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Ambient Temperature Removal of Problematic Organic Compounds from ISS Wastewater

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ABSTRACT

Small, highly polar organics such as urea, alcohols, acetone, and glycols are not easily removed by the International Space Station's Water Recovery System. The current design utilizes the Volatile Removal Assembly (VRA) which operates at 125°C to catalytically oxidize these contaminants. Since decomposition of these organics under milder conditions would be beneficial, several ambient temperature biocatalytic and catalytic processes were evaluated in our laboratory. Enzymatic oxidation and ambient temperature heterogeneous catalytic oxidation of these contaminants were explored. Oxidation of alcohols proceeded rapidly using alcohol oxidase; however, effective enzymes to degrade other contaminants except urea were not found. Importantly, both alcohols and glycols were efficiently oxidized at ambient temperature using a highly active, bimetallic noble metal catalyst. Adsorption onto activated carbon formed from pyrolyzed polymeric beads was shown to be the most practical method for acetone removal.

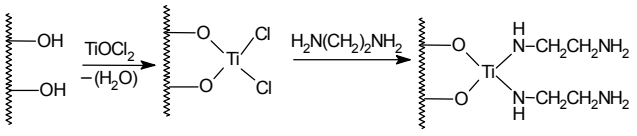
INTRODUCTION

Most contaminants within wastewater streams generated aboard manned spacecraft can be effectively removed by adsorption and ion exchange (IX), a process known collectively as Multifiltration (MF). Those which remain in MF effluents are generally highly polar low molecular weight organics such as urea, straight chain alcohols, isopropyl alcohol, acetone, glycols, etc. More than a decade ago, work began which resulted in the development of two unique composite beds which catalyzed the conversion of low molecular weight alcohols and urea to ionic constituents at ambient temperature, and then retained the reaction byproducts on IX resins. While the performance of these two Immobilized Enzyme Bioreactors was quite good, in the context of the current requirements for the International Space Station (ISS) water processor, they suffer from two primary deficiencies: (1) they were not designed to process a composite wastewater stream; and (2) the Immobilized Alcohol Oxidase Bioreactor was not effective against several problematic contaminants including isopropyl alcohol, acetone, ethylene glycol, propylene glycol, and other minor organic constituents. The purpose of this investigation was to establish the feasibility of additional methods for the decomposition and/or removal of these problematic contaminants, as the basis for the development of Advanced Immobilized Enzyme Bioreactors for the ambient temperature treatment of MF effluent aboard ISS. The investigation focused on the evaluation of additional immobilized enzyme systems, new heterogeneous catalysts, and novel sorbents. Six of the most problematic contaminants were studied: methanol, ethanol, acetone, isopropyl alcohol, ethylene glycol, and propylene glycol. Ambient temperature methods for the treatment of each of these contaminants were identified.

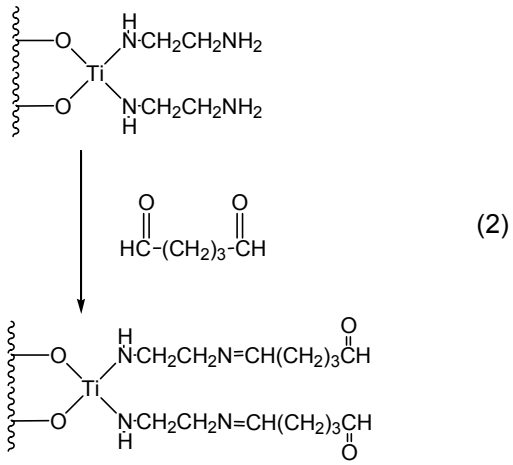
EXPERIMENTAL SECTION

ENZYME IMMOBILIZATION

Enzymes were immobilized onto diatomaceous earth for use in a heterogeneous bioreactor. The diatomaceous earth support was prepared for enzyme immobilization using the titanium activation technique [1,2] with ethylene diamine and glutaraldehyde bridging groups given by (1) and (2).



(1)



(2)

The enzymes were subsequently immobilized by Schiff base formation between an amino terminus or lysine residue of the enzyme and a free aldehyde group linked to the support. The aqueous enzyme preparations were added directly to the activated supports as received from the suppliers (enzymes were received in buffer solutions with pH between 7.0 and 7.8). The oxidase enzymes were immobilized on Celite R-648 media using the titanium activation procedure. Platinum (2% w/w) was co-immobilized to facilitate the decomposition of hydrogen peroxide produced as a reaction by-product since hydrogen peroxide is known to denature oxidase enzymes over time [3,4].

CATALYST PREPARATION

The bimetallic catalyst (RP-121) was created by aqueous impregnation of activated charcoal with platinum and ruthenium salts followed by reduction under mixed gas at 500ºC.

PREPARATION OF NOVEL HYDROPHOBIC COATINGS ON SORBENTS

Several novel sorbent materials with hydrophobic coatings were prepared to determine if improved aqueous phase sorption of acetone could be achieved. The hydrophobic coatings were intended to maintain gas filled pores within the sorbent media through minimization of surface wetting by the aqueous phase. This strategy seeks to take advantage of the much higher sorption capacities of common carbonaceous materials for acetone removal from the gas phase, as opposed to aqueous media. Higher sorption capacities in the gas phase are primarily due to decreased competition for sorption sites by water.

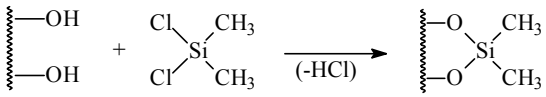
This approach was taken using Carbosieve SIII (a carbogenic molecular sieve), 580-26 coconut-shell based granular activated carbon from Barneby and Sutcliffe (surface area = 1800 m^2/g), and Ambersorb 572 pyrolyzed polystyrene-co-divinylbenzene beads from Rohm and Haas (surface area = 1000 m^2/g) as starting materials. Three hydrophobic coatings were tested. The coating materials included a polytetrafluoroethylene (PTFE) emulsion, and two silylation reagents: dimethyldichlorosilane and n-octadecyldimethylmethoxy-silane

PTFE Coated Sorbents

In separate batches, activated carbon granules and Ambersorb 572 beads were immersed in an emulsion containing ~2.4% PTFE based on the sorbent weight. Upon immersion in the PTFE emulsion, hydrophobic regions on the surface of the sorbents destabilized the emulsion and attracted sections of the $(-CF_2CF_2-)_n$ polymer. These fluoropolymeric segments were then deposited onto the sorbent surfaces. The sorbents were thoroughly rinsed with distilled water and dried at 110°C followed by firing at 300°C under nitrogen for 20 minutes to drive off the wetting agent and bind the PTFE to the surface [5]. In a variation of this approach, the Ambersorb 572 beads were first soaked in hexane to exclude water from internal pores and then exposed to the PTFE emulsion to bind PTFE to the external surface.

Preparation of Hydrophobic Sorbents by Silanization

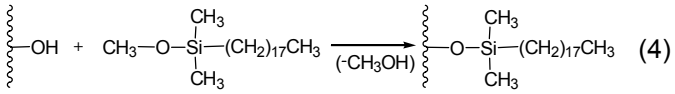
The silanization procedure for the molecular sieve, Carbosieve SIII, utilized 2.19 grams of sorbent placed in a glass column and confined by glass wool end plugs. The column was first rinsed with 200 mL of methanol, followed by 200 mL of toluene. Then 200 mL of a 10% dichlorodimethylsilane solution in toluene was passed through the column at 7.8 mL/min, reacting according to (3). The column was then rinsed with 80 mL of toluene and air dried at 110°C, followed by 4 hours at 200°C under nitrogen to remove residual solvent. Following silanization, the sorbent weight increased to 2.42 g, indicating a substantial surface coverage of dimethylsiloxane groups.



(3)

The Ambersorb 572 pyrolytic activated carbon beads were silanized using n-octadecyldimethylmethoxysilane. The methoxy portion of this molecule reacted with surface hydroxyls on the activated carbon, forming a covalent linkage as shown below in (4). The reaction was carried out in ethanol and catalyzed by the addition of a small amount of sulfuric acid. The C_{18} linkage provided excellent hydrophobicity due to the increase in the alkyl group length. In addition, the larger size of the precursor inhibited penetration of the surface coating into

the interior pores of the sorbent. Following silanization, adsorbed toluene and ethanol were removed by heating in nitrogen to 200°C for one hour.



(4)

CONTINUOUS FLOW CONTAMINANT CHALLENGES

The apparatus used for a variety of continuous flow experiments is illustrated schematically in Figure 1. Primary system components include feed reservoir, peristaltic pump, one or more fixed beds in series, followed by the effluent reservoir. Fixed beds employed in various experiments included immobilized enzymes, heterogeneous catalysts, solid phase reactants, ion-exchange resins and other sorbent media. For acetone challenges both feed and effluent reservoirs were closed to prevent loss through volatilization.

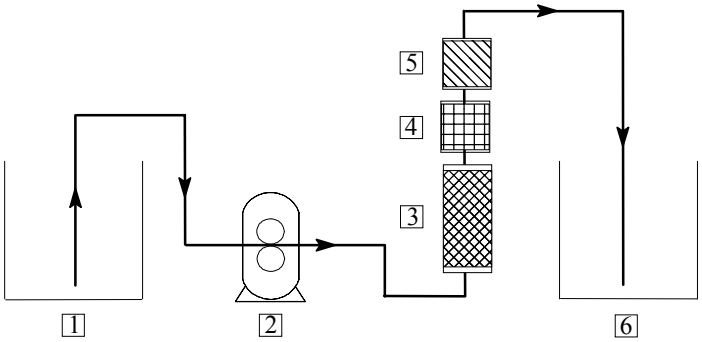


Figure 1. Continuous Flow Test Apparatus: 1- Influent Reservoir, 2- Peristaltic Pump, 3- Fixed Enzyme Bed, 4- Fixed Catalyst Bed, 5- Sorbent Bed, 6- Effluent Reservoir.

ANALYTICAL METHODS

Gas chromatography was used for quantifying methanol, ethanol, acetone, isopropanol and acetaldehyde. An HP 5710A gas chromatograph with a flame ionization detector and a SP1000 packed bed column was used isocratically at 90ºC for separating and quantifying analytes.

Total Organic Carbon (TOC) analyses were used for quantifying ethylene and propylene glycols. An Astro 2001 TOC analyzer was used. Since this analysis does not differentiate between organic analytes, the amount of glycols present in a composite mixture must be determined by difference once the levels of the other ingredients have been determined using gas chromatography.

RESULTS AND DISCUSSION

FIXED BED IMMOBILIZED ENZYME EXPERIMENTS

To confirm efficacy of the enzyme immobilizations, a fixed bed containing 1 g of alcohol oxidase was fed an aqueous stream containing 7.9 mg/L ethanol over a range of flow rates. The relationship between ethanol oxidation and bioreactor residence time is illustrated in Figure 2. Complete conversion of ethanol is evident for contact times ≥ 17 seconds. The results of similar experiments tracking the decomposition of methanol are given in Figure 3. Subsequently, similar beds with other oxidase enzymes were challenged with an aqueous mixture containing 8 mg/L each of acetone, isopropyl alcohol (IPA), ethylene glycol, and propylene glycol. Effluent concentrations of each of these analytes were determined using gas chromatography, with the exception of the glycols which were quantified by taking Total Organic Carbon (TOC) measurements and determining the glycol level by difference. The additional immobilized enzymes included: galactose oxidase, glucose oxidase, ascorbate oxidase, pyruvate oxidase, and amino acid oxidase. Each of these were packed into individual fixed beds containing 1 g of media. The feed solution was sparged with oxygen to bring dissolved O_2 levels to ≈ 40 mg/L. Samples were collected at flow rates of 0.153, 0.729, 1.75, and 3.57 mL/min. No conversion of IPA or acetone was observed.

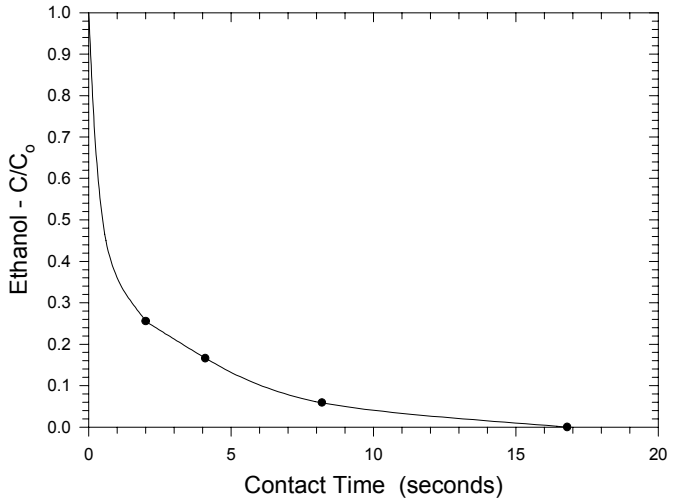


Figure 2. Alcohol Oxidase Catalyzed Ambient Temperature Decomposition of 7.9 mg/L Ethanol Solution.

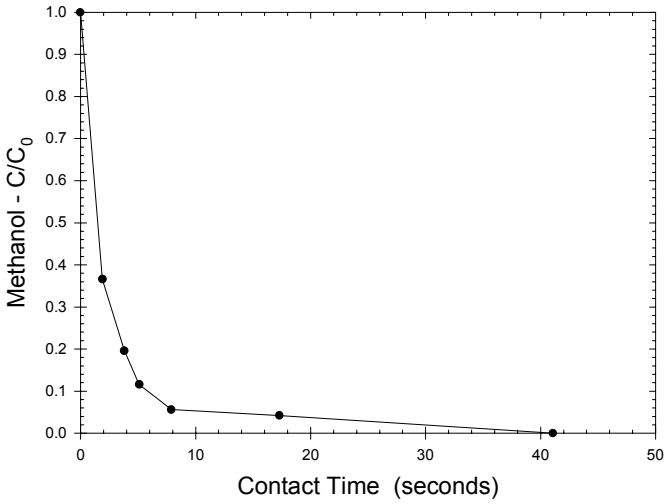


Figure 3. Alcohol Oxidase Catalyzed Ambient Temperature Decomposition of 7.9 mg/L Methanol Solution.

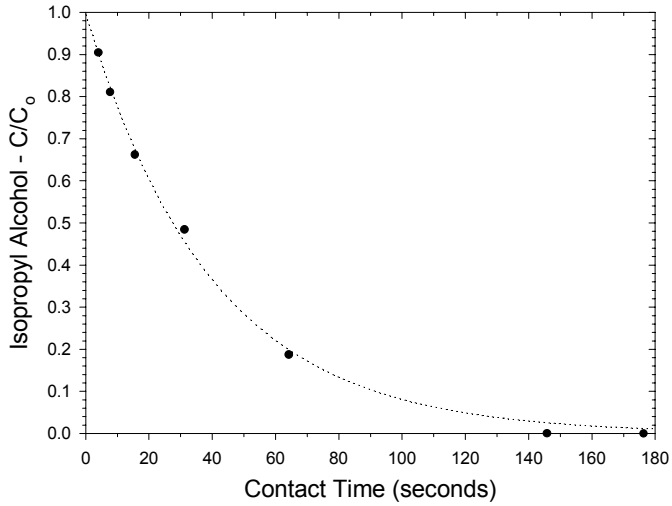


Figure 4. Isopropyl Alcohol Oxidation over RP-121

HETEROGENEOUS CATALYSIS

The original immobilized enzyme bioreactors, developed in the late '80s and early '90s utilized a 1% platinum catalyst bed downstream from the immobilized alcohol oxidase bed to convert the product aldehydes to the corresponding carboxylic acids, which as ionic constituents, are effectively removed from the aqueous stream via mixed IX resins. Since that time, workers in our laboratory have developed significantly more active broad spectrum oxidation catalysts. The most active of these is RP-121, a bimetallic platinum-ruthenium catalyst supported on activated carbon [6-9]. Because alcohol oxidase does not catalyze the destruction of IPA, a fixed bed microreactor containing RP-121 was used to promote the ambient temperature oxidation of this contaminant. A fixed bed containing 20 cm^3 of catalyst was challenged with an aqueous influent containing 7.9 mg/L IPA over a range of flow rates. Figure 4 illustrates the relationship between IPA conversion and reactor residence time at 25°C. Decomposition of IPA, as indicated by the disappearance of the IPA gas chromatographic peak, was achieved for residence times longer than 2.5 minutes.

The decomposition of glycols was initially investigated using a composite bioreactor consisting of a 1.7 cm^3 immobilized galactose oxidase bed, followed by a 1.7 cm^3 RP-121 catalyst bed, a 1.6 cm^3 strong base IX resin (Picopure 400), and a strong acid cation exchange resin (Picopure 100), in series. The intention was for the enzyme bed to catalyze the oxidation of glycols to aldehydes, followed by oxidation of aldehydes to organic acids in the noble metal catalyst bed, followed by sorption of the ionic products by the mixed ion-exchange resins.

The composite bioreactor was challenged with a 22.2 mg/L glycol solution at an initial flow rate of 0.4 mL/min. Activity of the system was monitored by effluent TOC concentration. The system initially resulted in complete decomposition of the glycol. Subsequent experiments revealed that, while galactose oxidase is known to have some activity toward glycol oxidation, the RP-121 bed was responsible for virtually all of the observed catalytic oxidation. The enzyme bed was removed from the system with no effect in the overall destruction of the glycols. The relationship between reactor residence time and decomposition of ethylene glycol is shown in Figure 5.

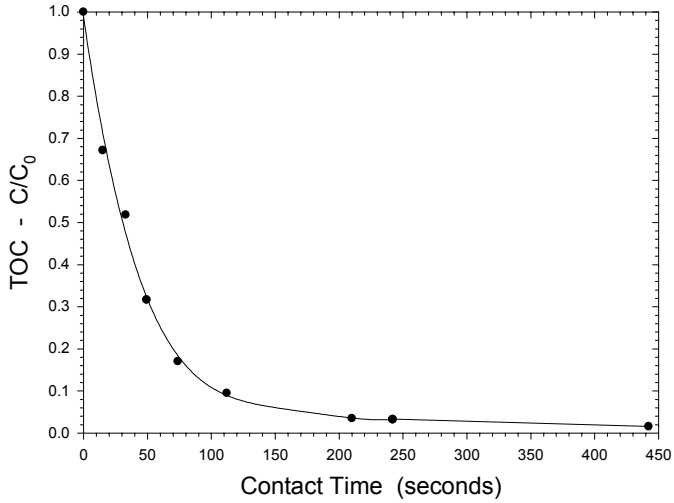


Figure 5. Ethylene Glycol Oxidation over RP-121

The ambient temperature oxidation of propylene glycol over the RP-121 catalyst was evaluated in sequential beds containing the RP-121 catalyst, strong base anion exchange resin (Picopure 400), and strong acid cation exchange resin (Picopure 100). The bed volumes were 7.5, 2, and 2 cm^3, respectively. The challenge solution contained 20.7 mg/L propylene glycol (TOC = 9.8 mg/L).

In the first challenge, the influent was saturated with air for a dissolved oxygen concentration of ~8 mg/L. The fractional TOC in the effluent versus contact time is shown in Figure 6. At long contact times, greater than 95% of the TOC due to propylene glycol was removed by combined oxidation and ion exchange.

The oxidation followed first order kinetics initially, but at longer contact times a TOC reduction limit appears to have been reached. Lower oxidation rates at longer contact times were attributed to insufficient dissolved oxygen. Consequently, a second challenge utilized 20.7 mg/L propylene glycol containing ~40 mg/L of oxygen. The experimental results are shown in Figure 7. The oxidation closely followed first order kinetics with a least squares correlation coefficient, r^2 = 0.9983. The first order reaction rate constant is 0.0551 s^{-1}.

These results indicate rapid oxidation of propylene glycol at ambient temperature, forming constituents which are effectively removed by ion exchange. Importantly, propylene glycol was present in the humidity condensate feed to the potable water MF train during Stage 4/5 potable water processor tests, and was identified as a major constituent of the MF train effluent [10,11].

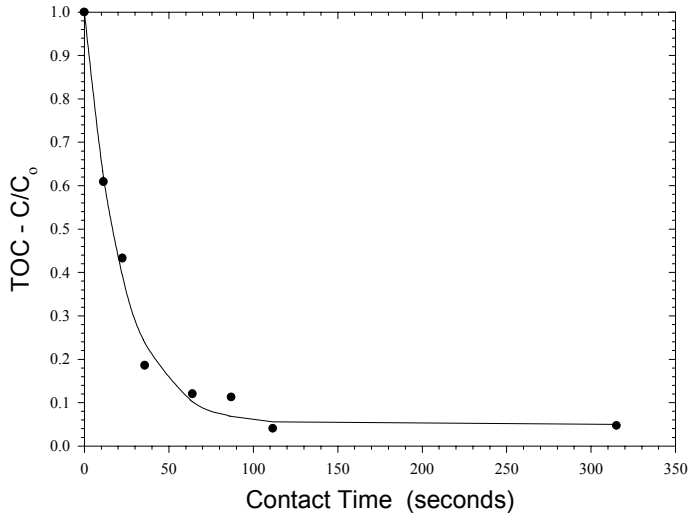


Figure 6. Propylene Glycol Oxidation over RP-121

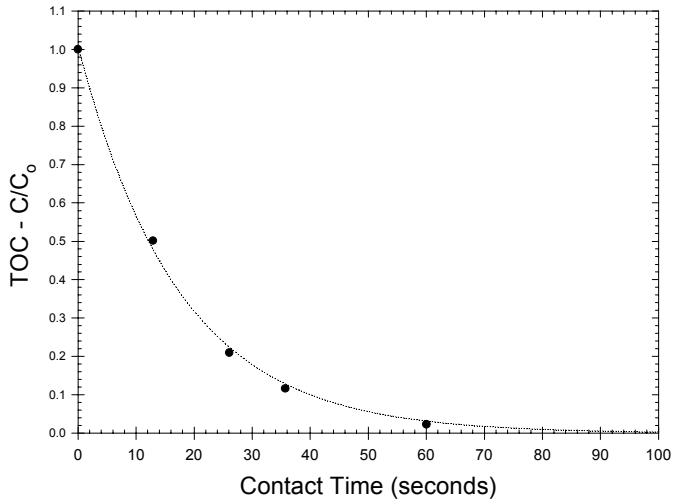


Figure 7. Oxidation of 20.7 mg/L of Propylene Glycol (1,2-propanediol) over RP-121 Catalyst Using Oxygen as the Oxidant.

ACETONE SEPARATION USING HYDROPHOBIC SORBENTS

Since the enzymatic or heterogeneous catalytic oxidation of acetone proved unsuccessful, its removal by sorption was evaluated. Although several forms of activated carbon have been proven to be effective in the gas phase, the aqueous removal of acetone by these sorbents has been less successful. The poorer sorption from an aqueous environment is attributed to competition of water molecules for binding sites. As a strategy to improve acetone sorption, these media were coated with hydrophobic surface coatings to prevent liquid water from entering the pores. Even when these media are in direct contact with water, their interiors remain unwetted, allowing gas phase equilibria to drive the acetone sorption. Several hydrophobic carbonaceous sorbents were evaluated. In each case, a thin hydrophobic coating composed of bound aliphatic or other hydrophobic organic groups covers the surface of sorbent media. The hydrophobic surface layer prevents water from penetrating into the interior pores of the sorbent. In principal, acetone will diffuse from the aqueous phase through the hydrophobic surface coating into the gas-filled pores where sorption equilibrium strongly favors partitioning to the solid phase from the gas.

This approach was evaluated for three sorbents: (1) Carbosieve SIII, a carbogenic molecular sieve with a pore size which favors acetone adsorption; (2) a high surface area activated carbon (~ 1,800 m^2/g); and (3) Ambersorb 572, a high surface area carbonaceous material formed by the pyrolysis of polystyrene-co-divinylbenzene beads (surface area = 1000 m^2/g). Three hydrophobic coatings were tested: polytetrafluoro-

ethylene (PTFE), dimethyl-siloxane, and n-octadecyl-dimethylsiloxane.

Fixed beds containing 2 g of each uncoated and hydrophobically coated sorbent were challenged with 15.8 mg/L of acetone at a flow rate of 1.0 mL/min. Acetone levels as a function of cumulative throughput were determined by gas chromatography. All sorbents showed lower sorption capacities for the coated sorbents compared to the uncoated media. As an example, the breakthrough curves for coated and uncoated Ambersorb 572 are shown in Figure 8. The reason for lower acetone capacities on the hydrophobically coated sorbent was unclear, although slow gas adsorption kinetics, pore blockage, and passivation of the sorption site by the hydrophobic species were considered potential mechanisms.

An unexpected result of these experiments was the relatively high acetone loading capacity of uncoated Ambersorb 572 which adsorbed 0.95% of its weight in acetone. This is much higher than was achieved with other carbonaceous sorbents, especially given the relatively low acetone concentration. This significant sorption capacity strongly suggested the possibility of removing dissolved acetone at ambient temperature with sorbents, provided that the capacity is predictable and the sorbent bed size falls within acceptable limits. Superficially, the ability to adsorb ~1 g of contaminant per 100 g of sorbent is close to the nominal 3% loading of MF beds. As a result, an integrated system containing untreated Ambersorb 572 as an acetone sorbent was tested.

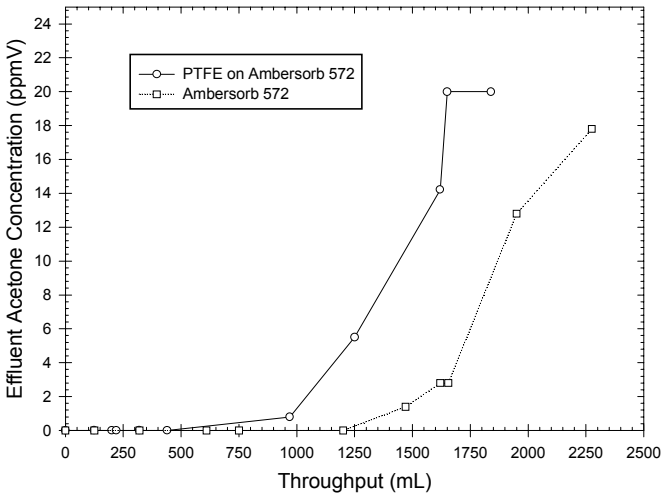


Figure 8. Acetone Breakthrough Curves for Uncoated and PTFE Coated Ambersorb 572 Beads.

INTEGRATED COMPOSITE IMMOBILIZED ENZYME BIOREACTOR TESTS

The combination of alcohol oxidase and RP-121 fixed beds was shown in preliminary tests to oxidize primary alcohols and glycols, yielding by-products that are easily removed by ion exchange. In addition, the RP-121 catalyst also oxidizes isopropyl alcohol, forming acetone. Thus the effluent from these two beds in series contains acetone as the primary remaining contaminant. Under these conditions, the removal of acetone by sorption becomes much more feasible since competition with other sorbates is eliminated. Also, as a single component system, sorption becomes much more predictable. An integrated system was assembled to evaluate this concept. The system contained sequential beds designed to remove all contaminants in the challenge solution, with the exception of acetone, followed by a single sorbent bed designed to remove acetone. A schematic of the integrated system is shown in Figure 9. The sequence of media consisted of a 1 cm^3 bed of alcohol oxidase, followed by a 10 cm^3 (4.84 g) bed of the RP-121 catalyst, a 2 cm^3 bed of strong base anion exchange resin (Picopure 400), a 2 cm^3 bed of strong acid cation exchange resin (Picopure 100), and a 10 cm^3 (4.38 g) bed of Ambersorb 572. The challenge solution contained 5 mg/L each of methanol, ethanol, acetone, isopropanol, and ethylene glycol. The flow rate was maintained at 1 mL/min for most of the test, although flow rates as high as 3.7 mL/min were used. The TOC concentration of this solution was 12.5 mg/L, with acetone and isopropanol which when oxidized forms acetone representing approximately half of the organic carbon (6.1 mg/L).

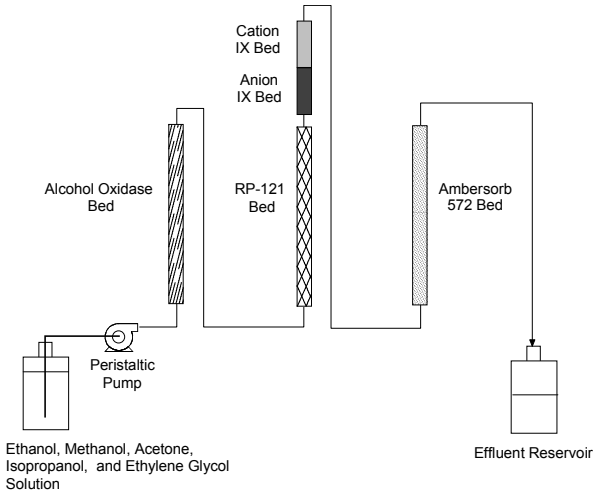


Figure 9. Integrated Bioreactor with Acetone Separation by Adsorption.

The TOC levels of the effluent were then monitored as a function of throughput. The results of this experiment are shown in Figure 10. The effluent TOC concentrations were less than 0.5 mg/L, the NASA potable water limit, during the first 4000 mL of

throughput. The values ranged from 0.17 to 0.47 mg/L. After 4000 mL of throughput, the effluent TOC level began to rise, indicating breakthrough of acetone. The total adsorbed acetone was calculated, assuming that the total acetone influent to the Ambersorb 572 bed was the sum of the influent acetone plus the isopropanol level. Based on this assumption, the total acetone concentration at the inlet to the Ambersorb 572 bed was 9.83 mg/L (TOC = 6.1 mg/L). Since acetone breakthrough occurred after 4000 mL of throughput, 4.38 g of Ambersorb 572 adsorbed 39.3 mg of acetone, or 0.90 % by weight. This correlates well with the results of an earlier experiment (see Figure 8) in which the Ambersorb 572 sorbent was fed 15.8 mg/L of acetone and the sorbent loading was 0.95 % by weight. These results indicated that the performance of a sorbent bed placed at the end of sequential enzyme, heterogeneous catalyst, and ion exchange beds is both predictable and practical in terms of bed size.

A sorbent bed with an acetone sorption capacity of ~1% by weight can process the expected levels of acetone plus oxidized isopropanol present downstream of the MF train, without an excessive increase in the overall quantity of expendable sorbents. For example, if the mass of expendable sorbents required to process water by MF is 3% by weight, then 1000 g of water will require 30 g of sorbent. If the acetone plus oxidized isopropanol concentration in the water is 10 mg/L, then 10 mg of acetone must be adsorbed by the Ambersorb 572 sorbent. Based upon a 1% sorption capacity, this will require 1 g of sorbent, which corresponds to 3.3% of the total expendable sorbent requirement.

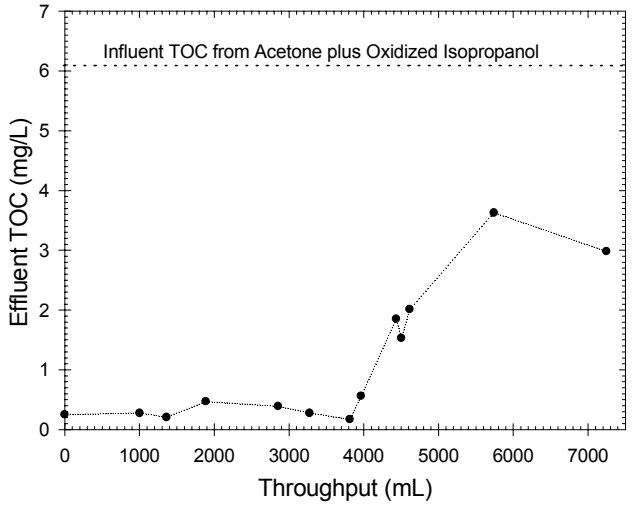


Figure 10. Effluent TOC for Integrated System with Acetone Removal by Ambersorb 572.

CONCLUSION

A simple ambient temperature composite immobilized enzyme bioreactor system can be employed to remove all problematic organic contaminants present in an ISS composite wastewater simulant. Furthermore, these preliminary studies indicated that the system mass and volume will be reasonable in comparison to the current generation of expendable sorption media employed in the ISS water processor. Significant accomplishments included the identification of effective ambient temperature catalytic methods for oxidation of ethylene glycol, propylene glycol, and isopropyl alcohol; and demonstration of acetone removal by adsorption. An integrated system with subsystems for enzyme catalyzed oxidation, heterogeneous catalytic oxidation, and removal of ionic reaction by-products was evaluated and shown to be fully capable of treating simulated ISS MF effluents to produce water meeting NASA's TOC limits for drinking water.

ACKNOWLEDGMENTS

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