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Journal of Hazardous Materials B73 (2000) 129–142

**Journal of  
Hazardous  
Materials**

www.elsevier.nl/locate/jhazmat

## Oxygen uptake rate inhibition with PACT™ sludge

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Received 26 February 1999; received in revised form 13 October 1999; accepted 14 October 1999

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### Abstract

Oxygen uptake rate (OUR) experiments were performed with sludge from six laboratory-scale, continuously fed, activated sludge and PACT™ reactors (sludge ages of 4-, 8-, and 12-days) to evaluate the sludge's resistance to inhibitory compounds. Three inhibitory compounds with varied ability to sorb on activated carbon were tested: 3,5-dichlorophenol (3,5-DCP, strongly adsorbed), phenol (moderately adsorbed), and zinc (poorly adsorbed). The inhibitory compound concentration that reduced the unacclimated sludge's specific oxygen uptake 50% from its maximum rate was determined (IC<sub>50</sub>). For the organic compounds, PACT™ sludge resisted acute inhibition better for all sludge ages; sorption studies indicate that phenol sorbed onto the PACT™ sludge could account for the IC<sub>50</sub> difference at the higher sludge ages. With 3,5-DCP, the 4- and 8-day-old PACT and activated sludge solids sorbed similar amounts of 3,5-DCP at concentrations near the IC<sub>50</sub> values, yet the PACT™ sludge exhibited higher IC<sub>50</sub> values; biomass differences may have accounted for the improved resistance to inhibition. With the poorly adsorbed zinc, no difference in IC<sub>50</sub> or sorption was noted with the 4-day-old sludge. For the 12-day-old sludge, the PACT™ sludge was much more resistant to zinc exposure, with changes in the biomass rather than sorption on carbon the apparent reason. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Activated carbon; Activated sludge; Adsorption; PACT™; Inhibition; 3,5-Dichlorophenol; Phenol; Zinc

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### 1. Introduction

DuPont developed the PACT™ process in the early 1970s to remove color from industrial wastewater. Powdered activated carbon (PAC) was added to an activated

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sludge reactor to remove compounds that were not degraded by the microorganisms and to provide treatment that could only be obtained with tertiary treatment processes.

Laboratory, pilot, and full-scale studies demonstrated the process's improved performance compared to activated sludge (Osantowski et al. [1], Dietrich et al. [2], Chao and Shien, [3]) PACT™ is claimed to have the following benefits over conventional activated sludge systems:

1. Improved process stability during shock loads by adsorption of soluble organic compounds;
2. Improved COD removal by adsorption of non-biodegradable organic compounds;
3. Improved color removal;
4. Improved sludge settling, thickening, and dewatering characteristics;
5. Improved hydraulic capacity because of either increased removal rates or operation with higher mixed liquor biomass levels;
6. Improved nitrification by either adsorbing inhibitors or providing a surface for the attachment of nitrifiers;
7. Improved removal of EPA priority pollutants.

The primary objective of early PACT™ research was to determine the carbon's ability to remove biologically resistant organic compounds. Although these advantages were reported in a number of studies, there is a lack of understanding of the process mechanisms responsible for these benefits. Many PAC and activated sludge studies focused upon the mechanisms involved in increasing organic removal; little information is available on the PACT™ system response to inhibitory substances. The objective of this study is to determine whether PACT™ sludge resists inhibition better than activated sludge when exposed to inhibitory compounds. Three inhibitory compounds with different adsorption characteristics were tested to determine if a compound's ability to sorb is important. Sub-objectives to meet this goal were:

- To determine whether the  $IC_{50}^1$  value for each specific inhibitory compound was greater for PACT™ sludge or activated sludge.
- To determine whether the carbon concentration and sludge age combination impacted the  $IC_{50}$  value.

## **2. Background**

The PAC-activated sludge system appears simple, with some organic compounds adsorbing on the PAC and others biodegrading; however, a number of synergistic PAC/biomass interactions have been proposed. Various authors have stressed apparent

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<sup>1</sup> Inhibitor concentration that reduced the sludge's oxygen respiration rate 50% from the inhibitor-free value.

synergistic effects due to simultaneous biological oxidation and carbon adsorption, these effects result in decreased effluent BOD and COD (DeWalle et al. [4], Flynn [5], Roberataccio et al. [6]). Some effects are:

- PAC enhances the biological assimilation and subsequent mineralization of organic compounds — enhanced bioactivity;
- Biomass can degrade organic compounds adsorbed on the PAC and thereby regenerates the PAC for further adsorption — carbon bioregeneration;
- Poorly biodegraded organic molecules can adsorb and be broken into smaller molecules by easily adsorbable extracellular enzymes, these molecules desorb and are utilized by the microorganisms;
- Metabolic End Products (MEP) produced from cell activity can be removed by adsorption.

Mechanisms to explain the enhanced bioactivity include the alteration of the microbial population and/or the protection of the microorganisms by the adsorption of toxic compounds. Enhanced bioactivity, degradation of slowly degradable materials, bioregeneration and adsorption of MEP have been studied, analyzed, and discussed in many research papers. Much of the early research overlooked the possible enhanced biooxidation that could result from adsorption of inhibitory organic compounds.

DeWalle et al. [4], Flynn [5,7], Robertaccio et al. [6] found sludge age and carbon dose to play a significant role in the distribution and quantity of specific organic compounds. Flynn [7] and Hals [8] only found synergism with slowly biodegradable and adsorbable organic matter, this was important for understanding the enhanced process for priority pollutant removal.

### 3. Experimental design

#### 3.1. Materials

##### 3.1.1. Inhibitory compounds

Compounds were selected to exhibit a range of abilities to adsorb. The compounds were as follows.

*3,5-Dichlorophenol* (3,5-DCP) represents a well-adsorbed, inhibitory compound; it is a reference toxicant for the oxygen uptake rate (OUR) test (OECD [9]). A 50% reduction in activated sludge activity should result with 5 to 30 mg/l of 3,5-DCP (OECD [9]). Adsorption data were not found for 3,5-DCP, but the less soluble 2,4-dichlorophenol's adsorption capacity is 147 mg/g at 1 mg/l solution concentration (Kuo-Ching et al. [10]); 3,5-DCP should adsorb slightly less. This compound adsorbs well, inhibits activated sludge, and is a reference toxicant.

*Phenol* was chosen as a moderately-adsorbed inhibitory compound. Phenol is known as a noncompetitive inhibitor of heterotrophic organisms, with activated sludge inhibi-

tion at 520 mg/l (Volskay and Grady [11]). Several studies indicate phenol's adsorption strength, with most loadings ranging from 15 to 80 mg/g at 1 mg/l solution concentration (Peel and Benedek [12], Faust and Aly [13]).

Zinc was selected to be a non-adsorbed inhibitory compound. Zinc adsorption data are limited, but one study indicates a loading of 0.6 mg/g at the 1 mg/l level (Mishra and Chaudhury [14]). Inhibitory data with zinc and heterotrophic organisms were not available, but zinc effectively inhibits nitrifiers at 11 mg/L (Pantea-Kiser [15])

### 3.1.2. Biomass

Sludge was obtained from six parallel internally-clarified, laboratory continuous-flow reactors. The reactors were seeded with the City of Akron's mixed liquor and operated for 2 months prior to collecting preliminary operating data. Each reactor's volume is 6.9 l, including the internal clarifier, and had a synthetic waste flow of 13 l/day (the reactor volume was 5.1 l). Mixed liquor dissolved oxygen was measured daily and was around 7 mg/l. The pH in each reactor was in the range of 7 to 8. All reactors were assumed to have reached steady-state after two months acclimation. Sludge age was controlled by wasting a constant volume of sludge once per day. The reactor conditions at this time were:

Reactor number	1	2	3	4	5	6
Carbon addition	None	PAC	None	PAC	None	PAC
Calculated PAC conc., mg/l	0	750	0	1510	0	2260
Sludge age, days	4	4	8	8	12	12
Mean TSS, mg/l	1296	2028	2090	2908	2816	4784
Standard deviation, mg/l (% of mean)	43.5 (3.4)	64.2 (3.2)	65.3 (3.1)	52.6 (1.8)	104 (3.7)	63.9 (1.3)

The mean solids concentrations are average values obtained over a 10-day period after steady-state was assumed to be achieved. The solids varied less than 4% (standard deviation as percentage of the mean value), greater than the single analyst MLSS test method percentage of about 1% obtained on a single sample (APHA et al. [16]).

The PAC concentrations were calculated using the equation derived from a PAC mass balance around a completely mixed activated sludge reactor, assuming no PAC loss in the effluent

$$C = \frac{C_i \theta_C}{\theta_H} \quad (1)$$

where  $C$  = equilibrium mixed liquor carbon concentration, mg/l;  $C_i$  = influent carbon concentration, mg/l;  $\theta_C$  = solids retention time or sludge age, days;  $\theta_H$  = hydraulic retention time, days.

Using the calculated PAC concentrations to estimate the biomass concentrations for the PAC-activated sludge reactors [biomass = TSS – PAC concentration] results in similar biomass concentrations (no significant difference at the 95% confidence level). During the testing phase, biomass was determined experimentally. During the acclimation phase, sludge bulking occurred, with microscopic examinations finding a large amount of filamentous bacteria. The reactors were treated to control the filaments, so the microbial population and sludge age were likely to have been impacted. For the 4- and 12-day sludge, the treatment was several weeks before testing; with the 8-day sludge, treatment was 1 to 2 weeks prior to testing (the treatment consisted of settling the solids, decanting the supernatant, and adding substrate so the beginning of the process was like a selector reactor). After the reactors were assumed to have reached steady-state, the reactors were operated for several months with only dissolved oxygen, temperature, flow, and pH monitoring — during this period, sludge was obtained for testing.

### 3.1.3. Activated carbon

Calgon Carbon's WPL bituminous coal-based PAC was added at 100 mg/l.

### 3.1.4. Synthetic wastewater

For the continuous-flow reactors that provided the sludge for the batch OUR tests, a concentrated feed solution was prepared and stored in the refrigerator at 4°C (Table 1). The concentrate (150 ml) was added to a container and diluted to 55 l with city water. The feed COD was about 600 mg/l. The pH of the freshly prepared concentrate was 7–7.4. Fresh concentrate was prepared when required, usually every 3 days.

The synthetic waste used for the batch OUR tests differed from the continuous flow reactor waste (Table 2A); its COD was estimated to be  $1056 \pm 42$  mg/l (mean and standard deviation). The nutrient solution was prepared separately from the synthetic

Table 1  
Synthetic wastewater for flow reactors  
This concentrated solution diluted with Akron City water to 55 l.

Components	Amount (grams or as indicated)
Peptone	11
Yeast extract	8.25
Beef extract	1.38
Non-fat milk	8.08
Diethylene glycol	2.75 ml
Urea	1.65
NaCl	0.38
CaCl <sub>2</sub> · 2H <sub>2</sub> O	0.22
MgSO <sub>4</sub> · 7H <sub>2</sub> O	0.13
K <sub>2</sub> HPO <sub>4</sub>	0.65
Water	900 ml

Table 2

Synthetic waste for inhibition tests

Both solutions were diluted to 1.0 l with Akron City water.

(A) Substrate solution	
Substrate compounds	Amount (g)
Peptone	0.5
Yeast extract	0.3
Beef extract	0.5
Non-fat milk	0.25

(B) Nutrient solution	
Nutrient compounds	Amount (g)
NaCl	0.007
CaCl <sub>2</sub> · 2H <sub>2</sub> O	0.004
MgSO <sub>4</sub> · 7H <sub>2</sub> O	0.002
K <sub>2</sub> HPO <sub>4</sub>	0.072

waste (Table 2B). Fresh concentrates of the synthetic and nutrient solutions were prepared as required (usually 4–5 days) or whenever the concentrate appeared cloudy, indicating microbial contamination.

### 3.2. Methods

#### 3.2.1. OUR

Specific oxygen uptake was used to estimate the inhibitor's effect on the sludge. OUR was measured using a Gilson Model 5/6H Oxygraph, which contains a reaction cell, a mixer, a Clark-type oxygen electrode, and a chart recorder. The Oxygraph records mg-O<sub>2</sub>/l in the sample cell vs. time, the slope of the resulting straight line is the OUR in mg-O<sub>2</sub>/L-h. Specific oxygen uptake rate (SOUR) is OUR divided by the biomass concentration.

Activated sludge from the continuous flow reactor was aerated for 1 h with oil-free air to oxidize any remaining substrate. The sludge was centrifuged to give a MLVSS concentration 10 times higher than the activated sludge reactor's MLVSS (mixed liquor volatile suspended solids). This concentrated sludge was shaken for 30 min on a shaker to insure uniform consistency. A mixture of 1 ml of sludge and 9 ml of solution (a combination of nutrient solution and synthetic waste to give the desired COD) was used to determine the OUR. When testing for inhibition, 9 ml of the synthetic waste and inhibitor solutions replaced the 9 ml of solution. After mixing the sludge and solution, an aliquot was immediately transferred to the reaction cell for oxygen measurement — measurement began about 30 s after mixing. Oxygen was monitored for 2 to 3 min and respiration rates were calculated from the slope.

#### 3.2.2. Biomass determination

For conventional activated sludge, the biomass concentration is estimated with a volatile suspended solids test. When PAC is added to the system, the suspended solids

include PAC. The PAC concentration is similar to the biomass concentration, and PAC cannot be separated from the biomass. Consequently, a separate determination of the PAC concentration is needed if the adsorption and biodegradation mechanisms are to be properly quantified. In this study, PAC and biomass concentrations were determined separately using a nitric acid technique that digests the biomass in the PACT sludge with concentrated nitric acid. An advantage of the nitric acid technique is its ability to solubilize a large amount of the biomass with only a small effect on the PAC. Studies have shown that 90% of the biomass is solubilized while only 5% of the PAC is solubilized (Zimpro/Passavant [17]). The nitric acid method was used to determine the biomass concentrations in *both* PACT and activated sludge reactors to provide consistent biomass measurements.

### 3.2.3. Adsorption tests

The OUR procedure was followed, except the aliquot was immediately transferred to a vacuum filter with Whatman GF/C glass fiber filter paper to separate the solution from the solids. Specific chemical analysis was then performed for 3,5-DCP, phenol, or zinc.

### 3.2.4. Analytical method summary

3,5-DCP, HPLC method (Barbeni, et al. [18]) (acetonitrile used instead of methanol).  
Chemical Oxygen Demand Method 5220 C. Closed reflux Titrimetric Method (APHA et al. [16]).

OUR (OECD [9])

Phenol, bathochromic shift method (Kennedy et al.[19])

Total Suspended Solids, Method 2540-D (APHA et al. [16])

Volatile Suspended Solids, Method 2540-E (APHA et al. [16])

Volatile Carbon/Biomass Determination. Nitric Acid Digestion Method (Zimpro/Passavant [17])

Zinc, Method 3500-F (APHA et al. [16])

## 4. Results and discussion

### 4.1. Synthetic waste OURs

The inhibition tests were to be obtained when at the maximum OUR, so substrate concentrations wouldn't complicate the study. To determine the waste concentration needed to obtain the maximum OURs, OUR tests were performed with each sludge using nine to 12 initial synthetic waste concentrations. All sludge exhibited a maximum OUR at a COD of 300 mg/l synthetic waste or lower. Substrate inhibition was not observed at COD increases up to 900 mg/l (the upper limit tested) except for the 8-day activated sludge, where considerable scatter was observed with a decreasing OUR at higher substrate levels. The 8-day activated sludge and PACT sludge were recovering from bulking problems and they are unlikely to represent steady-state conditions. Other indications that differences existed with the 8-day biomass, is that the biomass in the

PACT reactors were smaller than the corresponding activated sludge, which was not the case for the other sludge ages (Table 3). In addition, the SOURs for both 8-day sludges do not follow the expected pattern, decreasing SOUR with increasing sludge age. So the 8-day sludge age results are suspect. These tests resulted in the selection of a synthetic waste COD of 300 mg/l for the inhibition testing. Ten replicate OUR tests were performed at 300 mg/l (except for the 4-day PACT sludge), five replicates were performed 1 day and five the next. The mean and standard deviations from these tests indicate the test is quite reproducible (Table 3).

#### 4.2. Inhibition tests

The inhibition test was designed to determine  $IC_{50}$  for 3,5-DCP, phenol, and zinc by monitoring SOUR changes resulting from increased inhibitor concentrations. This method has been used as a practical and sensitive indicator in microbial toxicity assays (OECD [9], Larson and Schaffer [20]). A series of reaction mixtures was prepared with 300 mg/l of synthetic sewage COD, sludge, and varying concentrations of the inhibitor. Two control SOURs were determined for each sludge (no inhibitor), with the average representing  $SOUR_{max}$ . A SOUR value was obtained for each inhibitor concentration,  $I$ . Eq. 2 is used to determine the inhibition coefficient,  $K_I$ , which is the  $IC_{50}$  value.

$$SOUR = \frac{SOUR_{MAX}}{1 + \frac{I}{K_I}} \quad (2)$$

Eq. (2) was rearranged and  $[(SOUR_{MAX}/SOUR) - 1]$  regressed against  $I$  to obtain  $K_I$ ; all  $IC_{50}$  values and their associated 95% confidence intervals were obtained in this manner (Table 4). The variation in SOUR is very well represented by Eq. 2 as the model-generated curve indicates (Fig. 1, using activated sludge from Reactor #1 and 3,5-DCP).

##### 4.2.1. 3,5-DCP

OECD recommends 3,5-DCP as a reference toxicant to ensure that activated sludge biomass is appropriately sensitive — the  $IC_{50}$  should be between 5 and 30 mg/l (OECD [9]). Therefore, analyzing sludge inhibition with 3,5-DCP indicates whether the continuous-flow reactor's activated sludge has acceptable sensitivity. Increasing 3,5-DCP

Table 3

Oxygen uptake rate reproducibility

10 replicate OURs were performed, five 1 day and five the next.

Reactor type/no.	Biomass conc. (mg/l)	Substrate conc. (mg/l)	Mean and Standard deviation	
			OUR (mg/l-min)	SOUR (day <sup>-1</sup> )
AS #1	1000 ± 97	300	1.34 ± 0.04	1.93 ± 0.09
PACT #2	1527 ± 50	400	1.30 ± 0.08	1.23 ± 0.09
AS #3	1876 ± 75	300	1.37 ± 0.06	1.05 ± 0.04
PACT #4	1708 ± 61	300	1.76 ± 0.24	1.48 ± 0.09
AS #5	1820 ± 163	300	1.63 ± 0.12	1.29 ± 0.09
PACT #6	2373 ± 231	300	1.38 ± 0.11	0.84 ± 0.04



Table 4

IC<sub>50</sub> concentrationsIC<sub>50</sub> values from regression of linearized Eq. 2 with 95% confidence intervals.

Reactor type/no.	Biomass conc. (mg/l)	Sludge age (days)	3,5-DCP (mg/l)	Phenol (mg/l)	Zinc (mg/l)
AS #1	1000 ± 97	4	16.4 (14.5–18.7)	637 (578–710)	62.9 (53.2–77.0)
PACT #2	1527 ± 50	4	23.8 (21.9–26.0)	855 (701–1096)	57.5 (51.0–65.9)
AS #3	1876 ± 75	8	29.3 (26.0–33.5)	1016 (916–1141)	47.6 (44.4–51.7)
PACT #4	1708 ± 61	8	27.6 (24.2–32.1)	1335 (1184–1530)	30.3 (25.3–37.8)
AS #5	1820 ± 163	12	14.0 (12.8–15.4)	862 (784–958)	35.0 (31.9–38.8)
PACT #6	2373 ± 231	12	27.5 (24.7–31.1)	947 (815–1129)	90.9 (82.2–102)

exposure resulted in significant decreases in oxygen consumption rate (e.g., Fig. 1). The activated sludge IC<sub>50</sub> values agree well with the values specified by the OECD in its microbial toxicity test, with values of 16.4, 29.3, and 14.0 mg/l (Table 4). The 8-day sludge's IC<sub>50</sub> was significantly greater (95% confidence) than the other two values, probably related to the sludge's bulking. These values compare well with the results for this compound obtained by others (Volskay and Grady [11], Larson and Schaffer [20], Broecker and Zahn [21], Klecka [22]).

The IC<sub>50</sub> values measured for the PACT reactors for the 4-, 8- and 12-day-old sludge were 23.8, 27.6 and 27.5 mg/l of 3,5-DCP. The significantly higher IC<sub>50</sub> values (95% confidence, excluding the 8-day activated sludge value) indicate an increased resistance to the inhibitory effect of this poorly degradable compound using unacclimated sludge. The PACT sludge is more resistant due to either different biomass or sorption of the inhibitor by PAC during this test, or a combination of the two.

3,5-DCP adsorbs readily; therefore, the activated carbon was expected to reduce the adverse effect of the inhibitor. But several factors could interfere with activated carbon's ability to adsorb the 3,5-DCP:

- the PAC is already saturated with reactor organic compounds and organisms (the PAC is at steady-state in the reactor) and cannot sorb much additional material,

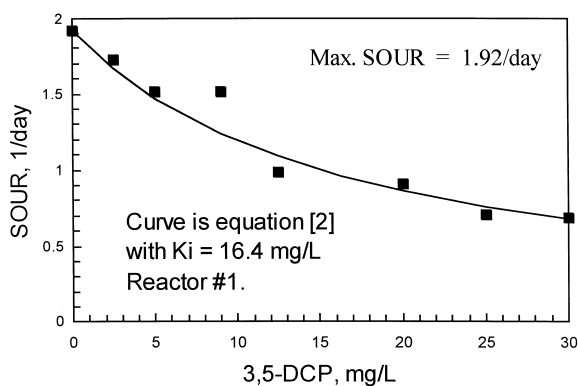


Fig. 1. SOUR variation for dichlorophenol.

- little time is available for adsorption (about 30 s elapse from the time the chemicals are added until the start of the OUR test); therefore, there isn't much time for adsorption on activated carbon to occur, and
- a significant quantity of competing organic compound is available in the waste added with the inhibitor (COD of 300 mg/l), so the 3,5-DCP would be one of many added organic components.

Sorption tests were to determine if PACT sludge sorbed (adsorbed on the surface or transported into the PAC or cells) more 3,5-DCP than the activated sludge (Table 5). For the 4-day-old sludge, the activated sludge resulted in lower 3,5-DCP concentrations than PACT sludge in the concentration ranges of the  $IC_{50}$  values (15.3 and 28.1 mg/l). At the highest concentration tested (50.3 mg/l), the PACT sludge sorbed more, resulting in lower solution concentrations. For the 8-day sludge, sorption was similar for both sludges. For the 12-day sludge, the PACT sludge (with its considerably greater carbon concentration) resulted in lower 3,5-DCP concentrations. These sorption tests were performed months after the OUR tests; therefore, the sludge differed somewhat from the sludge used in the OUR tests. Sorption of the 3,5-DCP on the PAC in the short time involved in an OUR test may not protect the biomass until the much higher PAC levels of the 12-day sludge age system (nearly 3000 mg/l PAC vs. 2000 mg/l for the 8-day sludge). Differences between PACT and activated sludge microbial populations are likely to be responsible for PACT's better resistance to inhibition — differences that are observed in the SOURs obtained in the reproducibility tests (Table 3). The maximum SOUR for activated sludge is significantly greater than for PACT sludge for both the 4- and 12-day sludge. Sorption on PAC cannot be ruled out, and may have resulted in less 3,5-DCP available to be sorbed by the microbial population. A better means of determining the amount of material available to the organism is needed.

#### 4.2.2. Phenol

Phenol was selected for testing because it sorbs moderately and is biodegradable; it is also an extensively studied compound. Adding phenol results in decreases in OUR, with

Table 5  
Adsorption of 3,5-DCP

Sludge age (days)	3,5-DCP (mg/l)		
	Initial	Activated sludge final	PACT final
4	15.3	6.6	7.8
	28.1	16.9	22.2
	50.3	43.7	32.3
8	15.3	9.0	8.3
	28.1	15.1	16.6
	50.3	32.9	29.2
12	15.3	8.2	6.3
	28.1	18.2	14.8
	50.3	34.6	28.0

much greater concentrations of phenol required to inhibit SOUR than found for 3,5-DCP (more than an order of magnitude larger). Phenol  $IC_{50}$  values for the activated sludge varied from 637 to 1016 mg/l of phenol (Table 4); the greatest value was obtained with the 8-day sludge which had experienced bulking problems and had a higher biomass concentration than expected. Volskay and Grady found an average  $IC_{50}$  of 600 mg/l phenol (Volskay and Grady [11], while Klecka found it to be 713 to 919 mg/l [22]). Therefore, inhibition data obtained for the activated sludge reactors agree with the results of phenol inhibition obtained by others, except that the 8-day sludge has a higher value.

The  $IC_{50}$  values measured for PACT sludge were greater than for the corresponding activated sludge reactor (855 to 1335 mg/l), anywhere from 10% to 34% higher. Because of the high phenol solution concentrations and the presence of the activated carbon, PAC sorption would be expected to reduce the SOUR based on phenol added, since at these much greater concentrations phenol becomes the major organic present relative to the substrate.

Sorption tests resulted in smaller phenol concentrations with the 8- and 12-day-old PACT sludge (Table 6) than activated sludge. The percent reduction in final phenol solution is similar to the percent increase in phenol  $IC_{50}$  values. Because very high phenol concentrations are required to inhibit sludge, differences in sorption are likely to be due to the activated carbon, and not just differences in uptake by the bacteria as may have occurred with the 3,5-DCP. If the sludge used for the OUR tests performed similarly to the sorption study sludge, sorption may explain the difference in  $IC_{50}$  values for the 8- and 12-day-old sludge when phenol is the inhibitory compound. Phenol sorption was not better for the 4-day-old PACT sludge; the smaller amount of carbon present did not provide significant sorption, although the sludge resisted phenol better as evidenced by the greater  $IC_{50}$ . The slower growing (smaller SOUR) PACT biomass may be responsible.

#### 4.2.3. Zinc

Zinc was selected because it adsorbs poorly and is non-biodegradable. Zinc was expected to be removed the same in the PACT and activated sludge systems; therefore,

Table 6  
Adsorption of phenol

Sludge age (days)	Phenol (mg/l)		
	Initial	Activated sludge final	PACT final
4	552	317	398
	1190	660	680
	2760	1380	1260
8	552	418	316
	1190	812	572
	2760	1400	1310
12	552	352	296
	1190	738	620
	2760	1550	1294

no differences in  $IC_{50}$  values were expected. Increasing zinc concentrations resulted in decreases in OUR. The activated sludge  $IC_{50}$  values ranged from 35 to 63 mg/l (Table 4), with the lowest value resulting at the highest sludge age. For the PACT sludge,  $IC_{50}$  values ranged from 30 to 91 mg/l of zinc, with the highest value at the highest sludge age. PAC did not increase the  $IC_{50}$  for 4-day-old sludge; there was no significant difference between the two. A significant difference results with the 8- and 12-day sludge. The activated sludge  $IC_{50}$  value decreased substantially from the 4-, 8- to 12-day sludge values, where less zinc is available per unit of biomass. The PACT sludge  $IC_{50}$  value increased substantially from the 4- to 12-day values, with the 8-day sludge value appearing very low. The 8-day PACT sludge's SOUR was higher than the other sludge age values (Table 3) and the sludge is not considered representative of steady-state sludge. The 12-day sludge had the greatest PAC concentration and the greatest  $IC_{50}$ ; the PACT system was more resistant to zinc inhibition.

Zinc was not expected to adsorb on the activated carbon, so sorption was not expected to help the PACT sludge. Sorption tests resulted in essentially no difference in zinc removal between activated sludge and PACT sludge with both the 4- and 8-day-old sludge (Table 7), with their 4-day  $IC_{50}$  values the same. For the 12-day-old sludge, zinc residual solution concentrations for the PACT system were quite similar to the 4- and 8-day-old sludge, so the substantially greater amount of PAC didn't increase the zinc removal. For the activated sludge, the residual zinc solution concentrations were substantially higher with the 12-day sludge. This older activated sludge, with greater biomass concentrations, was less able to sorb zinc and a smaller  $IC_{50}$  value resulted. The oldest PACT sludge seemed to sorb zinc to the same degree as the younger sludge, but a substantial increase in  $IC_{50}$  value resulted — the bacteria are better protected at these same concentrations. Because there is a greater amount of PAC (about 50% more than the 8-day sludge), the sorbed zinc may be associated with the PAC solids rather than the bacterial solids. If these bacteria behave like the activated sludge bacteria, they sorb less zinc; thus, the microbial population may actually have a much smaller amount of zinc associated with it. Tests should be developed to separate microorganism and PAC solids, so zinc levels could be measured independently.

Table 7  
Adsorption of zinc

Sludge age (days)	Zinc (mg/l)		
	Initial	Activated sludge final	PACT final
4	34	21	16
	150	31	31
	180	79	83
8	34.2	24	20
	149	33	36
	178	85	66
12	34.2	27	17
	149	51	30
	178	91	60

## 5. Conclusions

The following conclusions apply to unacclimated sludge used in acute inhibition tests, and are not meant to characterize full-scale PACT and activated sludge processes operating on continual exposure to these compounds. In the current tests, PAC had insufficient time to sorb much of the chemicals with the results a better indication of the biomass's susceptibility to the inhibitory compounds.

(1) The  $IC_{50}$  for 3,5-DCP is 14 to 16 mg/l for the 4- and 12-day-old activated sludge, well within OECD's acceptable 5 to 30 mg/l range. The PACT sludge  $IC_{50}$  values were 24 to 28 mg/l. Using the SOUR test, PACT sludge is less inhibited by 3,5-DCP for these two sludge ages.

(2) No statistical difference in  $IC_{50}$  was observed between the 4- and 12-day sludges with the 3,5-DCP.

(3) Sorption tests in the initial concentration range of the  $IC_{50}$  values (10 to 30 mg/l) indicated the difference in 3,5-DCP sorption between the activated sludge and the PACT sludge is insufficient to account for the difference in  $IC_{50}$ . Biomass differences are likely to be responsible.

(4) The 4- and 12-day-old activated sludge  $IC_{50}$  for phenol is 637 to 862 mg/l, while it is 855 to 947 mg/l for the PACT sludge. The PACT  $IC_{50}$  value was significantly larger than the activated sludge value. The  $IC_{50}$  values increased with increased sludge age.

(5) Sorption studies indicate that the PACT sludge results in a substantially lower phenol concentrations than the activated sludge for the 8- and 12-day-old sludge. This difference may be sufficient to account for the difference in  $IC_{50}$  values. Sorption could be responsible for the improved resistance to inhibitory compounds, but it doesn't explain the difference for the 4-day-old sludge.

(6) The  $IC_{50}$  for zinc is 63 and 35 mg/l for the 4- and 12-day activated sludge while the corresponding PACT values were 57 and 91 mg/l. There was no statistical difference between the activated sludge and the PACT  $IC_{50}$  values for the 4-day sludge. For the 12-day sludge, the activated sludge became more sensitive with a lower value (35 mg/l), while the PACT sludge was less sensitive, with a higher value (91 mg/l).

(7) Sorption studies indicate that the 12-day-old activated sludge sorbed considerably less zinc than the younger sludge, so higher solution concentrations resulted. PACT sludge removed the same amount of zinc at all sludge ages, yet the 12-day sludge was more resistant to inhibition than the younger sludge. A change in the biological solids is likely to cause the improved resistance to the zinc.

(8) Better test procedures are needed to separate specific chemicals from the biomass and the activated carbon in PACT sludge.

While these results were in response to acute toxicity tests, they indicate that the PACT process microbial populations are likely to differ from those in a similar age activated sludge process and that these organisms resist toxicity better. This indicates that the PACT process should resist shocks better whether the contaminant is adsorbable or not. When there is sufficient carbon (at high sludge ages) or when there is a significant input of contaminant, sorption may become an important aspect in the protection of the biomass response to an adsorbable toxicant.

## Acknowledgements

This project was unfunded; Marina Sher was supported on a City of Akron-sponsored project and Zhiyao Shen was supported by The University of Akron.

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