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2 **Removal of munition constituents in stormwater runoff: Screening of native and**
3 **cationized cellulosic sorbents for removal of insensitive munition constituents NTO,**
4 **DNAN, and NQ, and legacy munition constituents HMX, RDX, TNT, and perchlorate.**

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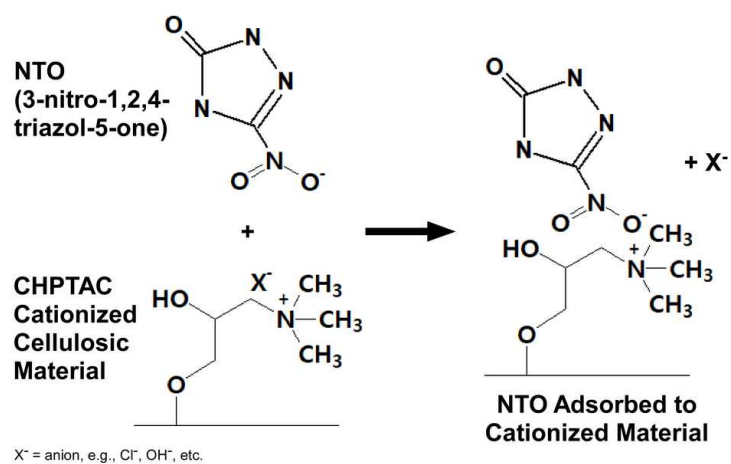
ABSTRACT

Technologies are needed to address contamination with energetic compounds at military installations. This research developed and evaluated novel and sustainable materials that can be used to remove munition constituents (MC) from stormwater runoff. Initial work focused on 3-nitro-1,2,4-triazol-5-one (NTO), as it is both highly soluble and ionized at environmentally relevant pH values. Screening cellulosic materials indicated that cationized (CAT) versions of pine shavings (pine, henceforth) and burlap (jute) demonstrated >70% removal of NTO from artificial surface runoff. CAT materials also demonstrated >90% removal of the anionic propellant perchlorate. NTO removal (~80%) by CAT pine was similar across initial pH values from 4 to 8.5 S.U. An inverse relationship was observed between NTO removal and the concentration of the major anions chloride, nitrate, and sulfate due to competition for anion binding sites. Sorption isotherms were performed using a mixture of the three primary legacy explosives (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexahydro-1,3,5-trinitro-s-triazine (RDX), 2,4,6-trinitrotoluene (TNT)), the three insensitive MC (nitroguanidine (NQ), NTO, 2,4-dinitroanisole (DNAN)), and perchlorate. Isotherm results indicated that effective removal of both legacy and insensitive MC would best be achieved using a mixture of peat moss plus one or more of the cationized cellulosic materials.

Keywords: 3-nitro-1,2,4-triazol-5-one (NTO), 2,4-dinitroanisole (DNAN), cationized cellulosic materials, perchlorate, RDX, surface runoff

49 TOC Art

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NTO
solution
only

+
Native
Cellulose

+
Cationized
Cellulose

51

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1. INTRODUCTION

Testing and training activities undertaken by the U.S. Department of Defense has resulted in contamination of soil and groundwater at military installations [1, 2]. The primary legacy explosives of concern include octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexahydro-1,3,5-trinitro-s-triazine (RDX), and 2,4,6-trinitrotoluene (TNT), as well as the energetic compound perchlorate. Additionally, several new explosive compounds are being phased in for use in insensitive munition (IM) formulations, including 3-nitro-1,2,4-triazol-5-one (NTO), 2,4-dinitroanisole (DNAN), and nitroguanidine (NQ). Soil concentrations of the legacy explosives range from the low $\mu\text{g/kg}$ range to the high mg/kg range [3], and include the presence of actual undetonated explosive residues [4]. Explosives concentrations in stormwater surface runoff have not been widely reported, but we have observed low $\mu\text{g/L}$ concentrations of HMX and RDX, and perchlorate up to more than 0.5 mg/L (unpublished data). As the IM are only now starting to come into wider use in testing and training, environmental concentration data are not available. Surface runoff concentrations are likely controlled by dissolution kinetics, total precipitation volume, and precipitation intensity, the latter controlling the entrainment and transport of small explosive residues as an undissolved solid phase. Previous work in our laboratory demonstrated dissolution and further disintegration of explosives of Composition B detonation residues under simulated precipitation, with average concentrations of approximately 0.5, 4, and 10 mg/L of HMX, RDX, and TNT in the resulting solution [5], highlighting that these compounds have a reasonable pathway as soil contaminants into surface runoff.

While the fate, transport, and toxicity of the legacy compounds have undergone considerable study [3, 6, 7], similar studies with the IM constituents have only begun relatively recently [8-11]. Although the IM constituents provide a higher level of safety for DoD personnel, they are also more water-soluble than the legacy explosives. This could result in lower retention in surface soil and higher transport to groundwater, as well as a higher probability of significantly higher concentrations in surface runoff during storm events. Additionally, the pK_a of NTO (3.7) indicates it will be negatively charged at environmentally relevant pH levels, and its low estimated K_{ow} (0.4-1.0) and K_d (avg. 0.6-1.5 across eight soils) values [9] indicate that hydrophobic sorption will likely not be effective. Rather, approaches more akin to anion exchange may be needed.

This research was undertaken to develop and evaluate sorbents and/or sorbent mixtures that effectively remove dissolved explosive and energetic compounds, with a focus on identifying materials that would be effective in remediation technologies for contaminated surface runoff. A range of inexpensive and sustainable materials were identified as effective sorbents, including cationized derivatives of several cellulosic biopolymers.

2. MATERIALS AND METHODS

2.1. Chemicals and media.

TNT, RDX, HMX, and NTO were purchased from Accurate Energetic Systems LLC (McEwen, TN). DNAN, NQ, and the cationizing agent 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All other chemicals were reagent grade or higher.

An artificial surface runoff (ASR) used for this work was based on the analysis of the major anions and cations in stormwater collected from an east coast U.S. Navy facility, and consisted of (mg/L): Na₂SO₄, 16; MgCl₂•6H₂O, 10; CaCl₂•2H₂O, 10; KCl, 18; NaCl, 10; (NH₄)₂SO₄, 2; Ca(NO₃)₂•4H₂O, 1.5. The pH of ASR was adjusted to 6 standard units (S.U.) with 0.5 N HCl and NaOH, as needed.

The materials screened included *Sphagnum* peat moss, as well as native and cationized versions of: pine sawdust, pine shavings, aspen shavings, cotton linters, chitin, chitosan, burlap (landscaping grade), coconut coir, raw cotton, raw organic cotton, cleaned raw cotton, and cotton fabric. Commercially cationized fabrics were also examined: Inman Mills 207433-145 (Inman, SC); Tintoria Piana 25% and 55% cationized cotton (Cartersville GA).

2.2. Cationization.

The cationization process for the various materials was based on the method of Fu et al. (2013) [12]. The chemical reaction between CHPTAC and cellulosic materials is illustrated in Figure S1. For small batches (3-6 g), the material to be cationized was packed into a 60 ml polypropylene syringe barrel. For each gram of material, a solution was prepared comprised of 1.7 mL CHPTAC solution (60 wt% CHPTAC), 1.4 mL 10 N NaOH, and 3.6 mL laboratory grade purified H₂O. This equates to a CHPTAC concentration of 150 g/L (0.8 M) in 2.13 N NaOH. The material was thoroughly wetted, then the syringe plunger was inserted into the barrel, the syringe was inverted, and the wetted material was compressed to remove air bubbles. The luer outlet of the syringe was then capped and the mixture reacted at room temperature for 18-24 h. The cationized material was then removed from the syringe and rinsed with tap water, collecting the solids via vacuum filtration onto a 100 mesh

120 stainless steel screen. The material was then transferred to a large glass beaker on a stir
121 plate. Once the material was dispersed in the water, the pH was adjusted to approximately 6
122 with HCl. After vacuum filtration, the material was given a final rinse in laboratory grade
123 purified water. The washed cationized material was then air dried and stored in a plastic bag
124 until use. Larger batches (20+ g) were prepared similarly, except that nested polypropylene
125 beakers, which allowed the upper beaker to act as a plunger to compress the material to
126 remove air bubbles from the reaction prior to incubation.

127 The effect of different CHPTAC concentrations and replacing the water in the
128 cationization solution with a solvent (isopropyl alcohol (IPA), tetrahydrofuran (THF), or
129 tetraethylene glycol dimethyl ether (TG)) [13] on the effectiveness of the cationized material
130 for NTO removal was also examined.

132 2.3. Batch screening.

133 The initial focus of the screening was identification of potential sorbents for DNAN,
134 NTO, and NQ. Testing was done with ASR with all three compounds at an approximate
135 concentration of 20 mg/L. Concentrations of the explosives were selected to ensure
136 collection of accurate and reproducible analytical data even in the event of a high percentage
137 of removal of the analyte by the sorbents. The basic screening was performed by mixing 0.2
138 g (air dry) of each sorbent material with 20 ml of ASR spiked with the target compounds in
139 40 ml clear glass vials sealed with teflon lined septa. A minimum of duplicate vials were
140 shaken horizontally at 200 rpm at room temperature (20-22°C). Preliminary screening
141 indicated that NTO (and the other target compounds) were essentially at equilibrium after 4
142 hours (data not shown), but experiments were standardized at an incubation period of 18-24 h.

Aliquots (1 ml) were transferred to 1.5 ml polypropylene tubes, centrifuged for 3 minutes at 14,000 rpm, and 0.5 ml of the cleared supernatant was then mixed with 0.5 ml of methanol prior to HPLC analysis as described below. The final pH of the controls and the treatments were routinely measured.

Additionally, the competitive effects of higher and lower concentrations of the major anions, and the effects of the initial solution pH on the sorption of NTO were examined. For competing anion effects, several CAT materials were placed in solutions containing DNAN, NTO, and NQ, and 0.1X, 1X, and 10X of the normal ASR concentrations of Cl^- , NO_3^- , SO_4^{2-} , and sampled and analyzed as described above. To examine pH effects, CAT pine was combined with ASR containing NTO at initial pH values of ~3.8 (e.g., the pH of ASR with NTO without any pH adjustment), 4.5, 5.5, 6.5, 7.5, and 8.5 S.U. (adjusted with 0.5 N NaOH).

The removal of the insensitive MC by CAT pine, CAT burlap, and CAT cotton was also examined in actual runoff from the east coast U.S. Navy facility that the ASR was based on. The runoff was allowed to settle for approximately 30 minutes, then the overburden water was combined with NTO, DNAN, and NQ, and the pH was adjusted to ~6.1 S.U. using 0.5 N NaOH. Sample and analysis was performed as described above.

As peat moss was previously demonstrated to be an effective sorbent for the legacy explosives [14], and that it a useful bulk material for biofilter applications, peat moss was mixed with some of the CAT materials to examine the effects on the extent of NTO sorption. Peat moss was combined with the CAT materials at ratios (w:w) of 1:1, 2:1 and 3:1 (peat moss:CAT material). Additionally, the effects of water extractable compounds in peat moss equivalent to the 3:1 peat moss:CAT material ratio was examined. Briefly, a peat moss

extract was prepared by mixing peat moss with water for several hours, then passing the solution first through coffee filters to remove larger particles. The resulting solution was then passed through glass microfiber filters with pore sizes of 5, 2.7, 0.7 and finally 0.45 μm . For one treatment, the extract was combined with NTO, ASR components, and water, and the pH was brought to ~6 S.U. For a second treatment, NTO, ASR components, and water were combined and brought to pH 6, then the peat extract was added, resulting in a solution with an initial pH of ~4.3 S.U.

Follow-on multipoint isotherms were performed with peat moss, CAT pine, CAT burlap and CAT raw cotton done with ASR containing RDX, TNT, DNAN, NTO, and NQ at ~10 mg/L, HMX at ~3 mg/L, and perchlorate at ~6 mg/L (molar equivalent of NTO).

2.4. Analytical.

The HPLC analytical methods for NTO and DNAN have been previously published [15]. NQ was analyzed using the same HPLC method as NTO, with detection at 217 nm. HMX, RDX, and TNT were analyzed by using HPLC according to a modified EPA Method 8330 using an Agilent 1100 HPLC (Santa Clara, CA) equipped with a Dionex 3000 (Sunnyvale, CA) PAD (photodiode array) UV-Vis detector to collect peak spectral data. The variable wavelength detector collected data at both 254 and 230 nm. The chromatography column used to separate the nitroaromatics was an Acclaim Explosive E1 C-18 reverse phase HPLC column (Thermo Scientific, Waltham, MA; 25 cm x 4.6 mm, 5 μm particle diameter). A methanol:water gradient was used as the mobile phase as follows: 0-3 mins (20:80); gradient ramp from 3.0-9.0 min (20:80 up to 38:62); 9.0-15.0 min (38:62); gradient ramp from 15.-20.5 min (38:62 to 43:57); 20.5-44.0 min (43:57); 44.0-51 min (80:20, to wash column); 51-

64 min (20:80) to re-equilibrate column at the end of each sample run. Perchlorate was analyzed by ion chromatography using a modified EPA Method 300.0.

Nitrogen content of native and cationized materials was determined using a CHNS elemental analyzer (vario EL Cube, Elementar, Langenselbold, Germany) in the Advanced Materials Characterization Lab at the University of Delaware. Briefly, each test material was pretreated at 105°C for 20 min and 10-mg moisture-free samples were prepared in replicates for CNHS measurement. Following catalytic oxidation, organic nitrogen was converted into N₂ and quantified by a thermal conductivity detector (TCD). Prior to analysis, the instrument was calibrated using a sulfanilamide standard run in triplicate.

2.5. Data analysis.

The adsorption data was fitted into the most widely used Freundlich and Langmuir and isotherm models. The Freundlich model can be expressed as

$$q_e = K_f C_e^{\frac{1}{n}} \quad (1)$$

where q_e is the equilibrium sorbed concentration (mg/g); C_e is the equilibrium sorbate concentration in solution (mg/L); K_f and n are the fitted Freundlich parameters of adsorption capacity ((mg/g)(mg/L)^{-1/n}) and adsorption intensity (unitless), respectively. The Langmuir model can be expressed as

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2)$$

where q_e and C_e are the same as in the Freundlich equation; q_m and b are the fitted Langmuir parameters of maximum adsorption amount (mg/g) and the energy of adsorption constant (L/mg), respectively. Experimental data was fitted using the custom nonlinear curve fitting functionality of KaleidaGraph (v4.5.2, Synergy Software, Reading, PA).

The amount of CHPTAC incorporated into the various materials was estimated based on the difference in the nitrogen content between the raw and cationized materials.

3. RESULTS AND DISCUSSION

3.1 NTO removal.

None of the native materials sorbed NTO, but cationization (designated as CAT henceforth) of all the materials demonstrated increased removal of NTO (Figure 1), albeit only slightly in the case chitin. CAT cotton linters and CAT pine shavings performed quite well, resulting in sorption of more than 70% of the initial NTO. The NTO removal reported herein by cationized cellulosic materials was significantly more than that reported for amine functionalized chitin (AFC) based on the information provided in the patent, e.g., 1800-fold more removal of NTO per gram of CAT pine compared to AFC [22]. The observed extent of NTO removal by CAT pine in these single point evaluations was similar to the extent of orthophosphate anion removal by cationized pine bark previously reported (e.g., ~90% removal at initial concentrations of <10's of mg/L) [21].

The commercially available cationized fabrics removed less than 20% of the NTO from solution (data not shown). The fabrics were designated as containing 25% and 50% of cationized cotton. These percentages would need to be multiplied by the degree of CHPTAC incorporation in the cationized cotton used, which was not provided by the manufacturer. Therefore, these fabrics likely had a much lower number of positively charged NTO binding sites than the CAT materials prepared in our laboratory.

The CHPTAC concentration used during the cationization process directly impacted the ability of CAT pine to remove NTO from solution (Figure 2). NTO removal increased as CHPTAC increased from 38 to 225 g/L, but then decreased at 300 g/L. CHPTAC concentration showed a positive relationship with CHPTAC incorporation based on the change in nitrogen content before and after cationization (Figure 2), and followed the same pattern as observed for NTO uptake, e.g., the CHPTAC incorporation decreased in the CAT pine produced with the 300 g/L compared to 225 g/L CHPTAC. Therefore, part of the lower NTO removal by the pine cationized using 300 g/L CHPTAC is a result of less CHPTAC incorporation (e.g., fewer cationic sites). The leveling off the NTO removal at higher CHPTAC concentrations is similar to previous work showing leveling off of dye uptake into cotton fabrics cationized with higher CHPTAC concentrations [12, 19]. The previous research did not use CHPTAC concentrations greater than 200 g/L, so the current result showing decreasing cationization above this concentration is a new finding. The reasons for the decreased cationization at the highest concentration was not further investigated, but may be due to increased self-reaction of the epoxide formed during the process (hence, less overall reaction of the epoxide with the cellulose). The authors of the previously published information did not go to as high a CHPTAC concentration as in this current work, so it is possible that they would also have seen a decrease in cationization, reflected in a decrease in dye uptake.

It was observed that the CAT materials tended to buffer the pH of the ASR test solution towards circumneutral values. With CAT pine, initial acidic pH values of 3.5 to 4 S.U. were brought to around 7, and an initial basic pH value of 8.5 was brought down to slightly above 7. (Figure 3). Due to this buffering effect, NTO removal was not affected by the initial pH of

the solution. Even at an initial acidic pH near the NTO pK_a of 3.7, where there would be a~50:50 mix of neutral (protonated) and charged (deprotonated) NTO, the uptake of the charged NTO would lead to further deprotonation of the remaining neutral NTO, thus resulting in additional sorption to the CAT materials. The exact mechanism behind the buffering ability of the CAT materials was not determined, but was assumed to be due to exchange between hydroxide anion associated with the positively charged sites on the CAT materials and anions in the solution (e.g., chloride), thus leading to acid neutralization. This is actually a secondary benefit of the CAT materials, in that circumneutral pH values are favorable for the biological processes required to transform and degrade both insensitive and legacy MC.

The combination of peat moss with CAT materials had mixed effects on NTO removal. A 1:1 ratio of CAT pine, CAT burlap, or CAT cotton did not significantly change NTO removal (Figure 4). With a 2:1 peat moss:CAT material ratio, little impact was observed for CAT pine or CAT burlap, but NTO removal by CAT cotton was reduced by over 50%. At 3:1 ratio, NTO removal was reduced by 20%, 46% and 61% with CAT pine, CAT burlap, and CAT cotton, respectively. When water extractable peat moss compounds equivalent to a 3:1 peat moss:CAT material ratio were included, NTO removal decreased by compared to no peat addition. The final solution pH decreased as the amount of solid peat moss increased (Figure 4). However, even with a 3:1 peat moss:CAT ratio, the final pH was still at least 0.5 S.U. above the pK_a of NTO, and the pH in the presence of peat extractables was similar to that with no peat present (e.g., >6.5 S.U.). Therefore, the observed changes in NTO removal were not due to NTO becoming a neutral species in acidic solution. Rather, we postulate that the effects of peat moss on NTO removal were attributable to competition between anionic

compounds (e.g., organic acids) and NTO for the positively charged sites on the CAT materials. These results are quite encouraging, given that the final application is expected to be a combination of peat moss plus one or more of the CAT materials. The competition between peat-derived anionic compounds and NTO would be expected to decrease over time as those compounds are leached and/or degraded.

Competition was also observed between the concentration of major anions (chloride, nitrate, sulfate) and the removal of NTO by CAT materials (Figure 5). A 10-fold decrease in the major anions resulted in approximately 2-fold more NTO removal, while a 10-fold increase resulted in 3- to 5-fold less NTO removal, relative to the control concentrations in 1X ASR. The range of anion concentrations measured in the Navy site runoff collected periodically over a year has indicated that major anion concentrations in natural runoff are never extremely high, and are more likely to be below the anion concentrations in the ASR used for this testing. Therefore, the performance of these CAT materials with respect to NTO removal is not expected to be affected by competing anions.

Taken in total, the removal of NTO is theorized to be predominantly by ionic interactions between the positively charged cationized materials and the negatively charged NTO molecule. As such, the application of simple ion exchange models would be expected to explain the interactions/removal of NTO by these materials.

The main application of cationization has been in the textile industry as a means to increase anionic dye uptake into cotton, improving both color depth and color retention upon washing [12, 16], and as strength-enhancing process in the pulp and paper industry [17]. Cationization of cellulosic materials has also been evaluated to remove anionic dyes in wastewater [18-20], and anions like orthophosphate from surface runoff [21]. A recent

patent described the use of amine functionalized chitin for the removal of MC from aqueous solutions, including NTO [22], but the current work is the first known report of cationized cellulosic materials for NTO removal.

3.2. DNAN removal.

The greatest DNAN removal was observed with peat moss, with pine and aspen shavings, burlap, and coconet coir exhibiting slightly lower DNAN sorption (Figure 1). In most cases, cationization of these materials resulted in somewhat lower DNAN removal. This is likely due to a combination of delignification of the materials by exposure to the NaOH [23], leading to loss of more hydrophobic zones. During the cationization process, the initial rinse from most of the materials had a brown/orange hue, indicative of aromatic lignin-like compounds. When pine shavings and burlap were treated with the same concentration of NaOH as used during the cationization process (e.g., mercerization), but in the absence of CHPTAC, DNAN removal was also reduced compared to the corresponding raw materials, and was only slightly higher than their cationized versions (Figure S4). Additionally, cationization leads to an increase in positively charged sites due to incorporation of CHPTAC, and a decrease in overall hydrophobicity, which could be less likely to bind DNAN. However, DNAN removal was not observed to significantly vary with CAT pine possessing varying levels of CHPTAC incorporation (Figure S5).

3.3. NQ removal.

None of the materials tested sorbed NQ to any significant extent (<10% removal). This is not entirely unexpected, given that previous research has indicated that NQ is poorly retained

in soil due to low sorption to natural minerals and organic matter [11, 24]. These findings are also in line with another report of low NQ removal by unmodified cellulose, chitin, and chitosan [25]. This indicates an area for additional research, as insensitive munition compositions, as well as several propellant formulations, have the potential to lead to NQ contamination of surface runoff on military ranges.

3.4. Legacy and insensitive MC isotherms.

Freundlich and Langmuir adsorption parameters are shown in Table 1. Initial single point sorption testing with legacy explosives indicated that CAT pine and CAT burlap removed approximately 20% of HMX, 10% of RDX, and 50-60% of TNT from solution. However, no sorption parameters for HMX or RDX with any of the CAT materials were obtained from the isotherm data. Additionally, no parameters for NTO were obtained with peat moss, or for perchlorate with peat moss or CAT cotton. Model fit r^2 values were generally greater than 0.9, although the fits for CAT cotton were significantly lower (~0.6).

The trend in the Langmuir maximum sorption amount (q_m) for NTO was CAT pine > CAT burlap > CAT cotton, with the CAT pine q_m approximately five times greater than CAT cotton (4.1 vs. 0.8 mg NTO/g sorbent). For TNT, the peat q_m was approximately three times greater than that for CAT pine (3.6 vs. 1.3 mg TNT/g sorbent). This follows what was observed during the single point evaluation.

4. CONCLUSIONS

The identification of cationized materials for the removal of the insensitive MC compound NTO from aqueous solution, combined with the previous findings regarding the

effectiveness of peat moss for removal of the legacy MC compounds HMX, RDX, and TNT, provide a foundation for further development of a passive treatment technology for MC in surface runoff. These data indicated that a combination of peat moss and CAT pine would be required to effectively remove both insensitive and legacy MC from aqueous solution (excluding NQ). Follow-on work will include flow-through column and bench-scale biofilter testing, to assess not only sorption effectiveness and sorbent longevity under the dynamic conditions expected to occur in the field, but also combining sorption with abiotic and biotic degradation processes to work toward a wholistic approach for removal and destruction of the legacy and insensitive MC in stormwater runoff.

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441

TABLES

Table 1. Freundlich and Langmuir adsorption parameters for insensitive and legacy explosives.

		NTO			DNAN			ClO ₄		
		K_f	n	r^2	K_f	n	r^2	K_f	n	r^2
Freundlich	Peat	- ^a	-	-	0.38 ± 0.05	1.71 ± 0.20	0.89	-	-	-
	CAT Pine	0.94 ± 0.05	1.61 ± 0.11	0.97	0.01 ± 0.01	0.70 ± 0.13	0.76	1.54 ± 0.06	2.42 ± 0.16	0.97
	CAT Burlap	0.41 ± 0.05	2.43 ± 0.41	0.82	-	-	-	0.53 ± 0.03	2.42 ± 0.26	0.92
	CAT Cotton	0.26 ± 0.06	2.53 ± 0.76	0.57	-	-	-	-	-	-
		q_m (mg/g)	b (L/mg)	r^2	q_m (mg/g)	b (L/mg)	r^2	q_m (mg/g)	b (L/mg)	r^2
Langmuir	Peat	-	-	-	2.57 ± 0.33	0.13 ± 0.03	0.92	-	-	-
	CAT Pine	4.07 ± 0.26	0.30 ± 0.04	0.99	-	-	-	3.63 ± 0.18	0.89 ± 0.13	0.97
	CAT Burlap	1.29 ± 0.12	0.36 ± 0.08	0.89	-	-	-	1.26 ± 0.06	0.76 ± 0.10	0.97
	CAT Cotton	0.83 ± 0.15	0.30 ± 0.15	0.58	-	-	-	-	-	-

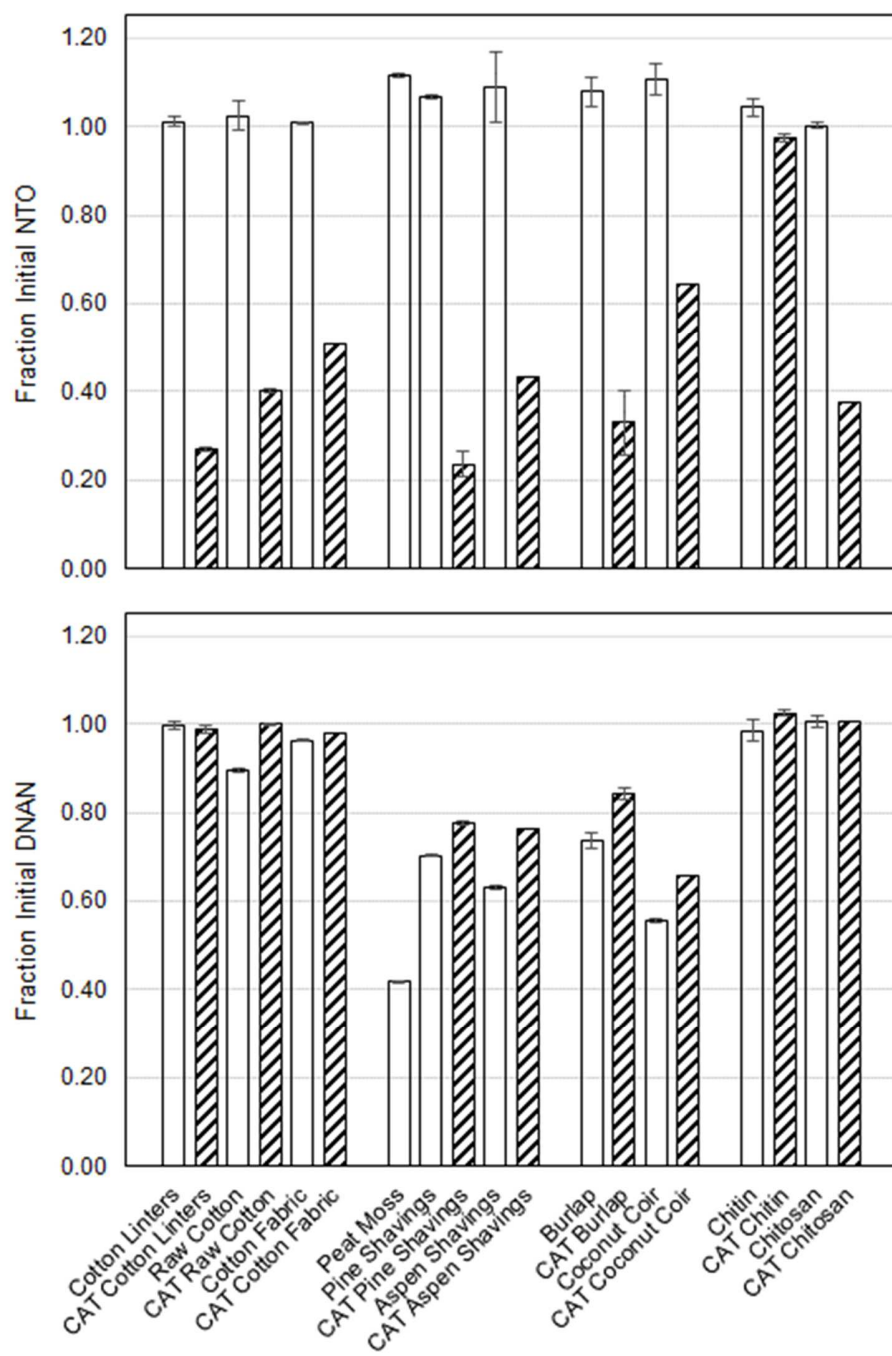
		HMX			RDX			TNT		
		K_f	n	r^2	K_f	n	r^2	K_f	n	r^2
Freundlich	Peat	0.08 ± 0.00	1.70 ± 0.18	0.91	0.11 ± 0.02	2.75 ± 0.63	0.69	1.21 ± 0.15	2.78 ± 0.67	0.81
	CAT Pine	-	-	-	-	-	-	1.02 ± 0.04	4.01 ± 0.44	0.93
	CAT Burlap	-	-	-	-	-	-	0.36 ± 0.02	1.59 ± 0.09	0.98
	CAT Cotton	-	-	-	-	-	-	-	-	-
		q_m (mg/g)	b (L/mg)	r^2	q_m (mg/g)	b (L/mg)	r^2	q_m (mg/g)	b (L/mg)	r^2
Langmuir	Peat	0.29 ± 0.04	0.39 ± 0.09	0.93	0.38 ± 0.05	0.23 ± 0.08	0.69	3.63 ± 0.18	0.89 ± 0.13	0.97
	CAT Pine	-	-	-	-	-	-	1.26 ± 0.06	0.76 ± 0.10	0.97
	CAT Burlap	-	-	-	-	-	-	-	-	-
	CAT Cotton	-	-	-	-	-	-	-	-	-

^a No successful model fit

FIGURES

Figure 1	Removal of NTO (top) and DNAN (bottom) from ASR. Data represent average of duplicates $\pm$ standard deviation.
Figure 2	Effect of CHPTAC concentration on removal of NTO by cationized pine shavings (top) and amount of CHPTAC incorporation based on change in nitrogen content (bottom).
Figure 3	Initial and final solution pH and removal of NTO by cationized pine shavings.
Figure 4	Impact of peat moss on removal of NTO from solution by CAT materials (top) and final solution pH (bottom).
Figure 5	Impact of major anions on removal of NTO from solution by CAT materials.

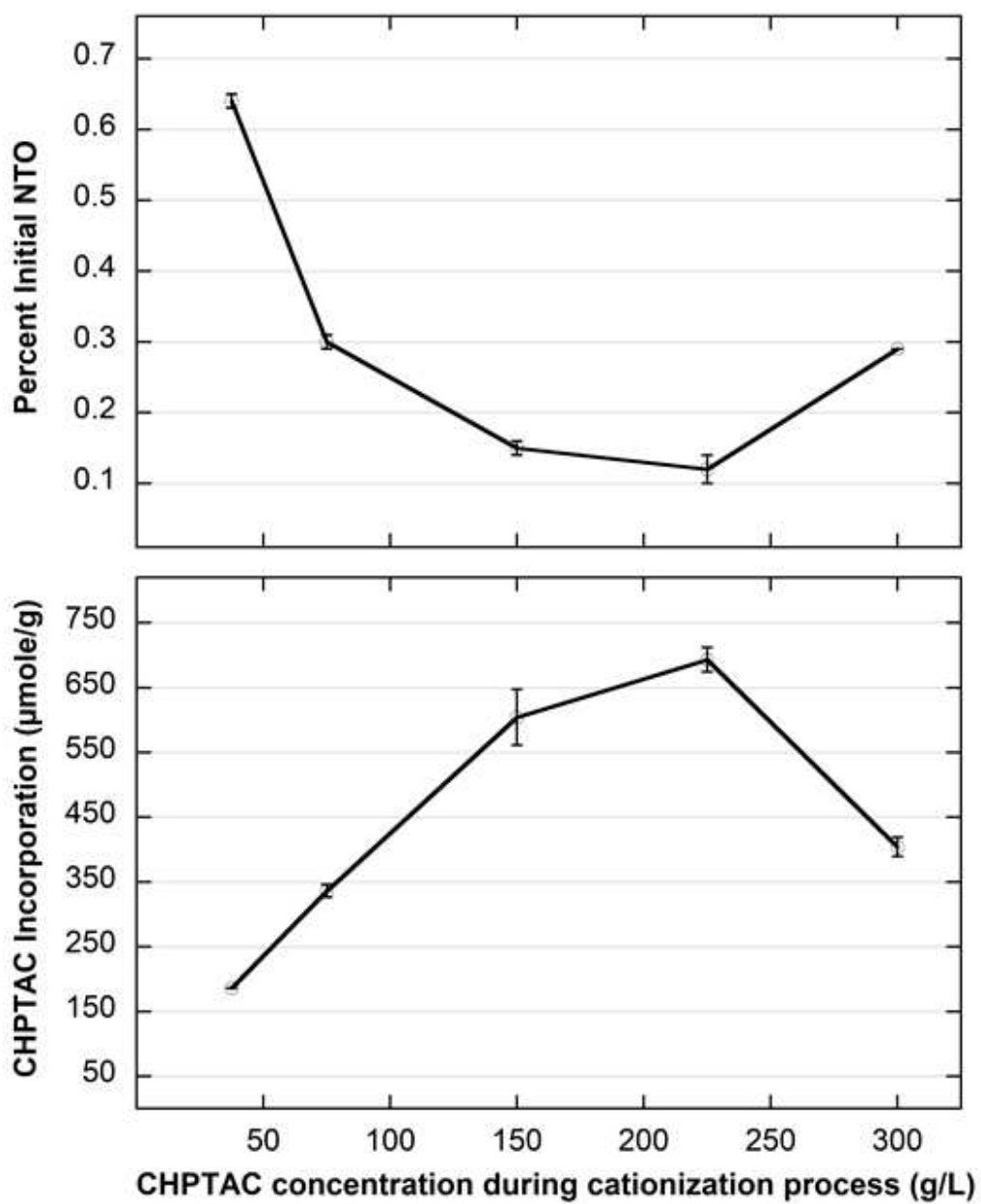
454 Figure 1.



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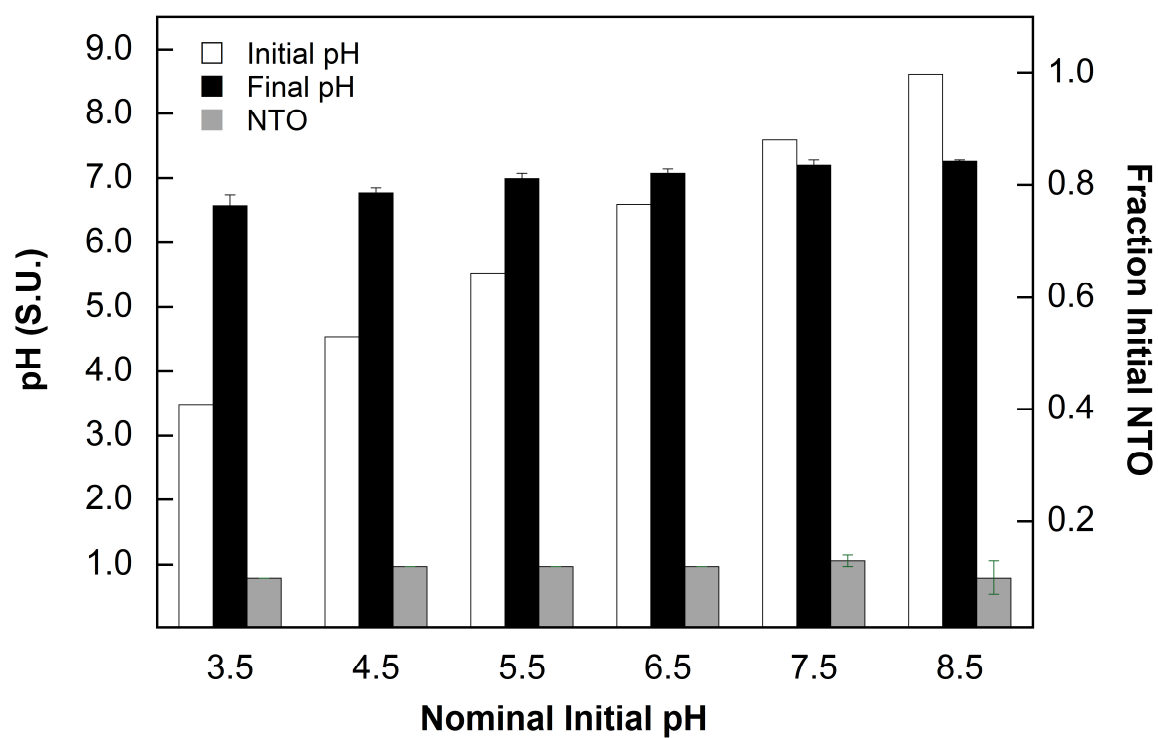
457 Figure 2.



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460 Figure 3.

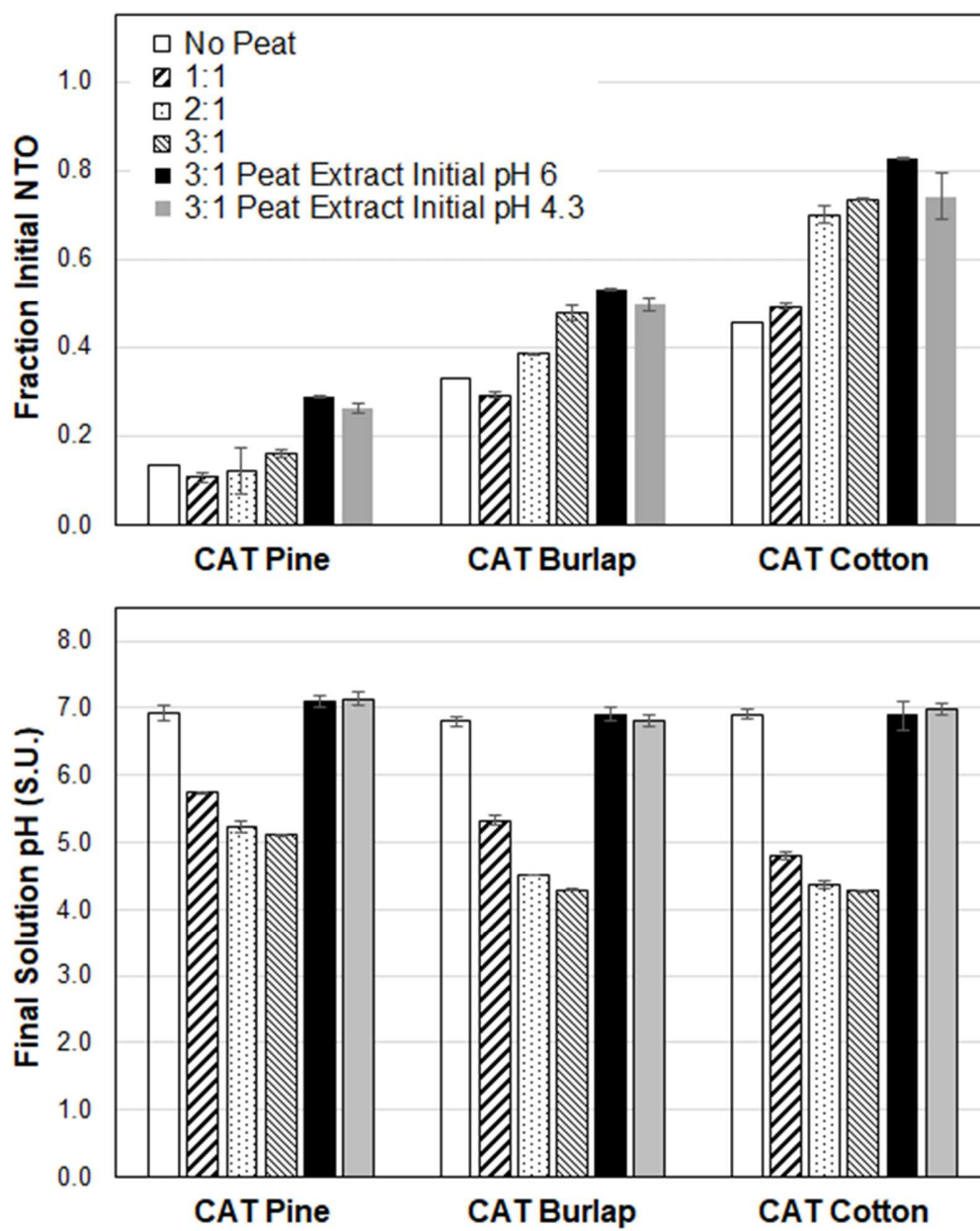


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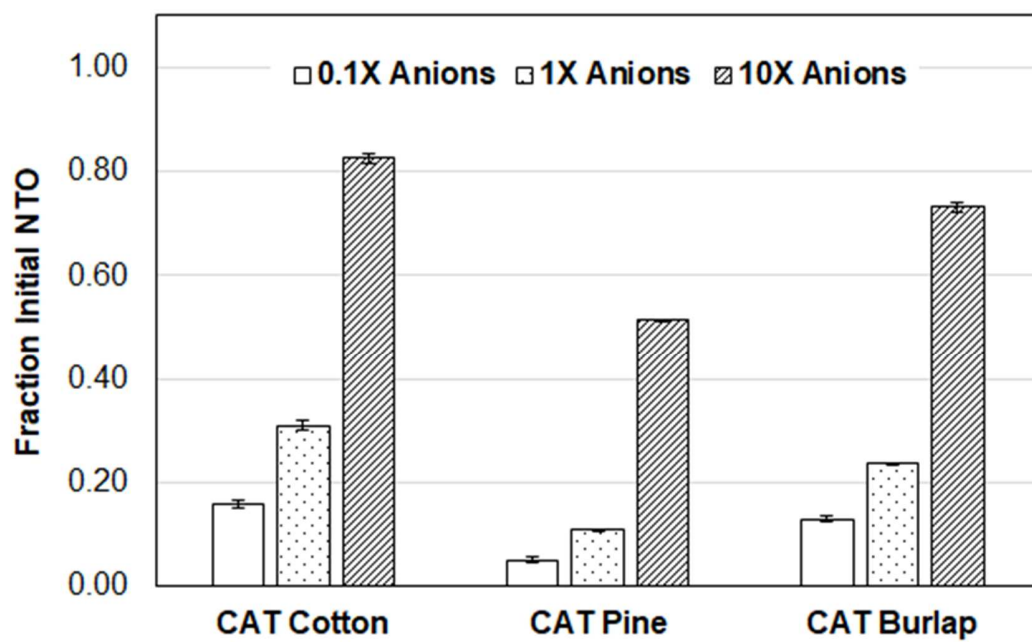
464 Figure 4.



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467 Figure 5.



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