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# EFFLUENT DISCHARGE
# CHEMICAL DEMILITARIZATION ALTERNATE TECHNOLOGY RESEARCH
# HD CHEMICAL NEUTRALIZATION AND BIO-TREATMENT



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A review was undertaken to establish technical regulatory guidance on the discharge of waste, to a Federally Owned, or Publicly Owned Treatment Works, resulting from the neutralization and biodegradation of HD mustard agent. This report is a review of specific and general pretreatment requirements, proper hazardous waste exclusion, and statute and regulatory prohibition on discharge of chemical warfare agent. A waste water discharge resulting from the proper treatment of chemical warfare agent, which destroys the agent and reduces toxicity, can meet applicable federal, state, and local discharge standards and laws.

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## PREFACE

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The work described in this technical note was authorized under Sales Order No. 5605L6R2-01, in support of the U.S. Army Chemical Demilitarization and Remediation Activity, Program Manager for Chemical Demilitarization Alternative Technologies Program. A recommendation for waste disposal is rendered to the program after technical review of federal, state, and local regulations. This work was started in September 1995 and completed in February 1996.

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CONTENTS

## FIGURES



## TABLE

## EFFLUENT DISCHARGE

## CHEMICAL DEMILITARIZATION ALTERNATE TECHNOLOGY RESEARCH

## HD CHEMICAL NEUTRALIZATION AND BIO-TREATMENT

1. PURPOSE

This paper will detail the necessary gates that must be opened to meet a regulatory compliant waste water discharge from the Alternate Technology (Alt Tech) chemical neutralization and bio-treatment operations to a Publicly Owned Treatment Works (POTW), or a Federally Owned Treatment Works (FOTW). The four major elements to be considered are: 1) Specific Pretreatment Standards. 2) General Pretreatment Standards for POTWs-Treatability and Toxicity, 3) Proper Hazardous Waste exclusion. 4) Statute and regulatory prohibition on discharge of radiological, chemical, or biological warfare agent.

2. PRETREATMENT BACKGROUND INFORMATION: PROHIBITED DISCHARGES

Standards for the discharge of pollutants to sewer treatment systems are governed by section 403 of the Code of Federal Regulations. This section is titled the General Pretreatment Regulations. The purpose of these regulations is to control pollutants which pass through or interfere with treatment processes in POTWs, (also may apply to FOTWs), and to protect the sewer system, treatment plant and water quality of the receiving stream. This is achieved by the following:

a. Specific numerical discharge standards - These are technological standards applied to specific pollutants to ensure treatability of that pollutant prior to discharge. Technological standards are developed by various methods including: Removal efficiency studies on specific pollutants, toxicity tests, and treatability tests. Numerical standards are site specific except for the following federally prohibited discharge standards: Flash point less than 140 degrees F, pH less than 5.0, and discharges that raise the waste water temperature of the treatment plant greater than 104 degrees F.

b. Specific narrative discharge standards - These standards are statements in the regulation which establish good operating conditions at the treatment plant. Prohibitions are stated against causing obstruction and structural damage in the sewer, causing the presence of toxic gasses and vapors in quantities that may cause worker health and safety problems, or causing the plant bio mass to die, etc.

c. General Prohibition on Pass Through - "Pass Through" is a legal term which means: A

discharge which exits the POTW into waters of the United States in quantities of concentrations which, alone or in conjunction with a discharge or discharges from other sources, is a cause of a violation of any requirement of a Clean Water Act (CWA) discharge permit (40 Code of Federal Regulations (CFR) 403.3 (n)).

d. General Prohibition on Interference - Interference is a legal term which means: A discharge which, alone or in conjunction with a discharge or discharges from other sources, inhibits or disrupts the POTW, its treatment processes or operations, or its sludge processes use or disposal which is a cause of the violation of the POTWs discharge permit. Interference is also caused when the planned use of sludge disposal or use is out of compliance with federal state, or local statutory provisions (40 CFR 403.3(I)).

3. DEFINITIONS AND APPLICATIONS (40 CFR 122.2)

a. National Pollutant Discharge Elimination System (NPDES) Permit is a national permitting system which regulates the discharge of pollutants into the waters of the United states. This system is used to permit the operations of POTWs and FOTWs.

b. Discharge of Pollutants means: Any addition of any pollutant or combination of pollutants to the "Waters of the United States"... This term does not include an addition of pollutants by any "indirect discharger".

c. Indirect Discharger means: a non-domestic discharger introducing pollutants to a "Publicly Owned Treatment Works".

d. Waters of the United States or Waters of the U.S. Means: All waters which are currently susceptible to use in interstate or foreign commerce, including all waters which are subject to the ebb and flow of the tide; ...including wetlands...all waters such as intra-state lakes, rivers. streams, mudflats, prairie potholes..... Waste systems including treatment ponds or lagoons designed to meet the requirements of the Clean Water Act....are not waters of the United States. (Read: Waters in sanitary sewer systems leading to POTWs are not waters of the United States).

e. FOTW means: (The following Definition is given in the Federal Facilities Compliance Act (FFCA).) A facility owned by any Agency or Department of the Federal government that treats wastewater, a majority of which is domestic sewage. Although "majority" is not defined in the FFCA, it is assumed that to qualify as a FOTW, the treatment plant must treat more than 50% domestic waste by flow volume.

f. POTW means: a treatment works which is owned by a State or municipality...This definition includes any devices and systems used in the storage, treatment, recycling and reclamation of municipal sewage or industrial wastes of a liquid nature.

4. PRETREATMENT REQUIREMENTS FOR DISCHARGE INTO A POTW AND AN FOTW

a. The NPDES permitting system establishes the requirements for general pretreatment guidelines, which includes numeric and narrative discharge standards. The purpose of pretreatment guidelines is to prevent "passthrough" and "Interference", protect the integrity of the sewer system and treatment plant, and preserve the water quality of the receiving stream.

b. All POTWs, that have a total design flow greater than 5 million gallons per day and receive industrial users pollutants which may passthrough or Interfere with the operation of the POTW, must develop a pretreatment program. Pollutants that are discharged to a POTW must be in compliance with general federal prohibitions (prevention of passthrough and interference), specific federal prohibitions (numeric and narrative standards), and specific local limits (developed as necessary, which includes the toxicity of the pollutant as it affects the operation of the POTW plant and as it affects the receiving stream).

There are additional special conditions for sending liquid waste to an off-site POTW which may contain hazardous waste. These conditions are governed by 40 CFR 437 - Effluent Guidelines, Pretreatment Standards, and New Source Performance Standards: Centralized Waste Treatment Category.

c. Waste subject to the Resource Conservation and Recovery Act (RCRA) can be discharged to a POTW only by being in compliance with all pretreatment regulations. In addition, the discharger shall certify that it has a program in place to reduce the volume and toxicity of hazardous waste generated to the degree it has determined to be economically practical. The RCRA waste is exempted from RCRA regulation and covered by CWA regulations by way of the domestic sewage exemption, which was established by Congress. The exclusion provides that solid or dissolved material in domestic sewage is not a solid waste as defined in RCRA. The waste generator must give notification, of intent to discharge RCRA waste to the POTW, to Federal, and State officials (40 CFR 403.12 p.1).

d. Discharges to Army Owned sewage treatment works, which are FOTWs, follow Army policy which states, "...discharges to Army-owned treatment facilities will comply with all pretreatment regulations applicable for discharges to POTWs" AR200-1, 3-3.e(1). This Army policy makes it a requirement for all FOTWs to follow all applicable POTW regulations but does not qualify FOTWs for POTW exemptions. Discharges to FOTWs are not automatically excluded from the definition of hazardous waste. However, the FFCA establishes hazardous waste exclusions in section 108 of the Act. Such discharges are exempt if four conditions are met:

1) "The solid or dissolved material and, subsequently, the wastewater discharge, is subject to a pretreatment standard issued under section 307 of the CWA and the discharge is in compliance with the standard." Which means: an effluent standard must be established for

all hazardous constituents in the waste, and the discharge must be in compliance with those standards.

2) "The solid or dissolved material and, subsequently, the wastewater discharge, comes from an industrial pretreatment facility in an effluent category for which the EPA Administrator has established a schedule for developing a standard." Which means: Hazardous wastes that is in a discharge which is subject to categorically specific effluent guidelines, and is treated in a pretreatment facility, is exempt.

3) "The solid or dissolved material is not covered under the first two conditions and it is not prohibited from land disposal under subsections (d), (e), (f), or (g) of section 3004 of the Solid Waste Disposal Act (SWDA) because it has been treated in accordance with subsection (m) of section 3004 of the SWDA."

The SWDA 3004(m) required EPA to develop levels and methods of treatment required for land disposal. These levels of treatment are found in regulation 40 CFR 148 and 40 CFR 268. This condition means that any waste discharged with the hazardous waste exclusion, to a FOTW, can not contain any constituents prohibited from land disposal, or it contains a land disposal-prohibited waste at a concentration below that found in the land disposal treatment standards.

4) "The solid or dissolved material is generated by a household or person which generates less than 100 Kilograms of hazardous waste per month. This exclusion does not hold if the solid or dissolved material would otherwise be acutely hazardous waste." This condition exempts small quantities of non acute hazardous waste generated by a person or a household.

## 5. SPECIAL CONSIDERATIONS FOR LIQUID WASTE DISCHARGED FROM MILITARY CHEMICAL/BIOLOGICAL TREATMENT SYSTEMS SUBJECT TO CWA

The Clean Water Act and the Code of Federal Regulations 40 CFR 122.4 prohibit "....The discharge of any radiological, chemical, or biological warfare agent or high-level radioactive waste..." This prohibition pertains to the discharge of subject waste to the "Waters of the United States". There are two issues that must be addressed as this prohibition applies to waste generated by the Alternate Technology Program: 1) Can Chemical/Biological warfare agent be successfully treated with the resultant waste discharged to the Waters of the U.S.? 2) Neither the CWA nor Federal regulation define "any". If it is assumed "any" means zero, what is the appropriate method to establish an enforceable zero discharge number?

1) The following legal opinion was issued by Environmental Law Advisor, P Gieseking, on the interpretation of section 301(f) of the CWA: "Section 301(f) of the CWA states that, "[notwithstanding any other provisions of this chapter it shall be unlawful to discharge any radiological, chemical, or biological warfare agent, ... into the navigable waters". Section 102 (a)

of the Marine Protection, Research and Sanctuaries Act (MPRSA) includes a similar provision that no permit for ocean dumping may be issued with respect to radiological, chemical, and biological warfare agents. A general counsel opinion from the U.S. Environmental Protection Agency (EPA), dated 21 April 1977, clarifies the application of section 102 (a) of the MPRSA to high temperature incineration of Herbicide Orange, an analogous situation to the neutralization and bioreaction of the chemical agent mustard. This opinion explains that the high temperature incineration of Herbicide Orange will not violate section 102 (a) of the MPRSA because the products of the incineration are not closely related to the original technical ingredients. The "nature of the waste changes dramatically" so that EPA does not consider the Herbicide Orange to be a chemical or biological warfare agent after the incineration." Preliminary waste characterization of HD neutralization followed by biodegradation show a similar situation with the HD hydrolysis products being dramatically different than the original HD.

2) The question of the CWA use of the word "any", meaning "zero", is addressed in the draft EPA document: National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels. This document is produced by EPAs office of wastewater enforcement and compliance.

The purpose of the document is to make recommendations for calculating interim "minimum levels" (MLs) when promulgated MLs for a particular analytical method do not exist. The ML is the concentration at which the entire analytical system must give a recognizable signal and acceptable calibration point. This concentration is based on the "Method Detection Point", which is the minimum concentration of analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, as determined by 40 CFR 136.

Water quality based effluent limits (WQBEL) are used when technology-based effluent guidelines are deemed not stringent enough to protect the quality of the receiving stream. The WQBELs are a system to control the release of toxic pollutants, "No toxic pollutants in toxic amounts." Guidance is given to express water quality permits as calculated WQBELs, based on health effects. When these limits are set below quantitation levels (MLs), the ML is used as the quantitation level and is included in the permit as a footnote to the WQBEL. According to EPA guidance, "Analytical results which fall below the ML should be reported as "0"." This gives the Alternate Technology Program guidance for discharge quantitation with a WQBEL set at "Zero". This approach is being used as a legally defensible compliance tool by EPA Region VI for dioxin limits.

## 6. PRETREATMENT EFFLUENT CHARACTERIZATION FOR HD NEUTRALIZATION AND BIO-DEGRADATION LAB SCALE SAMPLE BR8

Liquid waste discharged to any POTW or FOTW must meet National pretreatment standards: Prohibited discharges. Specific prohibitions include flash point, pH, technological based local limits, hazardous waste characterization (TCLP), narrative standards pertaining to material damage to the system, and health affects to workers. General prohibitions state the

prevention of passthrough and interference. Sample BR8 has been tested and is in compliance with specific applicable prohibitions, for discharge to the Edgewood Area Sewage Treatment Plant. The following will focus on the toxic nature of the waste stream in an attempt to satisfy the general pretreatment prohibitions of passthrough and interference, and ensure POTW/FOTW receiving stream water quality.

Munitions grade mustard (HD, 1% by volume) was hydrolyzed in water then neutralized with sodium hydroxide. The resulting hydrolysate was analyzed and found to contain thiodiglycol (92%) and a mixture of ethers and alcohols. The hydrolyzed mixture (fed stock) was placed into batch bio-reactors seeded with bio-mass from various water treatment facilities. Toxicity studies were conducted on the effluent from the bio-reactors and on hydrolyzed HD. Results were compared to determine if the biodegradation process effected the toxicity of hydrolyzed mustard. Toxicity was determined by conducting bio-assays using Artemia salina (brine shrimp), Photobacterium phosphoreum (MICROTOX), Daphnia magna (water flea) , Cyprinodon variegatus (sheepshead minnow) and sewage treatment plant bio-mass (Test results are presented in Table 1). The bio-reactor process decreased the toxicity of the hydrolyzed HD for the P. phosphorem, but did not affect it for the daphnia. In an attempt to prove that the salt concentration (NaOH used for neutralizing hydrolyzed HD) was the cause of toxicity to daphnia, assays were conducted using thiodiglycol in fresh water and in salt water. When daphnia were exposed to solutions of thiodiglycol without salt, the toxicity was reduced approximately 25 %. Also, the toxicity of salt water to daphnia was similar to hydrolyzed HD and bio-reactor effluent. The thiodiglycol and salt water test results suggest that the toxicity of bio-reactor effluents to daphnia are caused by the salt concentration.

Only preliminary range finding tests exposing sheepshead minnows to bio-reactor effluents have been run. The preliminary result indicate that the EC50 will range between 80 and 90 %. Since the possibility exist that the bio-reactor effluent will be discharged to the sanitary sewer, aquatic life at the end of the process pipe will be receiving non- acclimated batch exposures. Therefore the minnows were not pre- acclimated to the test solution. Much of the toxicity to the sheepshead minnow is assumed to be associated with acclimation effects and the lack of necessary dissolved minerals to maintain physiological salt balance.

Bio-mass samples from the Gunpowder Neck Waste Water Treatment Facility were grown in hydrolyzed mustard and in bio-reactor effluent (Figure 1 & 2). Bio-mass growth was stimulated in both the hydrolyzed HD and the bio-reactor effluent. On the average the hydrolyzed mustard stimulated bio-mass growth 6.5 %, while the bio-reactor effluent stimulated bio-mass growth up to 31 %. However, the differences in the mean growth values among treatment groups were not enough to exclude the possibility that the difference is due to random sampling variability. Therefore, the amount of stimulated bio-mass growth in hydrolyzed mustard as well as bio-reactor effluent was not significantly different than the control growth.

Waste load allocation and exposure limits to the Waters of the U.S. are determined by site specific criteria for both specific toxicants and treatment plant whole effluent-toxicity. The

criteria will be set by EPA and/or State standards and methodology.

7. CONCLUSIONS

a. Data analysis of sample BR8 show this sample to be in compliance with specific Federal discharge prohibitions: 40 CFR 403.5(b)

1) pH > 5.0

2) Closed Cup Flash Point less than 140 degrees Fahrenheit

3) Heat (Effluent Temperature) < 104 Fahrenheit

4) No damage to facilities and operations, adverse health affects, etc. is expected

5) Waste is expected to have no "Land Ban" listed chemicals after Bio-treatment (for FOTW discharge)

b. Toxicity data and bacterial growth study on the treatment plant bio-mass indicate this waste stream will be in compliance with the general prohibitions of passthrough and interference.

c. The sample was tested for RCRA hazardous constituents (TCLP) and with negative results. Characteristic hazardous properties are also not displayed. Hazardous waste exclusions must be met in States that have Agent listed as a hazardous waste because it is "derived from the treatment of a hazardous waste". The above guidance details the process of discharging hazardous waste to a POTW/FOTW. Each discharge exclusion process is site specific as it pertains to the hazardous constituent and the local treatment plant regulations.

d. Understanding of the statue and regulatory prohibitions on the discharge of warfare agent is addressed by legal review and the regulatory framework. The EPA has recognized that waste resulting from the treatment of warfare agent to a quantitative zero point, with the warfare agent being substantially changed in nature and toxicity, can be discharge to the waters of the U.S.

e. The Alternate Technology Program should proceed with all applicable waste characterization of treatment effluent, including toxicity studies. Preliminary testing results show HD/Water to be a possible candidate for a liquid waste water discharge to a POTW or FOTW.

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## REFERENCES


1. Code of Federal Regulations 40 Sections 122, 148, 266, 268, 403, 437.

2. Technical Support Document for Water Quality-based Toxics Control, EPA-440/4-85-032.

3. National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels, Draft 22 Mar 94.

4. Water Quality Information Paper No. 48, CHPPM, MCHB-ME-WMCH.

5. MEMORANDUM FOR AMCPM-CDO, Clean Water Act Interpretation, 12 Jun 95, AMSCB-GC.

6. Toxicological Data Provided by ERDEC, Research Technology Branch, Environmental Technology Team.

Table 1. Aquatic Toxicity Test Results

The results are presented as $EC_{50}$ values (% vol./vol. concentration that induce a response equal to 50 % of the control response) calculated by using a Least Squares Regression analyses and Probit analyses.

| Organism | Test Duration | Hydrolyzed HD | Bio-Reactor Effluents | 1 % Thiodiglycol in $H_2O$ | 1 % Thiodiglycol in NaOH | Salt $H_2O$ |
|---|---|---|---|---|---|---|
| MICROTOX | 5 min. | 1.4 % | N.T. | 44.6 % | 49.4 % | N.T. |
| Brine Shrimp | 24 hr | N.T. | N.T. | N.T. | 93.0 % | N.T. |
| Daphnia | 48 hr | 32.3 % | 33.3 % | 73.0 % | 17.9 % | 34.0 % |
| Fish | 96 hr | --- | 80 -90 % (Testing in Progress) | --- | --- | N.T. |
| Bio-Mass | 7 hr | N.T. | N.T. (Stimulated Growth) | --- | --- | --- |
| Salt Concentration | | 15 ppm | 16 ppm | 0 ppm | 16 ppm | 16 ppm |

N.T. - The solution was not toxic up to 100 %.

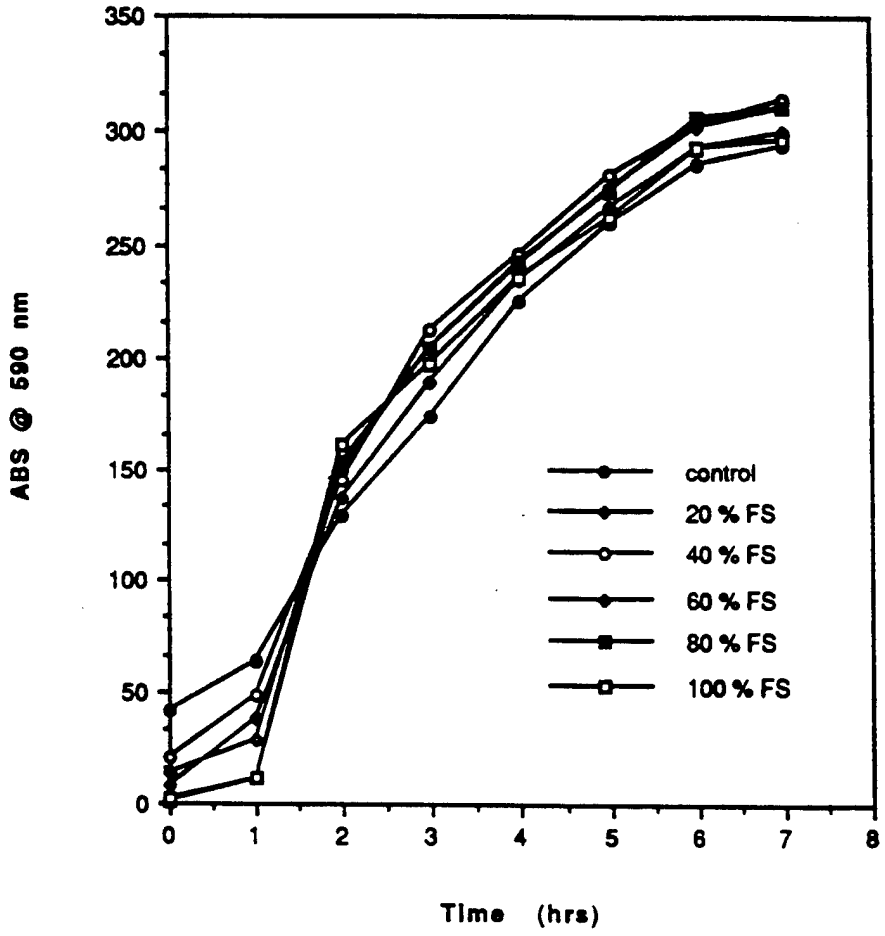


Figure 1. Treatment Plant Bio-Mass Growth on $H_2O$ Hydrolyzed HD

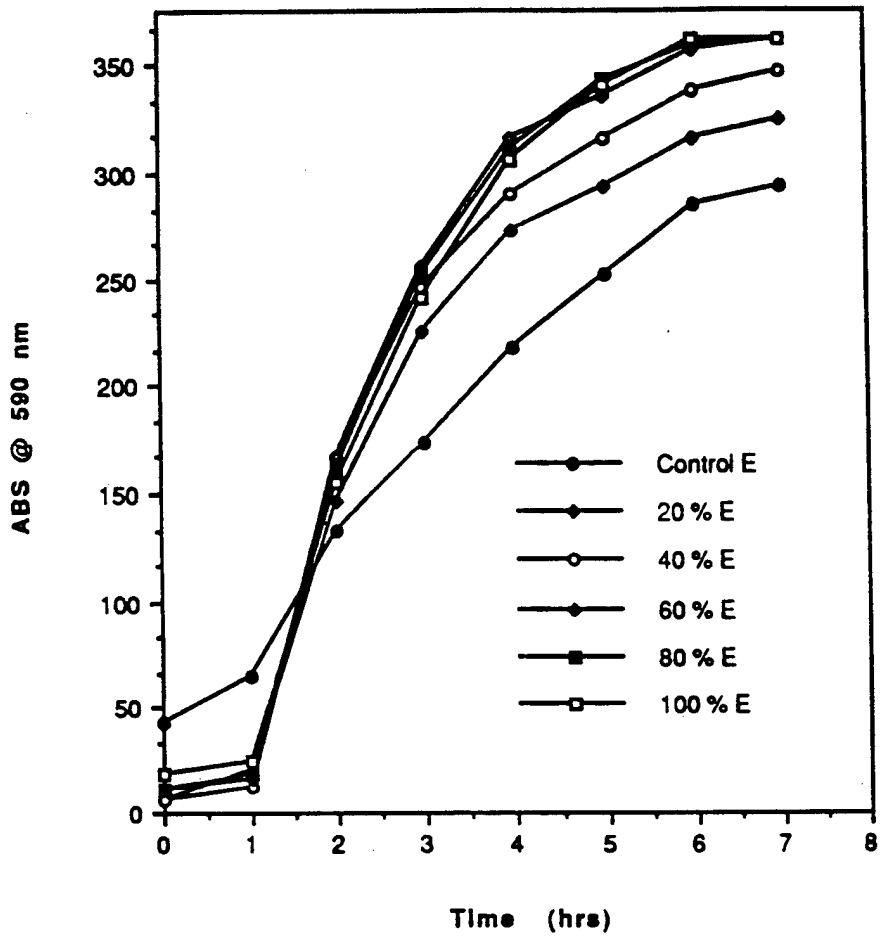


Figure 2. Treatment Plant Bio-Mass Growth on HD Bio-Reactor Effluent