August 4, 1999

Federal Energy Technology Center
AAD Document Control
U.S. Department of Energy
PO Box 10940, MS 921-143
Pittsburgh, PA 15236-0940

Dear AAD Document Control

Subject: Final Topical Report for "Removal of Organic Pollutants from Subcritical Water with Activated Carbon" – Task 1.1
DOE Contract No. DE-FC26-98FT40320; UND Fund 4401

Please find enclosed one copy of the final topical report for the subject project. A draft copy was submitted to the performance monitor on April 30,1999. No changes were required; therefore, we are enclosing the final report with the Request for Patent Clearance for Release of Contracted Research Documents and the electronic copy on diskette.

If you have any questions regarding this submittal, please call me at (701) 777-5124, fax at (701) 777-5181, or e-mail at slandis@eerc.und.nodak.edu.

Sincerely,

Sheryl E. Landis
Manager, Contracts and Intellectual Property
Business and Operations

SEL/mjj

Enclosures

FETC F 2050.4#
(02/98) OPI=PS10
(Previous Editions Obsolete)

U.S. DEPARTMENT OF ENERGY
Federal Energy Technology Center

REQUEST FOR PATENT CLEARANCE FOR RELEASE OF CONTRACTED RESEARCH DOCUMENTS

TO:

■ For Technical Reports
AAD Document Control
U.S. Department of Energy - FETC
MS 921-143
P.O. Box 10940
Pittsburgh, PA 15236-0940

For Technical Papers/Journal Articles/Presentations
Mark P. Dvorscak
U.S. Department of Energy
9800 S. Cass Avenue
Argonne, IL 60439
FAX: (630) 252-2779

♦Contract Agreement No.
DE-FC26-98FT40320

Name & Phone No. of DOE COR
Ms. Paula Flenory
(412) 386-4781

A. CONTRACTOR ACTION (CONTRACTOR COMPLETES PART A. 1-5)

1. Document Title: Task 1.1 – Removal of Organic Pollutants from Subcritical Water with Activated Carbon; Fund 4401

2. Type of Document: Technical Progress Report ■ Topical Report Final Technical Report
Abstract Technical Paper Journal Article Conference Presentation
Other (please specify): _____

3. Date clearance needed: _____

♦4. Patent information.

Yes	No	
	■	Is any patentable subject matter disclosed in the report?
	■	If so, has an invention disclosure been submitted to DOE Patent Counsel? If yes, identify disclosure number or DOE Case Number _____
	■	Are there any patent-related objections to the release of this report? If so, state the objections.

_____

_____

♦5. Signed _____ Date _____
(Contractor)

Name & Phone No. Sheryl E. Landis (701) 777-5124

Address Energy & Environmental Research Center, PO Box 9018, Grand Forks, ND 58202-9018

B. DOE PATENT COUNSEL ACTION

Patent clearance for release of the above-identified document is granted.
Other: _____

Signed _____ Date _____
(Patent Attorney)

♦ Must be completed by the contractor.

REMOVAL OF ORGANIC POLLUTANTS FROM SUBCRITICAL WATER WITH ACTIVATED CARBON

Final Topical Report

For the period April 15, 1998, through April 30, 1999.

Prepared for:

Paula Flenory

Federal Energy Technology Center
U.S. Department of Energy
PO Box 10940, MS 922-273B
Pittsburgh, PA 15236-0940

Cooperative Agreement No. DE-FC26-98FT40320
Performance Monitor: Paula Flenory

Prepared by:

Steven B. Hawthorne
Arnaud J. Lagadec

Energy & Environmental Research Center
University of North Dakota
PO Box 9018
Grand Forks, ND 58202-9018

99-EERC-08-02

August 1999

DISCLAIMER

EERC DISCLAIMER

ACKNOWLEDGMENT

This report was prepared with the support of the U.S. Department of Energy (DOE) Federal Energy Technology Center Cooperative Agreement No. DE-FC21-94MC31388. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors(s) and do not necessarily reflect the views of DOE.

TABLE OF CONTENTS

LIST OF TABLES

REMOVAL OF ORGANIC POLLUTANTS FROM SUBCRITICAL WATER WITH ACTIVATED CARBON

INTRODUCTION

The Energy & Environmental Research Center (EERC) has demonstrated that controlling the temperature (and to a lesser extent, the pressure) of water can dramatically change its ability to extract organics and inorganics from matrices ranging from soils and sediments to waste sludges and coal. The dielectric constant of water can be changed from about 80 (a very polar solvent) to <5 (similar to a nonpolar organic solvent) by controlling the temperature (from ambient to about 400 C) and pressure (from about 5 to 350 bar). The EERC has shown that hazardous organic pollutants such as pesticides, PACS (polycyclic aromatic hydrocarbons), and PCBs (polychlorinated biphenyls) can be completely removed from soils, sludges, and sediments at temperatures (250 C) and pressures (<50 atm) that are much milder than typically used for supercritical water processes (temperature >374 C, pressure >221 atm). In addition, the process has been demonstrated to be particularly effective for samples containing very high levels of contaminants (e.g., part per thousand). Current projects include demonstrating the subcritical water remediation process at the pilot scale using an 8-liter system constructed under separate funding during 1997. To date, subcritical water has been shown to be an effective extraction fluid for removing a variety of organic pollutants from soils and sludges contaminated with fossil fuel products and waste products, including PACS from soil (e.g., town gas sites), refining catalysts, and petroleum tank bottom sludges; PCBs from soil and sediments; toxic gasoline components (e.g., benzene) from soil and waste sludge; and phenols from petroleum refinery sludges.

The obvious need to clean the wastewater from subcritical water processes led to preliminary experiments with activated carbon placed in line after the extractor. Initial experiments were performed before and after cooling the extractant water (e.g., with water at 200 C and with water cooled to 25 C). Surprisingly, the ability of activated carbon to remove organics from the water is better at a high temperature than at room temperature. These initial results are opposite to those expected from chromatographic theory, since the solubility of the organics is about 100,000-fold higher in the hot water than in ambient water. At present, the physicochemical mechanism accounting for these results is unknown; however, it is possible that the lower surface tension and lower viscosity of subcritical water (compared to water at ambient conditions) greatly increases the available area of the carbon by several orders of magnitude. Regardless of the mechanism involved, the optimal use of activated carbon to clean the wastewater generated from subcritical water remediation will depend on obtaining a better understanding of the controlling parameters. While these investigations focused on the cleanup of wastewater generated from subcritical water remediation, the results also apply to cleanup of any wastewater contaminated with nonpolar and moderately polar organics such as wastewaters from coal and petroleum processing.

OBJECTIVES

- Determine the effect of water temperature on sorption efficiencies.
- Determine the importance of capacity versus elution for controlling breakthrough.
- Investigate different types of activated carbon.
- Attempt to understand the mechanism of sorption from hot water.
- Generate cleanup data on at least one real-world wastewater.

STATEMENT OF WORK

This project will determine the important controlling parameters for using activated carbon for cleaning subcritical water. Water temperature, carbon type, and the relative importance of elution versus retention will be determined by elution tests with a variety of pollutants (e.g., PACS, PCBs, and/or pesticides). Studies will be performed with standard mixes and with subcritical water extracts of real contaminated soils.

SPECIFIC DELIVERABLES

- Determination of the relative importance of capacity versus retention for causing breakthrough of the carbon traps.

- Determination of the relative abilities of three carbon types to remove organics from subcritical water.

- Determination of the ratio of soil cleaned to carbon needed for optimized systems (i.e., What quantity of pollutants and how much water can be cleaned with x amount of sorbent?).

- Proposal of theoretical model describing why, contrary to existing theory, activated carbon is more effective in hot water than at ambient conditions.

ACCOMPLISHMENTS

Experimental

System

Test water (either from soil extracts or with pure quinoline as described below) was pumped through the activated carbon (about 200 mg) which was loaded into a 0.5-mL Keystone cell (4.6 mm i.d. x 30 mm length) mounted vertically inside a gas chromatography (GC) oven. Water was run from the top to the bottom of the cell.

Experimental Procedures

For the study using subcritical water extracts from historically contaminated soils, pure HPLC-grade water was pumped at 1 mL/min (with an Isco pump) through 8 or 9 grams of PAH- or pesticide-contaminated soil at 250 C (loaded in an 6.94-mL cell inside a GC oven) and then through the activated carbon trap. The two cells were connected by 1/16-inch-o.d. stainless steel tubing.

For the study using a continuous feed of a pure standard in activated carbon, an aqueous solution of quinoline (0.67 mg/mL) was pumped at 1 mL/min (using Eldex metric pump A60S) through the activated carbon trap. For the studies on the effect of humic material on the retention of activated carbon, the quinoline solution was first pumped through a cell (6.94 mL, held at 250 C) loaded with 5–6 grams of non-polluted garden soil and then through the activated carbon trap.

Effluent water from the activated carbon cell was collected every 2, 5, or 10 minutes; extracted with methylene chloride; and analyzed by GC-flame ionization detection (GC-FID).

Determination of the Ratio of Soil Cleaned to Carbon Needed

Characteristics and Properties of the Activated Carbon Chosen

The first activated carbon tested was purchased from Fisher and manufactured by Barnebey & Sutcliffe Corp., Columbus, OH. It is an UU type “coconut shell carbon” having a surface area of 1150 m^2/g (B.E.T. N_2), 50 × 200 (75- to 300-µm)-mesh particle size, a packing density of 0.4–0.8 g/mL, an ash content of 5%, and a pH aqueous extract of 10 (ASTM D-3838). Two additional activated carbons were used in selected studies as described below.

Removal of Pesticides and PACS (extracted from historically contaminated soil) from Subcritical Water Using Coconut Shell Activated Carbon

Subcritical water extraction efficiently removes PACS and pesticides from soil, thus generating a wastewater contaminated with the original soil contaminants. In the present studies, the capacity of coconut shell activated carbon to remove pesticides (such as atrazine, alachlor, metolachlor, cyanazine, trifluralin, and pendimethalin, ranging in concentration from ca. 70 to 400 ppm) and PACS (ranging from naphthalene to benzo[*ghi*]perylene, with total PAH concentrations of ca. 2200 ppm) from the wastewater produced by the extraction of two historically highly contaminated soils have been determined at different temperatures.

The results, presented in Table 1, demonstrate that it is possible to remove pesticides and PACS from subcritical water using that type of activated carbon.

TABLE 1

Amount (mg) of Pesticides or PAHs Removed from Subcritical Wastewater by 200 mg of Coconut Shell Activated Carbon (the wastewaters were generated by extracting pesticide- or PAH-contaminated soil with subcritical water)

	25 C	100 C	175 C	250 C
Pesticides	0	11.6	23.2	–
PAHs	0	–	–	>17.6

Effect of Temperature on Removal

Contrary to expectations, the organics (pesticides and PACS) are better removed from the subcritical water extracts when the activated carbon temperature is high, while the ability of the carbon to remove the pollutants from the wastewater is reduced as the temperature of the carbon is decreased. At 25 C, the coconut shell activated carbon does not remove any significant amount of the pesticides or PACS from the wastewaters, while at 175 C, 200 mg of the activated carbon removes 23.2 mg of pesticides (Table 1) before breakthrough occurs (temperatures >175 C degrade the pesticides and, therefore, were not tested). At an activated carbon trap temperature of 250 C, a minimum of 17.6 mg of PACS have been removed from the subcritical wastewater produced by the extraction of the soil. For the soil contaminated with ca. 2200 ppm of PACS, the minimal ratio of soil cleaned to the amount of activated carbon required to completely remove the PACS from the wastewater is ca. 40 to 1 (with the activated carbon held at 250 C). Similarly, with the soil contaminated with ca. 1300 ppm of total pesticides, the ratio of soil cleaned compared to the activated carbon required to clean the resultant wastewater is ca. 90 to 1.

Results Are in Contradiction with Existing Theory

In contrast to our results with the soil extracts, literature reports based on pure compounds demonstrate that the capacity of activated carbon should be much better at lower (not higher) temperatures. Because of the contradictory results (activated carbon is more efficient in hot water than at ambient temperature), more experiments have been performed using with the coconut shell activated carbon as well as two additional activated carbons (described below). In order to mimic the studies from the literature, the effect of temperature on the retention of pure quinoline in water was first determined.

Experiments with Pure Solution of Quinoline

Quinoline was chosen as a model compound since it is aromatic (like all PAHs) and has reasonable solubility in ambient water (6700 mg/L at 25 C). A solution of quinoline was prepared (0.67 mg/mL) and injected through a trap of 200 mg of activated carbon (no soil is present for this experiment) at a 1 mL/min flow rate.

Determination of the Breakthrough of Quinoline at Different Temperatures for the Coconut Activated Carbon

Determination of the Breakthrough of Quinoline at Different Temperatures

The aqueous mixture of quinoline has been continuously injected into 200 mg of coconut shell activated carbon. As shown in Figure 1 of Appendix A, the breakthrough of quinoline occurs faster at high temperature than at low temperature, in agreement with literature reports. However, these results are in direct disagreement for the retention of pollutants from soil extracts (described above).

Capacity/Retention Versus Elution

At 25 C, the quinoline mixture was pumped through the activated carbon for 45 minutes, corresponding to 5 minutes before the breakthrough, and then pure HPLC water was pumped through for 95 more minutes at the same flow rate. No breakthrough was detected (Figure 2, Appendix A), which demonstrates that the ability of the activated carbon to retain solutes is limited by its capacity (i.e., total active sites), rather than its chromatographic retention (i.e., chromatographic repartitioning of retained solutes back into the water phase).

Use of Two Other Activated Carbons

Properties of the New Activated Carbons

Two different activated carbons were chosen for capacity studies. Centaur 20 × 50 (produced from bituminous coal) was manufactured by Calgon Carbon Corp., Pittsburgh, PA. Its total surface area is slightly smaller than the coconut shell carbon (about 800 m^2/g); its density is 0.58–0.62 g/mL; and the ash content is 8%. The final activated carbon is a home-made "North Dakota Lignite, Velva" (EERC) carbonized at 350 C and steam activated at 750 C. Its surface area is significantly smaller (252m^2/g) than the previous carbon types, and the ash content is 29.2%.

Determination of the Capacity for Each Activated Carbon and Ability to Remove Quinoline at High and Low Temperatures

Capacities of each activated carbon were determined for quinoline at 25 and 275 C. The results, presented in Table 2 showed that it is possible to remove quinoline from the subcritical water at 25 C with the coconut shell and the Centaur activated carbon. The coconut shell activated carbon has the better ability to remove quinoline from the water. Breakthrough occurs after 50 minutes (at 1-mL/min solution flow rate) which corresponds to about 33.3 mg of organic injected, while the Centaur 20 × 50 bituminous coal offers less capacity (or retention); i.e., breakthrough occurs after 15 minutes (10 mg of quinoline). The North Dakota lignite activated carbon hasn't remove any significant amount of quinoline from the water (<1.3 mg).

TABLE 2

Amount (mg) of Quinoline Removed by 200 mg of Activated Carbon (A.C.) from Subcritical Water Before Breakthrough (without soil)

	at 25 C	at 250 C
Coconut Shell A.C.	33.3	13.3
Centaur 20 × 50 A.C.	10.0	3.3
Lignite Velva A.C.	<1.3	<1.3

The capacity measured with quinoline in water solution at 25 C (without soil) is similar to reported literature values (Farley, J.A.; Hunter, G.B.; Crim, M.C. "Technical Feasibility and Conceptual Design for Using Supercritical Fluid Extraction to Extract Pesticides from Aged Soil," *Remediation* **1994,** 301–318), where the capacity of naphthalene was reported to be 50 mg removed by 200 mg of activated carbon.

***Influence of Soil (humic material) on the Breakthrough of Quinoline Using the Three Activated Carbon*s**

As described above, the results from the soil extraction (activated carbon at high temperatures has the highest capacity) and the pure compound studies (activated carbon at low temperatures has the highest capacity) are in direct conflict. Two major differences between the two studies exist: first, the soil extracts had complex mixtures of PAHs (or pesticides), while the pure compound study only contained quinoline in water. Second, the soil extracts contained soil organic matter as well as the PAHs (or pesticides). Therefore, in an effort to determine why the two studies give radically different results, the model quinoline study was conducted again as before, except that noncontaminated soil (6 grams of garden soil) was extracted at the same time so that the quinoline was exposed to the activated carbon in the presence of extracted soil organic matter.

Influence of the Temperature on Capacity

The results (Table 3 "with soil") demonstrate that, similarly to the experiments with the PAH- and pesticide-contaminated soils, the breakthrough occurs faster at 25 C than at 250 C. The capacity of the activated carbon is higher in hot water than in ambient water; for example, the coconut retains 10 mg of quinoline at 250 C while it only retains 3.3 mg at 25 C when the water contains soil organic matter.

The lower capacity of the activated carbon at lower temperature than at high temperature can then be explained by the presence of humic material extracted during the removal of the pollutants from the soil. A theoretical model describing why, contrary to existing theory, activated carbon is more effective in hot water than at ambient conditions is discussed in the next

TABLE 3

Amount (mg) of Quinoline Removed by 200 mg of Activated Carbon (A.C.) from Subcritical Water Before Breakthrough in the Presence of Extracted Soil Organic Material

	With Soil	
	at 25 C	at 250 C
Coconut Shell A.C.	3.3	10
Centaur 20 × 50 A.C.	<1.3	3.3
Lignite Velva A.C.	<1.3	<1.3

section. About 50% of the organic matter or humic material (5 to 8 wt% of the soil) was removed by the subcritical water.

Influence of Soil on the Capacity

It has to be noticed that, despite the fact that the capacity decreases while decreasing the temperature in presence of soil, at a certain temperature (25 or 250 C), the capacity decreases when soil organic material is added in the system before the activated carbon trap (compare Tables 2 and 3). For example, the capacity of the coconut shell activated carbon at 25 C without adding soil is 33.3 mg of quinoline, while with soil it is lowered to 3.3 mg.

Selection of Activated Carbon

The results in Tables 2 and 3 demonstrate that the coconut shell activated carbon is the most efficient activated carbon to remove organic solutes from subcritical water, regardless of the temperature or presence of soil organic material. Therefore, all subsequent studies were performed with that activated carbon.

Proposed Model Describing Why, Contrary to Existing Theory, Activated Carbon Is More Effective in Hot Water than at Ambient Conditions

Possible Mechanisms for the Effect of Soil Organic Material on Pollutant Retention on Activated Carbon

Two possible mechanisms could account for the effect of coextracted soil organic material on the retention characteristics of activated carbon. First, soil organic matter could quickly overcome the capacity of the carbon at low temperatures, but may not absorb at higher temperatures, thus leaving sorbent capacity for the more strongly bound solutes (e.g., the PAHs and pesticides). A second possibility would be that the soil organic material helps to solvate the

pollutants (e.g., like surfactants help dissolve hydrophobic organics) and thus keeps them in solution instead of allowing their sorption to the activated carbon.

The first possibility was rejected since the water exiting the activated carbon traps is clearer at 250 than 25 C, thus demonstrating that the retention of soil organic matter is higher at 250 than at 25 C. Therefore, the results indicate that the extracted soil organic matter acts like a surfactant which helps keep the PACS and pesticides in the water phase and reduces their sorption to the activated carbon at room temperature. The surfactant effect of the soil organic material is negated by at the 250 C water temperature, possibly because the polarity of the water is reduced at elevated temperatures, which could destroy the surfactant interactions of the extracted soil organic matter with the PACS (or pesticides).

Model Compound Sorption in the Presence of Soil Organic Material

If the surfactant effect proposed above is correct, adding extracted soil organic material to the water containing the quinoline model compound should dramatically reduce its retention on activated carbon at 25 C. This is demonstrated in Figure 3, Appendix A, where partial breakthrough of the quinoline occurs almost immediately when soil organic matter is included in the water. Note, however, that the breakthrough is only partial, and a fraction of the quinoline is retained. This early breakthrough is in contrast to the large retention of quinoline in pure water (Figure 3). In contrast to the results at 25 C, the retention of quinoline with and without the soil organic matter is fairly similar (Figure 3). Note that initial breakthrough (with soil organic matter present) is faster at 25 than at 250 C, but after the initial breakthrough occurs, much higher amounts of quinoline are eluted at 250 than at 25 C. These results all support the fact that the presence of soil organic matter in the subcritical wastewater acts as a surfactant at 25 C only, while this surfactant activity is largely destroyed when the activated carbon is held at 250 C.

The surfactant theory is also confirmed by a separate set of experiments (Figure 4, Appendix A), where the activated carbon was preloaded with humic material from the same garden soil (using more soil in order to saturate the sites of the activated carbon) at 25 and 250 C. Then the solution of pure quinoline in water was pumped through the activated carbon at either 25 or 250 C. The biggest reduction in capacity occurred when the activated carbon was preloaded with soil organic matter at 250 C, regardless of whether the quinoline solution was pumped through the activated carbon at 25 or 250 C. In contrast, when the activated carbon was preloaded at 25 C, the effect on the capacity for quinoline (at either 25 or 250 C) is not largely affected. These results clearly support the fact that soil organic matter is more strongly retained on activated carbon at 250 than at 25 C.

Summary of Results for Specific Deliverables

Organics such as pesticides and PACS can be efficiently removed from subcritical water using a trap of activated carbon. For pure quinoline in water, the capacity of the activated carbon controls the ultimate retention of quinoline at 25 C, but lower retention (elution) becomes more important at 250 C. However, the presence of soil organic matter in the water appears to enhance elution (rather than reduce the capacity of the activated carbon) if the carbon is at 25 C, appar-

ently because soil organic matter acts as a surfactant to keep the pollutant molecules in water solution. At 250 C, the ability of the soil organic matter to inhibit the sorption of the pollutant organics onto the activated carbon is dramatically reduced, which results in much later breakthrough of the pollutant organics from the activated carbon. Of the three activated carbons tested, the coconut shell-derived carbon had the best capacity and retention characteristics. For the extraction of soils contaminated with ca. 2200 ppm of PAHs, and ca. 1300 ppm of pesticides, the ratio of soil cleaned compared to the amount of activated carbon required to clean the wastewater was ca. 40 and 90 to 1, respectively.

APPENDIX A

FIGURES

Figure 1. Breakthrough of quinoline at different temperatures (coconut shell activated carbon trap)

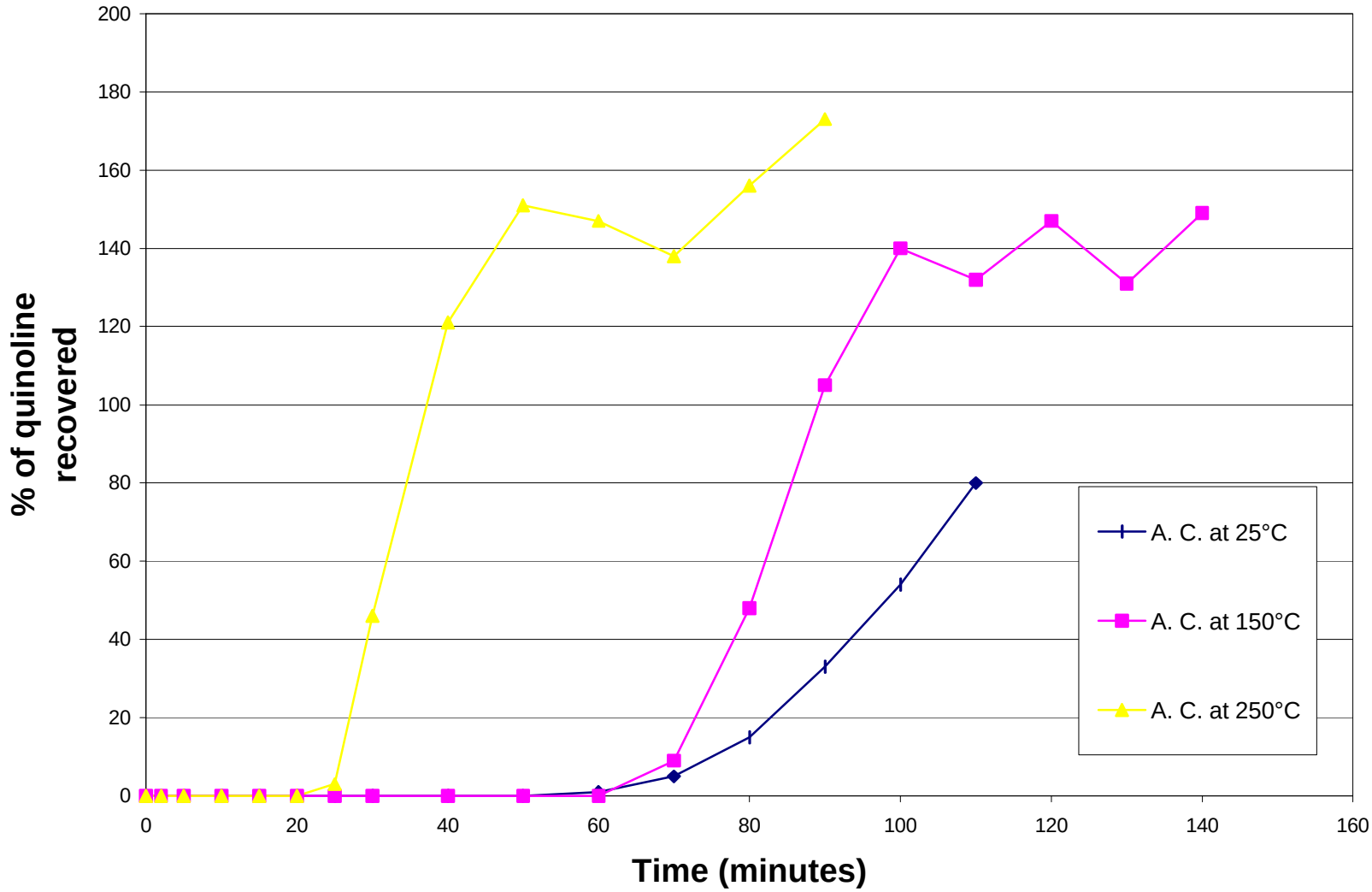

Figure 2 : breakthrough of quinoline with or without garden soil (coconut shell Activated Carbon trap)

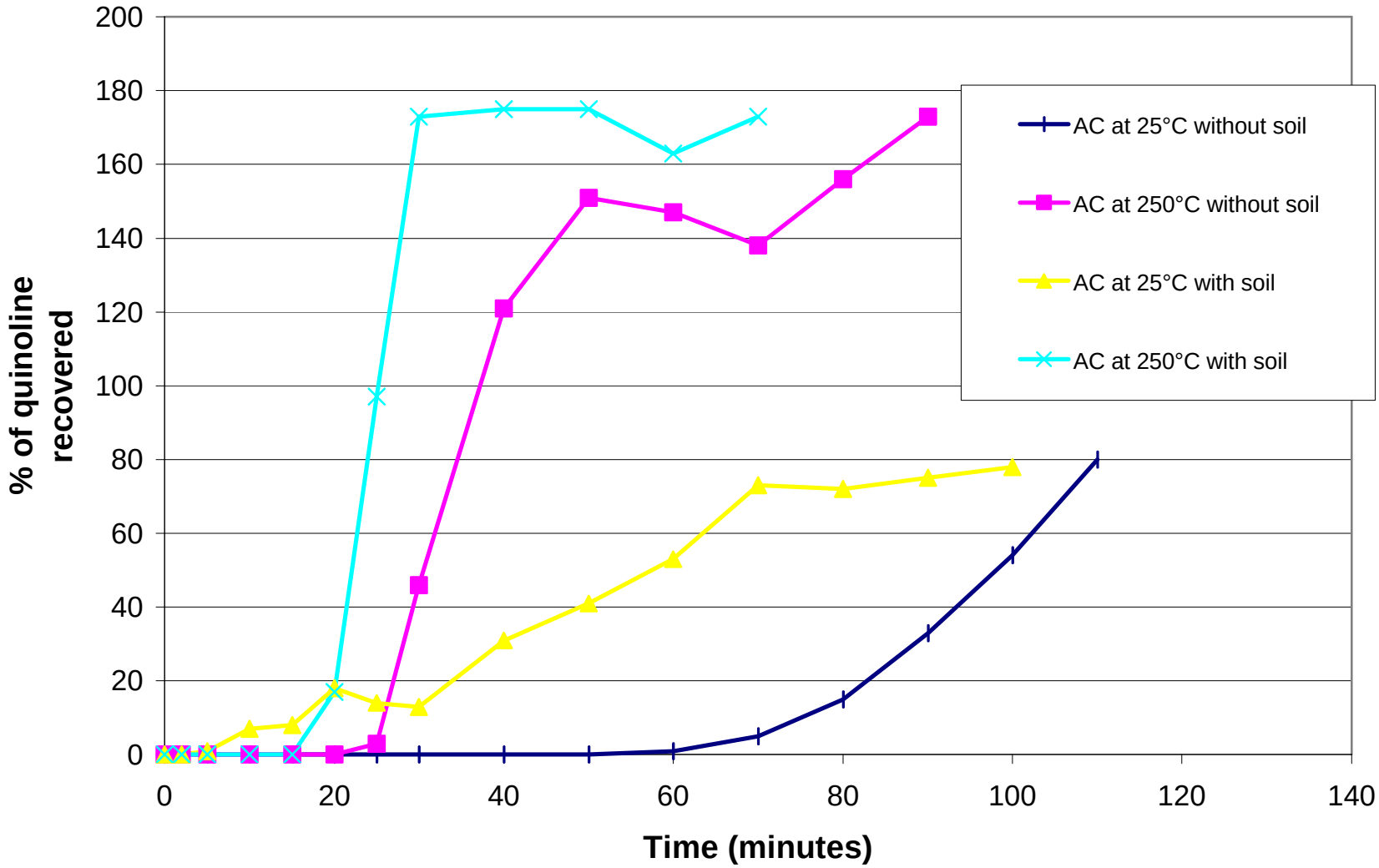

Figure 3: Breakthrough of quinoline, with preloading of humic material in the coconut shell Activated Carbon trap

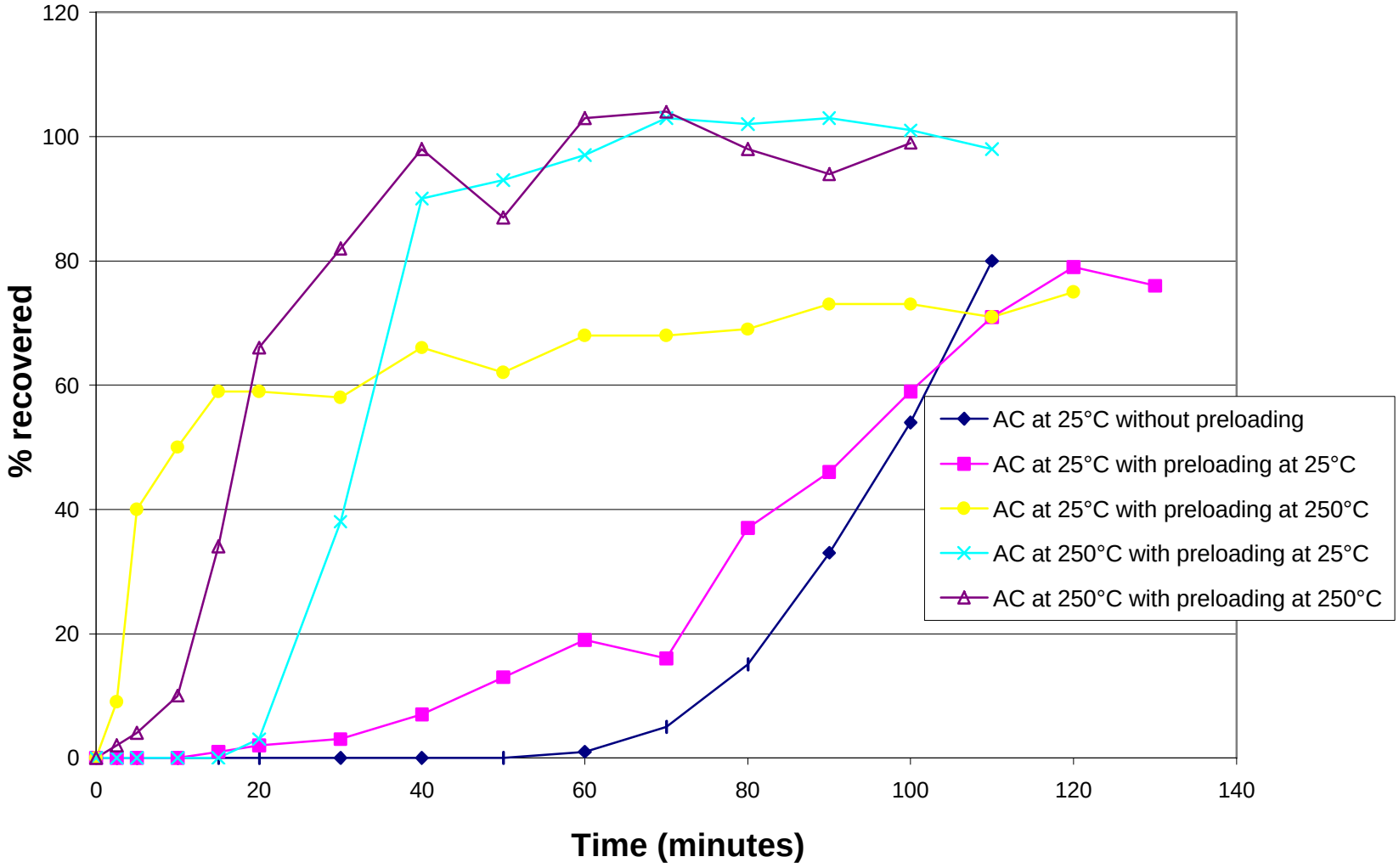

Figure 4: Breakthrough of quinoline continuously fed or fed for 45 minutes and then eluted with water (coconut shell Activated Carbon trap)