml/hr. The properties of XAD-2 and Filtrasorb-400 are listed in Table 1.

Table 1 Properties Of XAD-2 And Filtrasorb-400

Properties	Amberlite XAD-2	Filtrasorb-400
Surface Area, $\frac{m^2}{gr.}$	330	1125
Bulk Density, $\frac{lbs}{ft^3}$	42	25
Mean Particle Diameter, mm.	0.53	1.00

The concentration of α TNT eluted from each column is listed in Table 2.

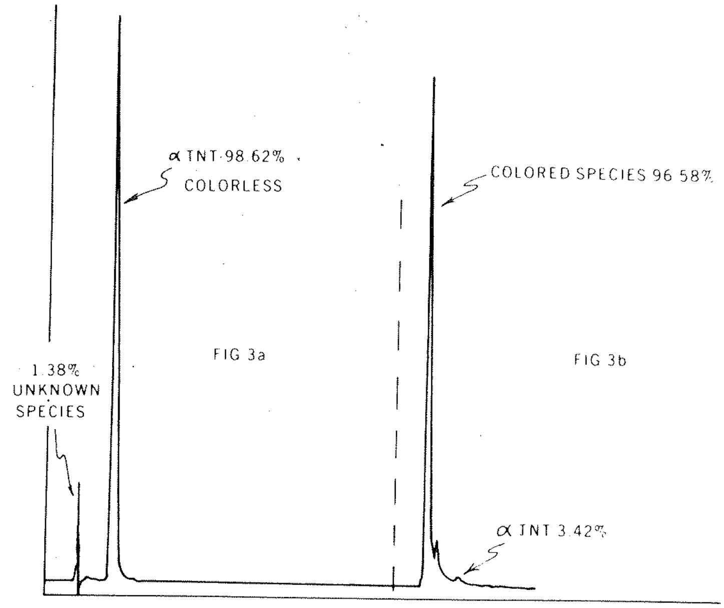

FIG 3 CHROMATOGRAM OF α TNT CONVERSION TO COLORED SPECIES

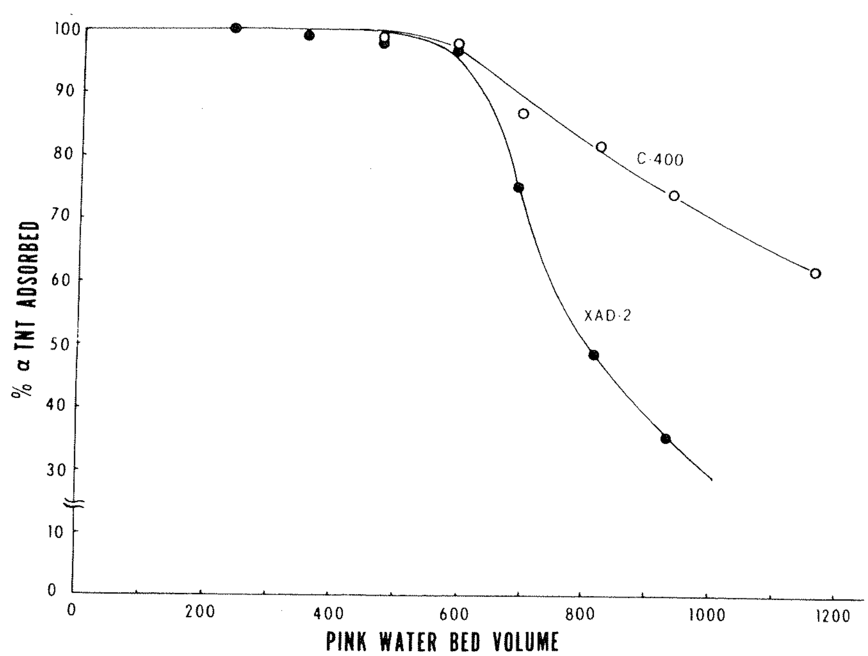

FIG 4 COLUMN ADSORPTION EFFICIENCY

Table 2 Eluted α TNT From XAD-2 And Filtrasorb-400 Columns

Influent α TNT - 34 ppm		Effluent α TNT - ppm	
Liters	Equiv. Adsorb. Bed Volumes	XAD-2	Filtrasorb-400
1	116	0.0	0.0
2	232	0.0	0.0
3	349	<0.5	<0.5
4	465	0.5	0.5
5	581	1.5	1.0
6	697	8.3	4.5
7	814	17.4	6.2
8	930	22.0	8.6
10	1162		12.8

Table 2 indicates that the breakthrough volume is the same for both the XAD-2 resin and the carbon column. The first breakthrough occurred after approximately 349 bed volumes of effluent. The concentration of α TNT leaking through at this stage was less than 0.5 ppm.

The table further shows that XAD-2 is as efficient as the Filtrasorb-400 up to almost 600 bed volumes. At this point the leakage endpoint of both adsorbents has exceeded allowable α TNT limits. Since the allowable limit of α TNT in disposed waters is expected not to exceed 0.5 ppm, both column materials are effective to meet the standards at a throughput equivalent to approximately 465 bed volumes.

To compare the adsorption effectiveness of XAD-2 and Filtrasorb-400 for pollutants present in the wash water, the amount of α TNT adsorbed compared to the total TNT present in the influent processed through each column was plotted as a function of the total flow through the columns. This is shown in Figure 4.

Figure 4 shows that at throughputs exceeding 600 equivalent bed volumes, the percentage of α TNT and other pollutants removed by the XAD-2 column is much less than that removed by Filtrasorb-400.

This is understandable since the fraction of active sites remaining for adsorption on Filtrasorb-400 would be relatively large

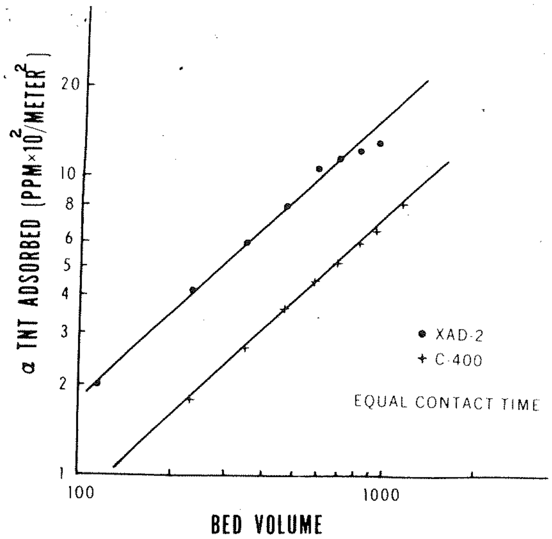

FIG 5 COLUMN ADSORPTION EFFICIENCY log-log

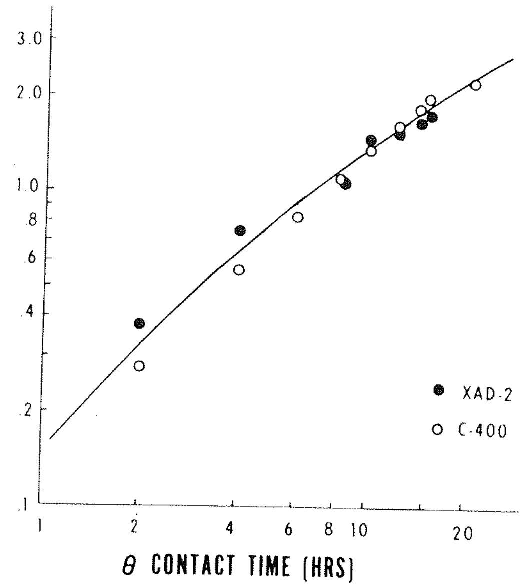

FIG 6 ADSORPTION RATE

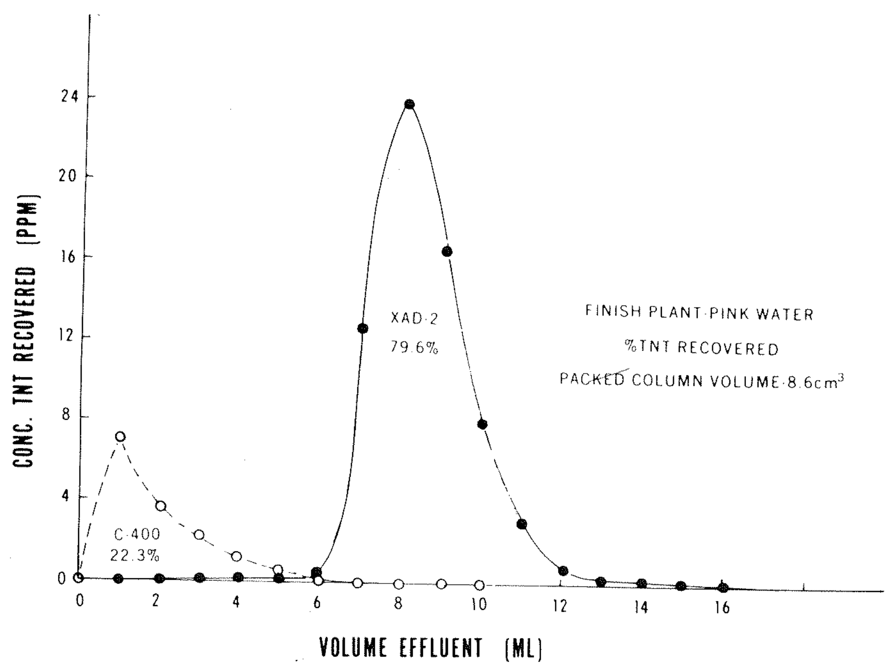

FIG 7 REGENERATION CURVES

while the active surface of the XAD-2 would be nearly saturated and not available for adsorption until regenerated. It should be noted that the initial active surface per gram of Filtrasorb-400 is 2.25 times that of XAD-2.

Because of the significant difference in active surface areas per unit weight of Filtrasorb-400 and XAD-2, it was of interest to compare the adsorption effectiveness of the two adsorbents on a unit surface basis. Figure 5 shows the quantity of α TNT adsorbed per square meter of surface for both adsorbents. These data show that for fixed throughputs of wash water containing 34 ppm of α TNT as contaminant, the XAD-2 appears to have better adsorbing characteristics than Filtrasorb-400.

One other parameter which should be factored into the evaluation of adsorption systems is the contact time between the material to be adsorbed and the active surfaces.

Figure 6 shows our experimental results normalized to reflect the adsorption rate of α TNT in parts per million as a function of contact time with the adsorbent surface in hours. These data indicate that the surface activity of Filtrasorb-400 and XAD-2 for α TNT are comparable.

In the selection of adsorbents to remove nitrobodies in polluted streams discharged from munitions manufacturing facilities, one must give serious consideration to techniques for disposing of the adsorbed pollutants and regeneration of the spent adsorbent bed. As indicated earlier, regeneration of XAD-2 has been found relatively simple. Studies at the Natick Laboratories show that acetone can easily strip the nitrobodies adsorbed from "pink" water quite rapidly.

To compare the regeneration characteristics of XAD-2 and Filtrasorb-400, fixed quantities of "pink" water containing 34 ppm α TNT and other color constituents were passed through equal bed volumes of Filtrasorb-400 and XAD-2. The adsorption cycle was followed by a stripping cycle in which acetone was used to regenerate each column. Figure 7 shows the percent recovery of the adsorbed nitrobodies as measured by the total α TNT in the eluant from each column.

It should be noted that the α TNT recovered from the XAD-2 column by flushing the adsorbent with approximately two bed volumes of acetone is approximately four times greater than the amount recovered from the Filtrasorb-400 column.

While the data thus far appear quite favorable, XAD-2 does allow some of the color components to pass through but Filtrasorb-400 shows that all color can be removed from the influent stream. Consequently, if the wash water from the α TNT finishing processes has changed color, it would be advisable to use a combination adsorption system in which XAD-2 can be used to remove nearly all pollutants in the effluent stream on a gross scale, and then finish the cleaning of the stream by removing the remaining color that may pass through the XAD-2 with activated carbon.

Conclusion

In summary, the results of studies with XAD-2 and Filtrasorb-400 as potential adsorbents for nitrobodies in wash waters from α TNT finishing processes at ammunition production plants and loading and packing plants show that:

1. XAD-2 is an effective adsorbent for nitrobodies containing primarily α TNT. This is particularly true for wash waters that have not been neutralized, and have not acquired the "pink-amber" color that results from structural changes of α TNT in the water.

2. The adsorption effectiveness of XAD-2 is comparable to that of Filtrasorb-400 for influent throughputs equivalent to approximately 600 adsorbent bed volumes.

3. Chemical regeneration of XAD-2 saturated with α TNT can be effectively accomplished with acetone. Chemical regeneration of Filtrasorb-400 has not been satisfactorily accomplished.

4. To effectively clean up the nitrobodies in wash waters from α TNT finishing processes and load and pack operations, XAD-2 should be used to adsorb the major fraction of nitrobodies and color producing constituents in the stream. The effluent of the XAD-2 column should then be passed through a polishing activated carbon bed to pick up any residual color that may pass through the XAD-2 column.