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Preliminary Investigation of Nitro-hydrolysis for Wastewater Sludge Treatment

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ABSTRACT

Activated sludge waste treatment facilities generate a waste stream, in the underflow, that consists of 3 to 5 wt% biosoilds that are not readily biodegradable and must be disposed of as a solid waste. Conventional disposal methods for this biosludge consist of landfills, land farming, wet air oxidation, and incineration, all of which add substantially to the cost of operating a municipal wastewater treatment facility. Bench-scale batch experiments were conducted with a 4.1 wt% biosludge stream obtained from the Knoxville Utility Board (KUB) Kuhawee treatment facility. These experiments demonstrated that treatment with dilute nitric acid at 180°C at 200 psia initiates a hydrolysis reaction that converts 40 to 82% of the biosolids to biodegradable substances suitable for recycle back to

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the treatment facility. The experimental design consisted of varying the nitric acid concentration from 1.5 to 11.2 wt% and the residence time between 5 and 20 minutes. At these conditions, the initial hydrolysis reaction is rapid, destroying most of the biosolids within 5 minutes. The products of this reaction consisted mainly of carboxylic acids that may be recoverable and sold commercially. The stoichiometry of the reaction was investigated and the kinetics was determined to be first order in nitric acid concentration. Results of these batch experiments performed on municipal sludge partially confirm the patent literature data that used a plug flow reactor and industrial sludge. Future work will expand this study to include a complete factorial design of this process by investigating four possible reaction variables: residence time, reaction temperature, acid concentration, and feed solids concentration in detail, with the objective of developing comprehensive kinetics for the process.

Key Words: Excess sludge; Sludge; Biosolids; Wastewater.

INTRODUCTION

The activated sludge process used by many municipalities and industries for removal of biological oxygen demand (BOD) from wastewater generates a solids waste stream, in the underflow, referred to as excess sludge.[1] The primary fates of the BOD are either conversion to water and carbon dioxide by cell metabolism or incorporation into the biomass.[1] The latter results in the production of an excess sludge that must be disposed of as a solid waste either by landfill, land farming, incineration,[2–4] or wet air oxidation.[5] It has been suggested in the patent literature[6] that contacting this waste stream with dilute nitric acid in a flow reactor at temperatures between 150 and 200°C can convert over 90% of the solids to biodegradable organic suitable for recycle to the activated sludge process. The reactor was pressurized, keeping the feed streams in the liquid state. Recycle of the entire reactor effluent stream to the activated sludge process will make an insignificant increase in the hydraulic loading of the waste treatment plant and will substantially reduce or eliminate the solids waste removal problem. The overall reaction is

$$\text{Sludge} + \text{HNO}_3 \rightarrow \text{Biodegradable organic} + \text{N}_2 \tag{1}$$

The organic materials produced in the process are mainly carboxylic acids, primarily formic, acetic, and propionic. It might be possible to optimize the process to economically convert this waste stream into acetic acid where a large commercial market is present.

This technology would be superior to existing methods, in that it is virtually a zero discharge process that would result in considerable energy saving over incineration and eliminate the air pollution problems associated with incineration. Landfills are expensive and can lead to long-term pollution concerns.[4] Land farming has risks associated with it that companies may not want to take on. For example, while DuPont still land farms its sludge, it is actively looking for an energy-efficient alternative because of potential future liability from this method. KUB currently land farms about 65,000 pounds of sludge per day (dry basis) that is transported 70 miles from the site. Because of the effects of the sludge on soil, KUB has to truck its solid waste further west of Knoxville. There are over 700 large municipal treatment facilities in the United States[2] that could use this process to substantially reduce their solid waste production. In addition, there are hundreds of large industrial sites with similar problems. Primary candidates are the petroleum and chemical industries; however, this process is applicable to any large industrial waste treatment process that produces excess biosolids. Companies like Tennessee Eastman may also be able to use this process to convert their waste stream to a usable product. Chemical companies have the technology to recovery acetic acid from an aqueous stream and many, like Tennessee Eastman, have an internal demand for this product.

Approximately 100,000 tons of biosludge are produced in the United States each day.[2] If this material were concentrated to 12.5 wt%, the concentration used by Eastman for incineration,[7] and sent to an incinerator a net input of 4.0×10^{14} BTU/yr would be required. Approximately one third of the sludge is actually incinerated nationwide,[2] resulting in an annual cost to industry and municipalities of approximately $662 million, just for the energy needed to run the incinerators. Incineration will also lead to air pollution concerns, and the capital cost of an incinerator is substantial. Chemical companies like Eastman that have the expertise to recover acetic acid from water and an internal demand for large quantities of acetic acid, may be able to economically utilize this process to convert their waste stream into a profitable product. Based on Eastman's sludge production rate of 50 to 55 tons/day,[7] dry basis, and an acetic acid price of $0.44/pound,[8] there is the potential to produce $5.6 million/yr of acetic acid.

BACKGROUND

This process was discovered in an attempt to improve the filterability of sludge.[6] While any strong acid can be used in the sludge destruction process, nitric acid is preferred because it blends into the chemistry of the waste treatment process.[1] High-molecular weight polymeric compounds make up most sludge. The sludge contains substances such as proteins, nucleic acids, and lipids, that degrade. An example of protein oxidation is[9]

$$\text{Aspartic acid} \Leftrightarrow \text{Oxaloacetic acid} + NH_4{}^+ \tag{2}$$

Proteins may make up 40 to 70% (dry weight) of a cell, while lipids make up 10 to 15%. Carbohydrates make up 15 to 35% of the cells. The products of oxidation can oxidize still further. Formic and acetic acids can both oxidize all the way to CO_2 and H_2O, shown as[9]

$$CH_2O_2 + 0.5O_2 \rightarrow CO_2 + H_2O \tag{3}$$

$$C_2H_4O_2 + 2O_2 \rightarrow 2CO_2 + 2H_2O \tag{4}$$

A general equation for biomass (sludge) oxidation is[1]

$$C_5H_7O_2N + 5O_2 \rightarrow 5CO_2 + 2H_2O + NH_3 \tag{5}$$

This stoichiometry estimated approximately 320 mg of acetic acid produced per g of sludge reacted for a flow reactor using an industrial sludge. Previous research[6] indicates that as much as 96% conversion of the biosolids may be achievable. Initial tests for the process indicated that the best performance was obtained at the reaction conditions of 200 psi and 180°C.

THEORY

To determine the reaction order for the reaction under consideration, some rate expressions must be assumed and then tested. One such rate expression would be a first-order reaction of the form

$$A \rightarrow \text{Products} \tag{6}$$

This type of reaction would then give a rate expression of

$$-r_A = \frac{-dC_A}{dt} = kC_A \tag{7}$$

By integrating this expression and substituting in the definition of fractional conversion (X_A),

$$X_A = \frac{N_{AO} - N_A}{N_{AO}} \tag{8}$$

we obtain the equation

$$-\ln(1 - X_A) = kt \tag{9}$$

To test the rate expression, we then perform a plot with time on the x axis and $-\ln(1 - X_A)$ on the y axis. If the reaction is first order with respect to the component under consideration, a straight line should be the best fit through the experimental data and should pass through the origin. The reaction may be first order with respect to a single component of the reaction.[10]

A similar test can be performed for a second-order bimolecular-type reaction of the type

$$A + B \longrightarrow \text{Products} \tag{10}$$

In this case, the rate expression would be

$$-r_A = \frac{-dC_A}{dt} = \frac{-dC_B}{dt} = kC_AC_B \tag{11}$$

With appropriate substitution and integration, we obtain

$$C_{AO}(M - 1)kt = (C_{BO} - C_{AO})kt \tag{12}$$

where

$$C_{BO} \neq C_{AO}$$

$$M = \frac{C_{BO}}{C_{AO}}$$

A plot of time on the x axis and $\ln\left\lfloor \frac{M-X_A}{M(1-X_A)} \right\rfloor$ on the y axis should give a straight line through the experimental data that passes through the origin. If $C_{AO} = C_{BO}$, then we can represent the reaction as

$$2A \longrightarrow \text{Products} \tag{13}$$

and then plot $\frac{X_A}{1-X_A}$ vs time to test the rate expression, which is[10]

$$-r_A = \frac{-dC_A}{dt} = kC_A^2 \tag{14}$$

In general,

$$-r_A = kC_A^{\alpha}C_B^{\beta} \tag{15}$$

so that by taking the logarithm of the above eq. 15, we have

$$\ln(-r_A) = \ln k + \alpha \ln C_A + \beta \ln C_B \tag{16}$$

and the coefficients may be obtained from regression of the data.

EXPERIMENTAL

Equipment

The equipment used in these experiments includes a hot oil bath (National Presto Industries Inc. of Eau Claire, WI—electric multicooker), a pressurized batch reaction tube (fabricated by The University of Tennessee), and a calibrated thermometer. The batch reactor was 5 inches in length, with an outside diameter of 0.75 inches and a wall thickness of 1/16 inches, giving an internal volume of 25.2 cm^3. The reactor was fabricated from 316 ss tubing with a rated working pressure of 3300 psi and a bursting pressure of approximately 8000 psi. The reactor was sealed with 3/4-inch swagelok fittings. A fritted disk filter, a filter flask, filter paper (Whatman International Ltd. of Maidstone, England), a 5-mL pipette and pipette bulb, a gravity filtration filter, and a graduated cylinder were utilized for analysis. Preliminary analysis on the sludge required a 600-mL beaker and a drying oven.

Materials

Great Value Vegetable Oil (Wal-Mart of Bentonville, AR) was used in the hot oil bath as the heat transfer medium. The nitric acid used had a concentration of 69.3% (Fisher Scientific of Fair Lawn, NJ). The sludge utilized in these experiments was obtained from the Knoxville Utility Board (KUB)—Kuwahee Wastewater Treatment Facility in Knoxville, TN. The sludge had a measured density of 1.014 g/mL and was stored in a refrigerator, at 7°C, to prevent degradation. This sludge sample had a solids content of 4.083 ± 0.105 based on 6 replicates, a value of 4.1 wt% was used for calculation purposes.

An elemental analysis was performed on the sludge solids (Galbraith Laboratories, Knoxville TN) giving the following compositions: carbon 41.14%, nitrogen 16.72%, oxygen 21.45%, hydrogen 12.37%, and remaining 8.32%. The remaining probably consisted of sand, dirt, metals, and other inorganics.

Procedures

The procedures used were similar to previous work.[11,12] A 100-mL sample of sludge was transferred into a beaker and weighed. The sample was then dried in an oven at 105°C to dehydrate the sample. The dried sample was then weighed to obtain the mass of dry solids in the original 100-mL sample. The fraction of the original sample that consisted of solids was then calculated. This procedure was repeated to give three replicates of the fraction solids. The average of the three tests was used as reported value. The sludge was stored in the refrigerator to preserve the properties and concentration of the sludge solution.

Preparation of a test sample included filling the batch reaction tube with 19.1 g of the 4.1 wt% sludge slurry. A measured volume of 69.3% nitric acid was then added to the reaction tube, and the cap placed tightly on to seal the reaction tube. The tube was shaken briskly to assure a good mixture of the reactants and was then submerged in the hot oil bath that had been preheated for 30 minutes and monitored to assure a constant reaction temperature of 180°C. The tube was allowed to heat up for 2 minutes, and then the reaction timer was started. The tube was left submerged in the hot oil for the measured reaction time and then removed and quenched in an ice water bath for 5 minutes to stop the reaction. The tube was opened and its contents transferred to a graduated cylinder. The contents were allowed to sit for about 2 minutes to allow the remaining solids to settle out, and the total product volume was recorded.

Approximately 5 mL of the liquid produced was gravity filtered through filter paper (110 mm) and sent for liquid analysis. Organic acids (formic, acetic, propionic, butyric, and valeric) and nitrate analyses were performed using high-pressure liquid chromatography. The mobile phase (filtered 5-nM H_2SO_4) was pumped at 0.6 mL/min through a 300-mm × 7.8-mm (8-μm particle size) RHM monosaccharide column (Bio-Rad Laboratories, Hercules, CA) held at a temperature of 65°C. A refractive index detector (Model 240, Waters Corporation, Milford, MA) held at 40°C was used for analysis. Each sample was prefiltered using a Acrodisc LC 13-mm syringe filter with 0.2-μm PVDF membrane (Pall Corporation, Ann Arbor, MI). The sample injection volume was 10 μL, and the resulting chromatograms were compared with injections of acids and nitrate standards. The remaining contents were vacuum filtered through a fritted disk funnel. All glassware and the reaction tube were washed into the funnel. The solids were then allowed to dry, and the fraction of the solids consumed in the reaction determined.

A second-order factorial design[13,14] was used for the experiments with acid concentrations of 1.5, 3.2, 6.1, and 11.2 wt% and residence times of 5, 10, 15, and 20 minutes.

RESULTS

Introduction

The results from this research are presented in the following section. The estimated stoichiometry is presented first, followed by a graphical test of a rate expression. The production of organic acids of interest, acetic, formic, and propionic acid, are discussed. Longer chain organic acids, such as valeric acid, were analyzed for, but their presence was negligible. The fractional conversion of each of the reactants as a function of reaction time and nitric acid concentration are discussed.

Stoichiometry

The amount of sludge used in the experiments was kept constant with reaction time and initial nitric acid feed as variables. The biomass term in eq. 5 was used to convert sludge to a molar basis. The analysis of the moles of sludge that react for each mole of nitric acid consumed can be found in Fig. 1. Figure 1 shows a large variation in the sludge-to-nitric ratio, going from 8 to about 2, generally decreasing with increased reaction time, indicating that the initial step in the sludge decomposition is completed rapidly under these conditions with subsequent degradation of nitric acid. The previously estimated stoichiometry predicted 0.80 moles of nitric acid consumed per mole of sludge reacted, using an industrial sludge as feed in a continuous system that consumed over 90% of

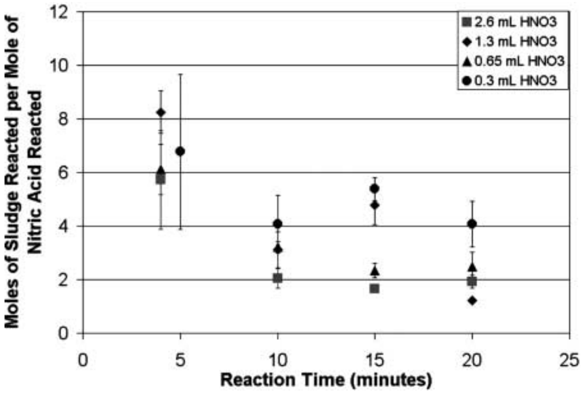

Figure 1. Stoichiometry estimation.

the sludge. There is some scatter in the data; however, it appears that the actual nitric acid loading and not the concentration is the key variable.

Test for Reaction Order

In performing an initial order of reaction analysis, with respect to nitric acid a significant amount of scatter appears in the data (Fig. 2). As can be seen in Fig. 2, the order of reaction with respect to the nitric acid gave straight lines through the data that pass nearly through the origin. This type of plot leads to the conclusion that the reaction is first order with respect to nitric acid. Similar graphical analysis for sludge contained a great deal of scatter and precluded any concise conclusions. Further tests are needed to determine the order of the reaction with respect to sludge.

Organic Acid Production

One objective of this work was to investigate the quantity of carboxcylic acids produced and possibly recovered from this waste stream. The production of acetic acid, with respect to the amount of sludge that reacts, is presented in Fig. 3. From Fig. 3, increasing reaction time does not increase the amount of acetic acid produced per g of sludge reacted. It should be noted that a small amount of acetic acid was already present in the sludge obtained from Kuwahee Wastewater Treatment Facility; the amount of acid initially present

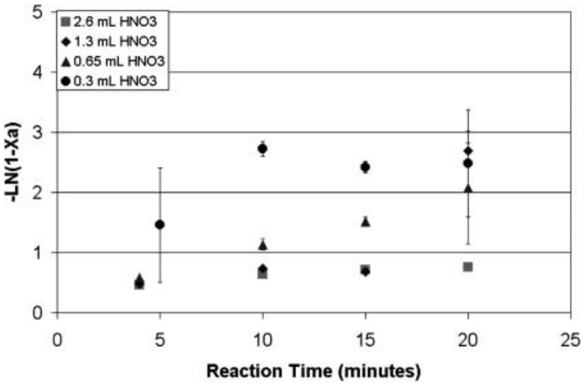

Figure 2. First-order rate test with respect to nitric acid.

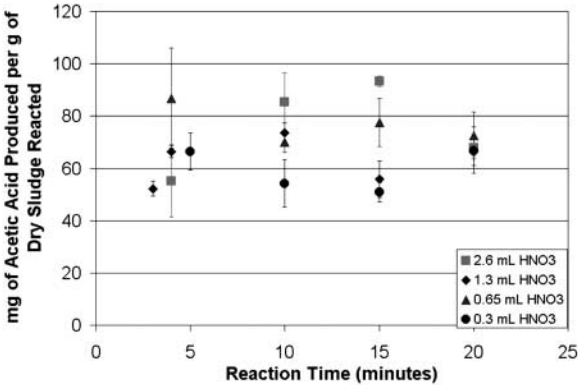

Figure 3. Acetic acid production.

has been subtracted from the total acid present in the analysis. The acetic acid in Fig. 3 is the acetic acid actually produced from the acid catalyzed hydrolysis of the sludge in the experiments. The 100 mg of acetic acid produced per g of sludge that reacted is about one third of the acetic acid production predicted by eq. 6. Equation 6 was based on data from a flow reactor using an industrial sludge, and it is unknown how much, if any, acetic acid was in this sludge stream prior to reaction.

The production of formic acid with respect to the amount of sludge that reacts is presented in Fig. 4. From Fig. 4, the reaction time does appear to affect the formation of formic acid, as does the initial amount of nitric in the reactor.

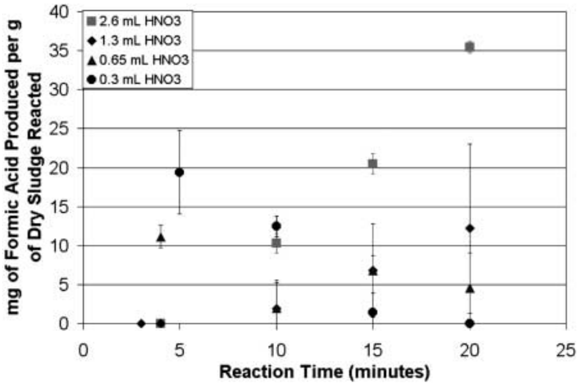

Figure 4. Formic acid production.

At low initial nitric acid input, as the reaction progresses, the amount of formic acid produced decreases to nearly zero. As the initial input of nitric acid increases, more formic acid is produced with increased reaction time. In fact, at an initial nitric acid input of 2.6 mL (11.2 wt%), the increase in the amount of formic acid produced appears to be linearly dependent on the reaction time up to about 20 minutes (the limit of these experiments). The turning point in the formic acid production appears to occur somewhere around an initial nitric acid input of 0.65 mL (3.2 wt%). The formic acid produced is corrected for any formic acid that was already present in the sludge.

The final organic acid that appeared in detectable quantities is propionic acid. The production of propionic acid, with respect to the amount of sludge that reacts, is presented in Fig. 5. From Fig. 5, the reaction time does not appear to greatly affect the amount of propionic acid produced. The production of the propionic acid with respect to 1 g of sludge reacted appears to range between 5 to 20 mg. The initial nitric acid input appears to increase the amount of propionic acid produced slightly in most cases. With 0.3 mL of nitric acid added to the reactor, approximately 10 mg of propionic acid are produced per g of dry sludge. With 2.6 mL of nitric acid added to the reactor, approximately 20 mg of propionic acid are produced per g of dry sludge.

Fractional Conversion of Reactants

The final analysis in this section comes from the fractional conversion of each of the reactants in the reaction (namely, sludge and nitric acid).

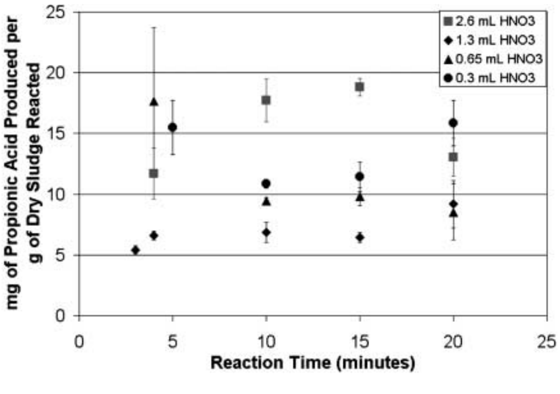

Figure 5. Propionic acid production.

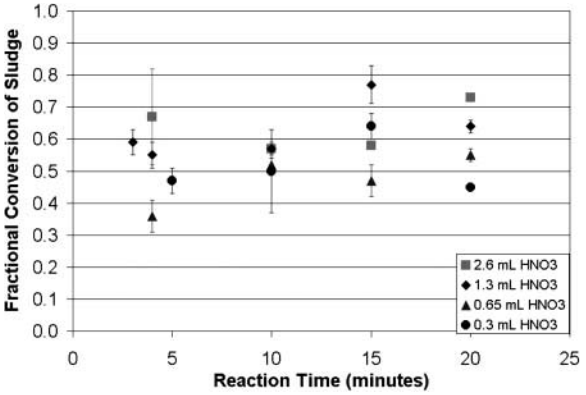

Figure 6. Fractional conversion of the sludge reactant.

The fractional conversion of the sludge, with respect to the reaction time and the amount of nitric acid initially present in the reactor, is presented in Fig. 6. A high-fractional conversion is desired. From Fig. 6, with a reaction time of about 5 minutes, between 40 and 65% of the sludge that is initially present is converted. An increase in the amount of nitric acid initially present in the reactor leads to an increase in the amount of sludge that is converted. With an increased reaction time of 20 minutes, approximately 50 to 75% of the initial sludge in the reactor is converted. Based on the elemental analysis of the dried sludge, 8.32% is inert material. If the kinetics are corrected for the inert materials, a maximum conversion of 82% is obtained. It appears from Fig. 6 that most of the reaction is over after 5 minutes for the high initial acid concentrations.

The fractional conversion of the nitric acid, with respect to the reaction time and the amount of nitric acid initially present in the reactor, is presented in Fig. 7 and is of concern, due to requirements on the concentration of nitric acid in wastewater. Figure 7 shows that increasing the reaction time will increase the amount of nitric acid converted to product. As expected, the amount of nitric acid initially present is also an important factor. At the low initial nitric acid input of 0.3 mL, nearly 95% conversion is achieved after 5 minutes of reaction time. The conversion remains constant after that, indicating that the nitric acid is the limiting agent and has reacted away. If the nitric acid used is increased to 2.6 mL, the initial-fractional conversion of nitric acid is about 35% at 5 minutes, and then the conversion planes off to about 50% at 20 minutes. This indicates that the sludge is limiting the reaction, and there is excess nitric acid present. Even though some sludge is still present

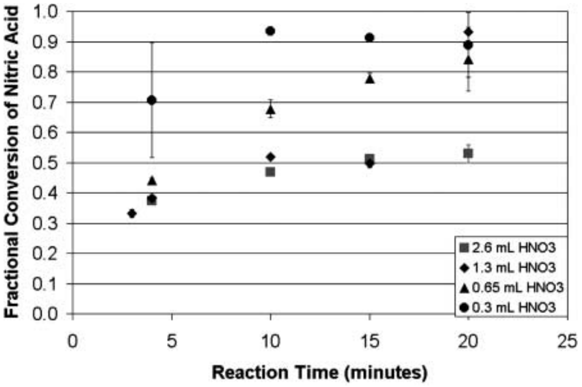

Figure 7. Fractional conversion of the nitric acid reactant.

in the system, the sludge does not appear to be reacting with the acid. This could be for many reasons, one of which could be the presence of metals and other contaminates in the sludge. The sludge that is left may not react at all. The behavior exhibited in Fig. 1 is explained in light of Figs. 6 and 7. The initial hydrolysis of the sludge is very rapid, resulting in sludge to nitric ratios of 6 to 8 in Fig. 1 after 5 minutes. The nitric is then consumed as this complex reaction sequence progresses. The sludge to nitric ratio continues to go down with increasing residence time.

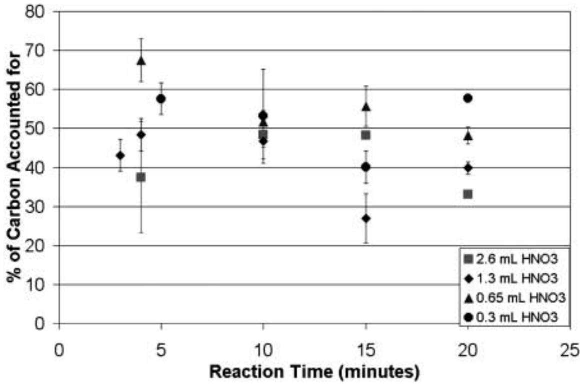

Figure 8. Amount of carbon that is accounted for in a carbon balance.

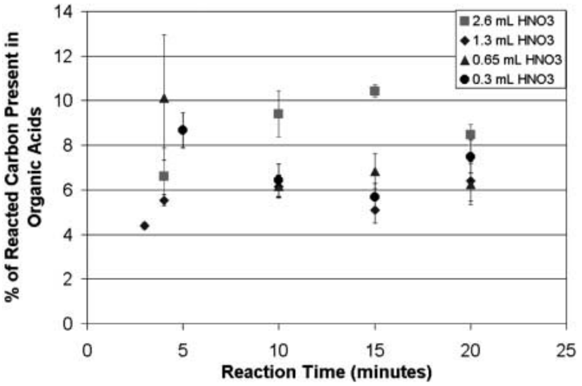

Figure 9. Percent of reacting carbon that appears in the organic acids.

Analysis of the reaction of wastewater treatment sludge with nitric acid to decompose the sludge to a useful product has a promising future. The sludge is being reacted away to reduce the amount of sludge that must then be disposed. The products of interest (specifically formic and acetic acid) are being produced from the reaction and an analysis of separation possibilities is needed.

In performing a carbon balance on the reactor, only 40 to 60% of the carbon is accounted for (Fig. 8). The carbon accounted for is in the unreacted sludge, and the organic acids produced in the reaction. The remainder of the carbon is believed to be in the form of carbon monoxide and carbon dioxide. The analysis of the off gas for these products is the topic of research that is currently underway at The University of Tennessee. Approximately 6 to 10% of the carbon that does react, appears in the organic acid products, as can be seen in Fig. 9.

CONCLUSIONS AND RECOMMENDATIONS

Conclusion

- The stoichiometry for the reaction involving sludge from KUB appears to be different from the stoichiometry for the reaction involving industrial wastewater sludge.
- With respect to nitric acid, the reaction appears to be first order.
- A measurable amount of acetic acid is produced from the reaction.
- A smaller but measurable amount of formic acid is produced from the reaction.

- A measurable amount of propionic acid is produced from the reaction.
- A significant amount of the carbon in the sludge appears to be exiting in the form of gases.
- Sludge destruction is relatively high (up to 82%).
- With low initial concentrations of nitric acid, all of the nitric acid is consumed in the reaction, with little to no residual.
- Approximately 8% of the reacted carbon results in organic acids.
- Results indicate that at a reaction temperature of 180°C, the initial step for sludge hydrolysis is very rapid, even at low acid concentrations.

Recommendations

- Analyze off gas from the reactor to complete a carbon balance.
- Develop a factorial experimental design incorporating reaction temperature and initial sludge concentration as additional variables.
- Determine experimentally the suitability of recycling the effluent from sludge hydrolysis back to the waste treatment unit.
- Quantify the composition of the unreacted sludge.
- Build a pilot scale system for continuous operation of the reactor.

NOMENCLATURE

Symbols

C_A	Concentration of component A	(g/L)
C_{AO}	Initial concentration of component A	(g/L)
C_B	Concentration of component B	(g/L)
C_{BO}	Initial concentration of component B	(g/L)
k	Rate constant	(L/mole-min)
M	Constant	(–)
N_A	Moles of component A	(moles)
N_{AO}	Initial moles of component A	(moles)
r_A	Reaction rate with respect to component A	(moles/L-s)
t	Time	(minutes)
X_A	Fractional conversion of component A	(–)
α	constant	(–)
β	constant	(–)

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