Nitrification enhancement in the powdered activated carbon-activated sludge process for the treatment of petroleum refinery wastewaters

Adam Ng, Michael K. Stenstrom, David R. Marrs

Several important developments have enhanced activated sludge process performance and energy conservation in the past 10 years. One of these is the addition of powdered activated carbon. Activated carbon has been added to remove biologically resistant organics, thereby providing levels of treatment which were previously obtainable only with expensive physiochemical treatment methods.

Early work in the powdered activated carbon-activated sludge (PAC-AS) process is described in various patents.[1,2,3] Since the development of the PAC-AS process, a number of evaluations have been made of the process' efficacy on various types of wastewaters.[4-11] The success of PAC-AS concept is demonstrated by the current operation of a number of full scale PAC-AS treatment plants in both the municipal and industrial sectors. Operational data from bench-, pilot-, and full-scale plants have provided evidence that PAC addition can have the following benefits over conventional activated sludge processes: improved organic removals; improved sludge thickening/dewatering characteristics; increased color removal; suppressed aerator foaming; and improved nitrification.

The primary objective of early PAC-AS research was to determine the removal ability of biologically resistant organic compounds using carbon. Although some or all of the advantages of PAC addition have been reported in a number of studies, there remains a lack of fundamental understanding of the process mechanisms responsible for observed benefits. This is especially true in the relatively few cases where improved nitrification was noted.

Among the first reports of enhanced nitrification in the PAC-AS process was that made by Stenstrom and Grieves,[6] who reported improved nitrification in 42-L reactors operated over a 15-month period at the Amoco Oil Texas City Refinery. Subsequent tests[12] showed that PAC reactors did not always nitrify better than non-PAC reactors. Over a summer period non-PAC and PAC reactors produced virtually identical nitrification rates; however, during the next cool period the PAC reactors nitrified more efficiently. During the latter phases of this research a reactor was operated with catalytic-cracker fines added in lieu of PAC. Nitrification efficiency in this reactor, and in another reactor operating with a very poorly performing carbon, was no better than the efficiency of the non-carbon control reactor. They concluded that the probable mechanism of nitrification enhancement was adsorption of inhibitory compounds, because reactors operating with non-adsorbing suspended solids nitrified no better than the control reactor.

Other investigators have reported variable findings with respect to improved nitrification in PAC-AS processes. Thibault, *et al.*[7] investigated increased treatment efficiencies caused by PAC addition, using 4-L bench-scale activated sludge units, fed with refinery wastewater. Their objective was to evaluate different carbon types and treatment performance using various carbon doses. They reported marginally improved organic removals independent of carbon dose. Both the PAC and non-PAC reactors did not nitrify throughout the study period. In addition, their results suggested that PAC addition could have detrimental effects on treatment efficiency because of desorption of accumulated toxin compounds during shock loadings. Bettens[8] conducted tests with PAC addition into full-scale activated sludge plants treating textile-finishing wastewaters. His results, based on observations of before and after PAC addition over a 3-year study period, showed that almost complete and stable nitrification was achieved only after many months of uninterrupted PAC dosing (50–100 mg/L influent). Moreover, denitrification ability improved. Bettens attributed the increased stability of the nitrification/denitrification system to the high concentration of nitrifying organisms attached to the carbon particles.

Comparison of rate ratios of nitrification in activated sludge-wastewater systems dosed with PAC or bentonite demonstrated enhancement capabilities.

In treatability studies of chemical production wastewaters, Leipzig[9] reported that stable nitrification was possible in PAC-AS pilot reactors operating at high mean cell retention time. Nitrification was variable and less efficient in parallel non-PAC reactors. Leipzig suggested that this was caused by the adsorption of inhibitory compounds or nitrifier attachment to the carbon surface, or both. Specchia and Gianetto[11] demonstrated increased nitrification/denitrification capacity from PAC addition in a full-scale industrial plant treating dye-works wastewater. Their comparisons were based on before and after PAC addition to the aeration basin (800 mg/L reactor PAC) over a 4-month period. The investigators suggested that the improved denitrification was caused by either low dissolved oxygen concentrations at the bottom of the aeration basin created by PAC addition, or to a high concentration of nitrifying-denitrifying bacteria on the surface of the carbon.

Previous reports have provided strong evidence that the addition of PAC can cause improved nitrification, especially under stressful conditions such as low temperature or the presence of inhibitory compounds, or both. Although mechanisms such as adsorption of inhibitory compounds and enhanced growth of nitrifiers on the carbon surface have been suggested for explaining improved nitrification, no studies have been attempted to elucidate the mechanism(s) by which the phenomenon occurs.

The major objective of this study[13] was to further define the mechanism of PAC-AS nitrification enhancement. Experiments were designed to emphasize the evaluation of the adsorption and surface growth theories because previous researchers have provided tentative support for these mechanisms.

EXPERIMENTAL DESIGN

Batch assays. Using nitrifying mixed liquor drawn from five bench-scale activated sludge plants treating refinery and synthetic wastewaters, a series of batch experiments were conducted to evaluate the influence on nitrification of PAC adsorption, the presence of inert suspended solids, and microbial acclimation. The general procedure was to compare the effect of an added adsorbable or non-adsorbable inhibitory compound on nitrification rates in assays from the following different reactor types: activated sludge (AS) and AS supplemented either with PAC or bentonite (BEN). Bentonite clay (aluminum silicate) is an inert suspended solid that is known to have suitable surface chemistry for microbial attachment (Stotzky,[14] Santoro and Stotzky[15]), but limited ability to adsorb organics.

Relative nitrification rates between assays with and without the added compound were computed for each reactor type and expressed as a ratio to form a basis of comparison among the different reactor types. Hence, if an adsorbable nitrification inhibitor was used and the nitrification rate ratio was significantly higher in PAC over BEN supplemented AS, the adsorption theory for nitrification enhancement was supported. Conversely, if equal or higher nitrification ratios were observed for BEN supplemented AS when a non-adsorbable nitrification inhibitor was added, the surface attachment theory was supported. Non-inhibitory compound use for testing verified experimental techniques, because ratios of nitrification rates should be close to unity for all reactor types.

The effects of the selected compounds on nitrification rates in acclimated and non-acclimated sludges were also examined parallel to the experiments already discussed This was done because our literature review[13] had suggested the acclimation ability may be an important variable in the degree at which nitrification inhibition is expressed.

Compound selection. An intensive survey of all known nitrification-inhibiting compounds and their carbon adsorption properties was made. Compounds were characterized either as adsorbable-inhibitory (AI), nonadsorbable-inhibitory (NAI), nonadsorbable non-inhibitory (NANI), or adsorbable-noninhibitory (ANI). From this survey a group of compounds was selected for experiments, based on the adsorptive and nitrification inhibition properties of the compounds, the likelihood of finding it in petroleum refinery wastewaters, and solubility considerations. Compounds selected were aniline (AI), phenol (AI), cyanide (NAI), acrylonitrile (NANI) and toluene (ANI). All of these compounds are traditionally associated with petroleum refinery or petrochemical processes. The presence of aniline, phenol, acrylonitrile, and toluene in the refinery wastewater used in this study was confirmed with gas chromatography/mass spectrometry. Cyanides were always less than 0.15 mg/L. The wastewater also contained no significant concentrations of heavy metals.

Continuous experiments. It is generally agreed that short batch tests do not give a good indication of how a given biological system will react under actual field conditions. Two consecutive continuous flow experiments were conducted to determine the long-term influences of PAC and BEN addition on activated sludge nitrification rates in the presence of aniline, a known adsorbable nitrification inhibitor.

EXPERIMENTAL METHODS

Reactors and associated apparatus. Five identical continuous-flow activated sludge reactors were operated simultaneously, treating either refinery or synthetic wastewaters. Of the five reactors, three received refinery wastewater (RW) as feed while the remaining two reactors received a glucose-ammonia based synthetic substrate (GA). Among the RW-fed reactors, PAC additions were made in one and bentonite additions in another, with the third acting as a control with no PAC addition. For the GA-fed reactors, PAC additions were made in one and the other served as a control. The PAC and the bentonite clay used in the study were obtained from single but separate suppliers. The operating processes for the reactors are shown in Table 1.

Each reactor was constructed of 1.2-cm (0.5-inch) plexiglass with a working volume of 12.2 L in the aeration section and 1.5 L in the solids-liquid separator section (Figure 1). The two sections were separated by a sliding baffle that fit snugly into slots to both sides of the reactor wall. Several holes were provided in the lid of the reactor: larger holes for a pH probe and access for maintenance purposes and smaller holes for influent feed, base addition, and air lines. A porthole on the side of the aeration section was used to withdraw mixed liquor for analysis and for the control of sludge age. Air, which was added through diffuser stones located near the bottom of the aeration section, provided oxygen for microbial activity and growth as well as turbulence for mixing purposes. Airflow rates, between 140 to 280 L/min (5 to 10 cu ft/min), were monitored independently in each reactor by routing the air through a rotameter before its introduction into the mixed liquor. Lower airflow rates were necessary at times to control reactor foaming and higher flow rates were occasionally required to provide adequate mixing. Even with the lowest airflow rates used, the dissolved oxygen concentration in

Table 1—Reactor conditions.

Feed	Reactor	Additions	Nomenclature used to identify reactor type
Glucose-ammonia	1	PAC	GPAC
	2	none	GCAS
Refinery wastewater	3	PAC	RPAC
	4	none	RCAS
	5	Bentonite	RBEN

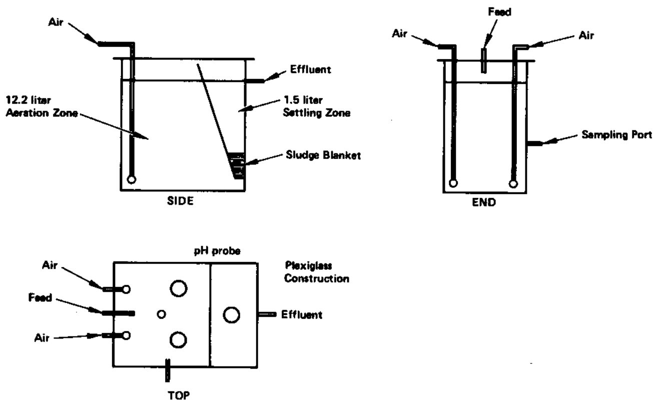

Figure 1—Schematic of reactor and associated apparatus.

the mixed liquor was above a level (3 mg/L) that would be expected to limit the growth of heterotrophs or nitrifiers at a high mean cell residence time (MCRT) environment. Each reactor had a pH controller which maintained pH from 7.0 to 7.2.

Synthetic wastewater composition and feed system. Because a large quantity of synthetic substrate was required, a dilution system was used to dilute concentrated feed before it was pumped into the reactors. A schematic of the dilution system is shown in Figure 2. The liquid level in the mixing reservoir was electronically sensed by two float switches which controlled both the concentrate feed pumps to the reservoir and an external solenoid valve for the flow of dilution tap water. The diluted substrate was pumped directly from the mixing reservoir, contained in a refrigerator at 4°C, into the reactors using a separate pump system. The feed was composed of glucose, ammonia, and other nutrients required to support the growth of heterotrophs and nitrifiers. The composition of the concentrated feed solution is shown in Table 2. The $CaCl_2$-$MgCl_2$ solution was separately pumped into the mixing reservoir to prevent the formation of calcium phosphate precipitates in the concentrate. The concentrate, prepared every 3 days, was diluted approximately 250 times during each cycle. The total steady-state influent ammonia-N concentration was calculated and measured to be 50 mg/L.

Refinery wastewater composition. Wastewater was obtained periodically from a West Coast oil refinery. The wastewater, drawn from the effluent side of dissolved air flotation units, was trucked from the refinery to the laboratory in 55-gallon polyethylene drums and stored in a walk-in refrigerator at 4°C. From there, the wastewater was automatically pumped, using an electronic filling/refilling system, into a refrigerated reservoir in the laboratory. From the reservoir, the wastewater was pumped into the reactors by a separate pump system. Because refinery wastewaters are generally lacking in phosphorus, phosphoric acid was added manually to the RW reactors daily (1 mg/L feed). No other nutrient was supplemented. For each batch of wastewater

Table 2—Concentrated feed and mineral solutions.

Component	Amount[a]
Concentrated feed (add to 1.0 L distilled water)	
Trace mineral solution	2 mL
$CaCl_2$-$MgCl_2$ solution	8 mL
K_2HPO_4	25.0
Yeast extract	10.0
Glucose	103.5
$(NH_4)_2SO_4$	10.0
NH_4Cl	45.0
Trace mineral solution (to 0.5 L distilled water)	
$FeCl_3$	19.5
$MnCl_2$-4 H_2O	4.75
$ZnCl_2$	3.30
$CuCl_2$-2 H_2O	2.05
$CoCl_2$-6 H_2O	2.90
$(NH_4)Mo_7O_{24}$-4 H_2O	2.10
Na_3 citrate	176.5
$Na_2B_4O_7$-10 H_2O	1.20
$CaCl_2$-$MgCl_2$ solution (to 0.2 L distilled water)	
$CaCl_2$	2.30
$MgCl_2$-6 H_2O	4.10

[a] Grams added unless otherwise noted.

Table 3—Results and comparisons of GC/MS analysis, concentrations in mg/L.

	Set 1	Set 2	Set 3
	Sept. 24, 1982	Dec. 28, 1982	Feb. 2, 1983
Aliphatic hydrocarbons			
Total alkanes (C_4 to C_{30})	0.701	0.341	2.78
Carboxylic acids (C_3-C_7)	18.3	19.8	8.8
Alcohols	0.12	—	0.428
Aldehydes	—	—	0.013
Ketones	0.65	1.11	1.05
Alicylic	—	—	5.61
Aromatic hydrocarbons			
Total phenols	21.14	18.62	43.1
Benzene and derivatives	8.13	4.89	5.35
Polynuclear aromatic	0.364	0.203	0.041
Heterocyclic hydrocarbons	2.94	0.913	0.635
Others			
1-methyl-2,3-dihydroindene	—	0.1	0.1
1-methyl-2-piperidione	—	—	0.26
4-octyne	—	0.39	0.78
dimethyldisulfide	0.25	0.24	0.12
dimethylphthalate	0.15	—	—

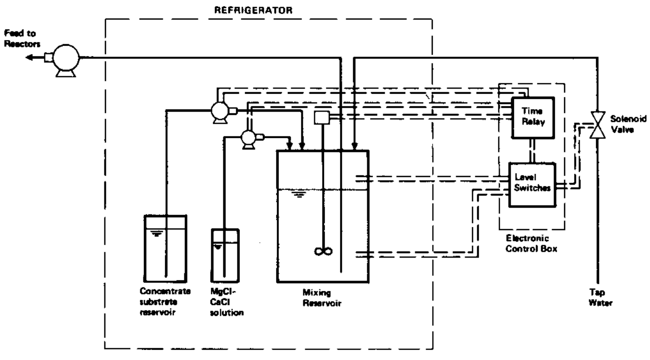

Figure 2—Schematic of substrate dilution system.

received, the pH, ammonia-N concentration, and soluble organic carbon (SOC) content was determined. In addition, adsorption isotherms, using PAC and bentonite as adsorbents, were determined for a single batch of wastewater. A GC/MS analysis was performed for base/neutral/acidic extractable organics in three separate batches of wastewater, to screen for potential nitrification inhibitors and to ascertain the general nature of the wastewater. The chemical characteristics of the raw refinery wastewater used throughout this study are shown in Table 3.

This refinery waste was selected in part because of its difficulty in fully nitrifying. Even though the plant's mean cell retention time and dissolved oxygen concentrations are well within the ranges normally considered acceptable for full nitrification, it frequently has difficulty nitrifying. Previous work[6] had shown that wastewaters having the greatest potential for inhibiting nitrification were the most likely to show benefits from PAC addition, and for this reason it was considered a good source of wastewater.

Experimental reactor operating conditions. The reactor operating conditions used during the experimental period are shown in Table 4.

Mixed liquor to seed the reactors was obtained from the Hyperion treatment plant in El Segundo, Calif. Appropriate volumes of PAC and bentonite were added as a slurry to the aeration section of the reactors daily. To ensure that steady-state conditions existed during the experimental period, all reactors were operated at the parameters specified above for a period of 2 MCRT's before the start of experimentation. With the exception of initial foaming problems encountered in the bentonite reactor, all reactors performed smoothly during this period, regularly achieving SOC removal efficiencies of greater than 95% for the GA-fed reactors and greater than 80% for the RW-fed reactors. Consistent NH_4^+-N removals were observed for the GA-fed reactors while NH_4^+-N removals for all RW-fed reactors were erratic (19–90%), especially during the first 6 weeks of operation. In the following 3 weeks, the refinery reactors consistently removed NH_4^+-N at efficiencies greater than 99%. Experimentation began following a period of stable nitrification.

EXPERIMENTAL PROCEDURES

Adsorption isotherms. Adsorption isotherm experiments were conducted to assess the relative adsorptive capacities of PAC and bentonite using refinery wastewater as the adsorbate. The procedure for the isotherms consisted of the following steps: PAC and bentonite were dried at 150°C for 3 hours and placed in a desiccator before use; appropriate amounts of PAC and bentonite were analytically weighed and placed into 150-mL Pyrex square bottles. Two bottles containing neither PAC or bentonite were retained as controls. Untreated refinery wastewater (125 mL) was added to each bottle, resulting in PAC or bentonite concentrations of 0.1, 0.2, 1.0, 2.0, 5.0, 10.0, and 20.0 g/L refinery wastewater and two controls. All bottles were stoppered, placed in a horizontal position on an orbital shaker, and agitated at 130 rpm for 3 hours at room temperature (27–29°C). At the end of the agitation period, the contents of each bottle was vacuum filtered through a 0.45-μm membrane filter and analyzed for SOC.

Batch assay procedures. Selected compounds and the concentrations used in the batch assays were aniline (10, 10 mg/L), phenol (10, 20 mg/L), toluene (10 mg/L), cyanide (1, 3, 3 mg/L as CN^-), and acrylonitrile (10 mg/L). The following procedure was used for all batch assays. Before each experiment, the NH_4^+-N and NO_3^--N effluent concentrations were determined for each reactor type. Mixed liquor, 430 mL, was withdrawn from each reactor into 500-mL Erlenmeyer flasks and an appropriate volume (1 to 3 mL) of a NH_4Cl solution was mixed into each flask to bring the concentration of NH_4^+-N to a predetermined level (60 mg N/L). Mixed liquor in each flask was divided equally into two 250-mL Erlenmeyer flasks. For each pair of flasks, an appropriate volume of a stock solution containing the test compound was added into one of the flasks to bring its concentration to the desired level, with the other flask retained as a control. All flasks (250 mL) were placed under a manifold and aerated for a specific period of time. Air was supplied through a disposable pipet at a flow rate of 100 L/h (3.5 cu ft/min) to ensure adequate dissolved oxygen concentrations and mixing at all times. Shortly after the start of aeration (typically 1–2 minutes), two separate 5- or 10-mL samples of mixed liquor were withdrawn from each flask with volumetric pipets. The mixed liquor samples were diluted to volume with an appropriate dilution solution in 100-mL volumetric flasks, capped, and stored for the analysis of ammonia and nitrate at the end of the aeration period. These samples were designated as t = 0 hour. Additional samples were taken throughout the aeration period. In the first two experimental runs with 10 mg/L aniline and 1 mg/L cyanide, the aeration period was 24 hours with sampling intervals ranging from 1.5 to 9 hours. In the following experiments, the aeration period was 9 hours with samples taken at t = 2, 4, 6, and 9 hours. Every hour throughout the aeration period, the pH was checked and adjusted, if necessary, to the range of 7.2–7.4 (using 0.05 or 0.1 *N* NaOH). The volume of caustic used was reported after each pH adjustment.

Continuous experiments with aniline. Two consecutive continuous flow experiments were carried out over a 2-month period using the three continuous flow RW fed reactors as experimental units. Consistent ammonia oxidation efficiencies of greater than 99% over a period of 1 week or longer for each reactor were a necessary prerequisite before the start of the initial experiment. This was to ensure that any observed effects could be attributed to the presence of added inhibitor, rather than to poor nitrification. In the initial experiment, all three reactors were subjected to a simultaneous aniline step and pulse input of 30 mg/L and a pulse input of 75 mg NH_4-N/L reactor (the reactor concen-

Table 4—Reactor operating parameters.

Reactor feed	Hydraulic retention time, days	Mean cell retention time, days	PAC or BEN added, mg/L feed	Calculated steady-state reactor PAC or BEN concentration
Synthetic wastewater	0.5	60	25	3000 mg/L
Refinery wastewater	1.0	60	50	3000 mg/L

tration was increased to 30 mg/L aniline and 75 mg/L ammonia by direct addition to the mixed liquor, as well as increasing aniline feed concentration by 30 mg/L). Immediately following this, the concentrations of ammonia and nitrate in the mixed liquor were sampled over time at regular intervals (every 2 to 8 hours) for 265 hours and then once a day for the next 3 weeks.

In the second experiment, the reactors, which had been operating at steady state with a continuous input of 30 mg/L aniline in the RW feed, were subjected to a simultaneous step and pulse of aniline and ammonia as before, except that the feed and reactor aniline concentrations were increased to 60 mg/L. The concentrations of ammonia, nitrite, and nitrate-N were monitored with time using sampling intervals of 2–3 hours up to the first 100 hours and once a day thereafter.

The general procedure for the continuous feed experiments consisted of the following steps. Before the start of experimentation, a separate pump system was installed for the continuous addition of aniline to the RW reservoir. This system consisted of a time-controlled pump operated via liquid level switches in the feed reservoir. At each reservoir filling cycle, a predetermined volume of aniline was pumped, diluted, and mixed with the incoming stream of RW. Aniline was pumped from a prepared concentrated stock solution contained in a flask adjacent to the reservoir. Before the start of each experiment, the RW reservoir was thoroughly cleaned by scrubbing and rinsing with hot water. Each experiment began with the reservoir at the start of a new filling cycle. Influent and effluent ammonia concentrations were measured for each RW-fed reactor. The RW feed pumps were turned on to give the step input of aniline. A 10-mL concentrated aniline solution was pipetted directly into the aeration section of each reactor to give an instantaneous aniline concentration increase. A 20-mL concentrated stock solution of ammonium chloride was pipetted into each reactor to give an instantaneous increase in reactor concentration to 75 mg NH_4-N/L. Two 10-mL mixed liquor samples were taken directly from the aeration section of each reactor at every sampling period. Samples were diluted to volume in a 100-mL volumetric flask with distilled water (for analysis NH_4^+-N) or with a dilution solution (for analysis of NO_3^--N). For nitrite samples, 100 mL of mixed liquor from each reactor was withdrawn and allowed to settle. Using a volumetric pipet, 1 or 2 mL of the resulting supernatant was withdrawn and diluted with distilled water into a 200-mL volumetric flask. The settled mixed liquor and supernatant were then promptly returned to the aeration section of each corresponding reactor. Throughout the entire test period, the pH was automatically maintained at 7.0–7.2. Cumulative caustic (1.0 N NaOH) usage was recorded for each reactor. Usual daily sludge wastage and PAC or bentonite additions were maintained throughout the experimental period.

ANALYTICAL METHODS

Ammonia-N. An ammonia specific ion electrode in conjunction with an ion analyzer was used to directly measure ammonia concentrations in the influent, mixed liquor, and effluent samples. The probe was calibrated at least once, using laboratory prepared standards, before and during each analytical run. All samples were preserved with 1 *M* HCl (0.1 mL/0.1 L of sample) and stored in capped volumetric flasks. Sample volume analyzed was 100 mL or aliquots diluted to 100 mL.

Nitrite-N. Nitrite-N was determined by a technique described by Method 419 in "Standard Methods".[16] All nitrite samples were preserved with 5 mg $HgCl_2$/0.1 L sample, filtered, and diluted with distilled water to cover the applicable range of the method (0.01 to 1.0 mg NO_2^-/L). Photometric determinations were accomplished using a spectrophotometer (1 cm light path) at 543 nm. Standard curves were obtained for each analytical run using serially diluted nitrite standards ($NaNO_2$).

Nitrate-N. A calibrated nitrate electrode with an ion analyzer was used for the determination of nitrate in all samples. Initially the cadmium-reduction method, Method 418C in "Standard Methods," was used. However, after an evaluation of the two methods for measurement of nitrate in RW derived samples, the probe method was determined to be a better choice based on the following observations. Although both methods suffered from unknown interferences present in the RW, the electrode method was at least as accurate as the Cd-reduction method and much faster and more economical than the Cd-reduction method. The efficiency of the Cd-reduction column decreased rapidly and eventually exhausted after only a few sample runs (8–9 samples). The degree of reduction in column efficiency or the point of exhaustion was difficult to detect or predict during analytical runs. This made it difficult to establish the proper time for corrective measures, such as Cd regeneration or granule replacement. Often a reduction in column efficiency was detected only after samples had already been analyzed.

When using the probe method, a constant ionic strength background must be maintained. The recommended ionic strength adjuster (ISA) for domestic wastewater samples is 2 mL of 2 *M* ammonium sulfate/100 mL sample, resulting in an ionic strength of 0.12 *M*. This ISA gave good accuracy and reproducibility (less than 5% variability) for the GA-fed samples, but poor to adequate results were obtained with the RW-derived samples. An alternate ISA (Milham[17]) used for the analysis of nitrates in soils was tested and provided more reproducible results for RW-derived samples. The modified ISA consisted of 16.66 g $Al_2(SO_4)_3 \cdot 18H_2O$, 4.67 g Ag_2SO_4, and 2.43 g NH_2SO_3 in 1 L of distilled water. The ionic strength background for this ISA was calculated to be 0.49 *M*. In this study, the modified ISA was used as a dilution liquid for the analysis of nitrates in RW-derived samples and the 2 *M* ammonium sulfate ISA was used for nitrate analysis in the GA-derived samples. The dilution liquid used in the later case was distilled water. All samples were preserved with 1 *M* boric acid (1 mL/100 mL sample).

Soluble organic carbon. All SOC determinations were made with an total organic carbon (TOC) analyzer that used a combustion-infrared method for the analysis of soluble and nonpurgable TOC. Samples were collected in clean glass bottles, preserved with concentrated HCl (pH less than 2) and stored at 4°C, if analysis was not immediate. All samples were either filtered (0.45 micron) or centrifuged and purged of inorganic carbon using HCl before analysis. A minimum of three consecutive replicates per sample were analyzed with the last two replicates averaged and recorded. The calibration solution standard was acetic acid and a new standard curve was obtained for each analytical run.

Mixed liquor suspended and volatile solids. Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) for each reactor was determined at various times throughout the study. For the GA-fed reactors, the solids were measured in accordance with Methods 209D and G in "Standard

Methods". For the PAC or bentonite supplemented reactors, MLSS concentrations were calculated using the following equation, based on the steady-state reactor concentration (C) of PAC or bentonite:

$$MLSS_{(biomass)} = MLSS_{(measured)} - C. \quad (1)$$

The MLVSS concentration was calculated by a similar steady-state equation:

$$MLVSS_{(biomass)} = MLSS_{(measured)} - C \times MLSS_{(biomass)} \times X, \quad (2)$$

Where

X = fraction of PAC or bentonite volatilized in MLVSS tests (assumed to be equal to the fraction of PAC or bentonite volatilized in a separate test with PAC or bentonite).

Alternately, Arbuckle *et al.*[18] proposed a method to determine biological solids concentration in PAC sludges operating under nonsteady-state conditions. The procedure requires the determination of MLSS, MLVSS at 400°C, and MLVSS at 550°C for PAC sludges and PAC by itself. In this study, the steady-state method was used to determine MLSS and MLVSS concentrations in the bentonite reactors and Arbuckle's method was used for the PAC reactors.

RESULTS AND DISCUSSION

Adsorption isotherms. Results of the RW adsorption isotherms are shown in Figure 3. For bentonite dose greater than 1250 mg (10 g/L), it was not possible to filter SOC samples and obtain a reproducible measurement. Data for the PAC isotherm indicated less-than-favorable adsorption equilibria for this particular wastewater, and in the case of bentonite, little or no adsorption capacity was observed. For the PAC isotherm, the equilibrium adsorption data correlated with the Freundlich isotherm model (r^2 = 0.8), resulting in calculated Freundlich parameters of K_f = 2.8 × 10^{-3} mg/g PAC at C_e = 1.0 mg SOC/L and n^{-1} = 2.58.

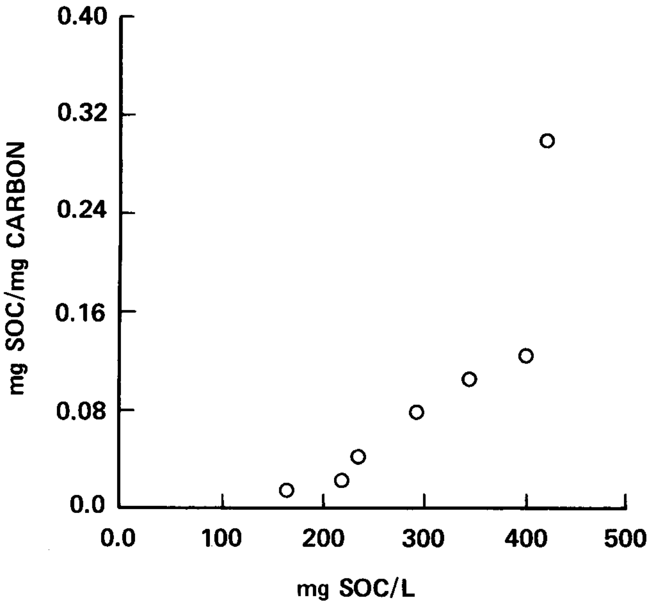

Figure 3—Refinery wastewater adsorption isotherms (blank SOC = 450 mg/L).

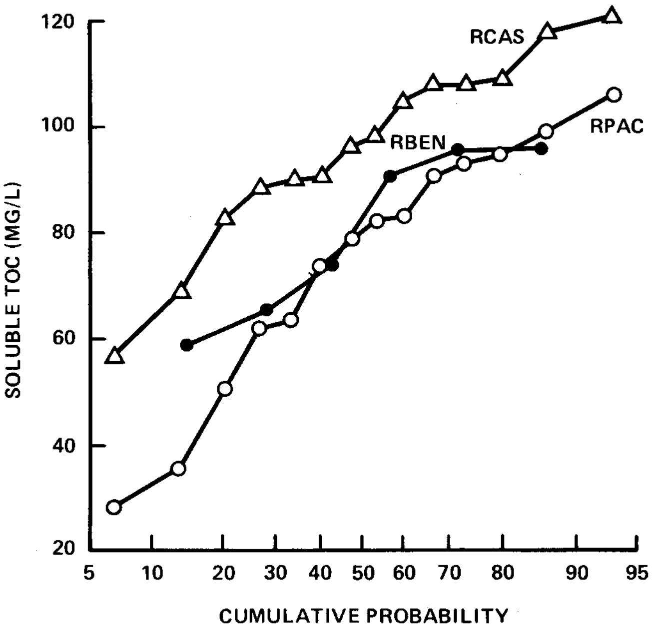

Figure 4—Cumulative effluent soluble organic carbon probability for refinery wastewater-fed reactors.

Calculated PAC adsorption parameters and data for SOC removals under PAC-AS equilibrium reactor conditions (when effluent SOC = ~80 mg/L; see Figure 4) suggest that, at the PAC dose used, the steady-state reduction in SOC caused by carbon adsorption should be less than 1.0 mg/L. However, steady-state operational data of effluent SOC (see Figure 4) indicated that the PAC and bentonite supplemented AS reactors consistently achieved greater SOC reductions than the corresponding control reactor. Increased organic removals caused by PAC addition are also consistent with observations cited in a number of studies. Mechanisms that have been proposed to explain this common observation are adsorption of influent substrate, enhanced biological assimilation, bioregeneration of adsorbed organics, and metabolic end product adsorption.

Results from the isotherm tests suggest that the increased SOC removals in the PAC and bentonite units were caused by some mechanism(s) other than the steady-state adsorption of influent substrate. Other mechanisms, such as enhanced biological assimilation (EBA) can be considered an explanation for increased organic removal. In other studies,[19-20] increased steady-state oxygen uptake rates or increased MLVSS is taken as evidence for EBA. In this study, steady-state data on oxygen uptake rates MLVSS concentration (see Table 5) taken at various intervals throughout the study period provided no definite evidence to support the existence of EBA. In fact, the MLVSS concentrations in the PAC and bentonite supplemented reactors were generally less than in the corresponding control reactor.

One possible mechanism that may account for the observed results is metabolic end product (MEP) adsorption. MEP are organics of microbial origin (metabolites, cellular components of lysed organisms). Studies by Schultz,[21] using radioactive labeled phenol substrates showed that 75% of the MEP produced from the biodegradation of phenol was irreversibly adsorbed by PAC. Other studies (as cited by Schultz) suggested that the adsorption of MEP may play an important role in PAC systems,

Table 5—Oxygen uptake rate and MLVSS data.

Oxygen uptake rates (mg O_2/L · h)				
GPAC	**GCAS**	**RPAC**	**RCAS**	**RBEN**
10.6	10.0	16.0	14.4	14.0
11.2	11.3	15.7	15.0	14.2
11.1	10.8	15.6	15.1	15.0
MLVSS (mg/L)				
3060	2520	2836	3059	2918
—	4440	—	—	—
4404	5262	4000	5998	3754
3021	4998	5634	6000	3770
4782	6296	6517	4844	3292
—	—	8396	5313	4443

Note— Arbuckle's method[16] was used to calculate MLVSS for the PAC reactors. Values for X_{400} = 0.0784 and X_{550} = 0.74 were determined experimentally. MLVSS for the bentonite reactors was measured and calculated by the steady-state method. Oxygen uptake rates were measured with an immersed DO probe in BOD bottles.

especially if the wastewater to be treated contains low amounts of adsorbable compounds. The less pronounced differences in SOC removals for the GA-fed reactors (see Figure 5) may be attributed to the difference in substrates fed. Glucose is a very simple and easily biodegradable organic, whereas the refinery wastewater contained a variety of complex compounds, many of which biodegrade very slowly. The differences in substrates no doubt influences the microbial population in the respective reactors, and thus may determine the nature and quantity of MEP produced. It should be noted that the bentonite-AS reactor performed as effectively as the PAC-AS reactor with respect to SOC removals at a solids retention time (SRT) of 60 days (Figure 4). If the MEP adsorption theory is applicable for this situation, a MEP isotherm study using bentonite should be undertaken.

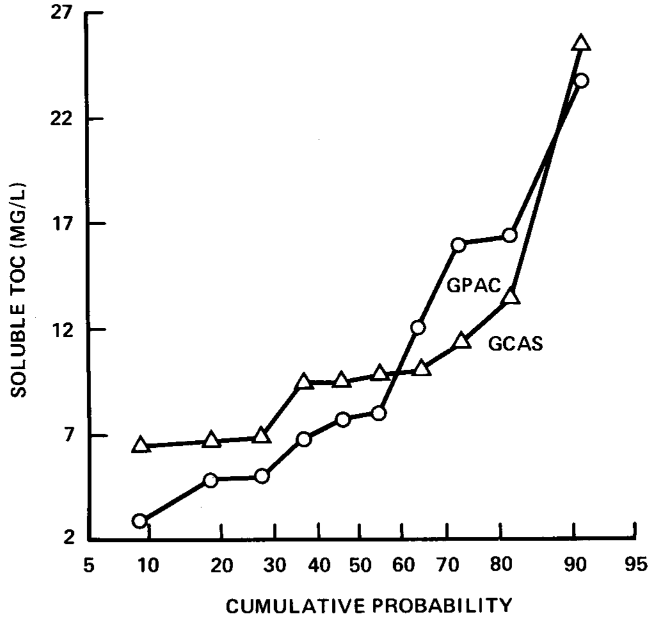

Figure 5—Cumulative effluent soluble organic carbon probability for glucose-ammonia fed reactors.

Batch inhibition assays. A series of nine batch experiments was performed. Figures 6 and 7 represent typical data generated from a single experiment. To interpret results, zero-order nitrification kinetics were used. Zero-order kinetics have been observed and used previously to describe nitrification by numerous investigators under various conditions.[22-27] Reported K_s values for ammonia oxidation in activated sludge processes typically range from 0.5 to 2.0 mg/L;[28-31] therefore, for ammonia concentrations above 2.0 mg/L, the kinetic expression for ammonia oxidation in a batch reactor becomes

$$\frac{d\mathrm{NH_4^+\text{-}N}}{dt} = -K. \tag{3}$$

If the ammonia oxidation rate is rate limiting, the nitrate production can be similarly expressed:

$$\frac{d\mathrm{NO_3^-\text{-}N}}{dt} = K. \tag{4}$$

Data analysis for all batch experiments included simple linear regression for determination of ammonia and nitrate reaction constants, *K*, and covariance analysis using the generalized linear models (GLM) procedure.[32] Covariance analysis tests for the heterogeneity of the slopes between the treatment group (assays with added compound) and the control group. This analysis was restricted to comparisons between test and control groups because they differ only in the presence or absence of the added compound. The calculated ammonia oxidation rate constants for all experimental runs are shown in Table 6. Included in Table 6 are the regression correlation coefficients, r^2, which indicate the degree of linearity (or zero-orderness) of the reaction. In general, for the RW assays, the *K* values for ammonia oxidation and nitrate production were not in stoichiometric agreement; nitrate production rates were usually higher than the corresponding ammonia oxidation rates. This may have been caused by excessive cellular lysis from the added compound or by the analytical difficulties associated with the measurement of nitrate in this particular type of wastewater (see Analytical Methods).

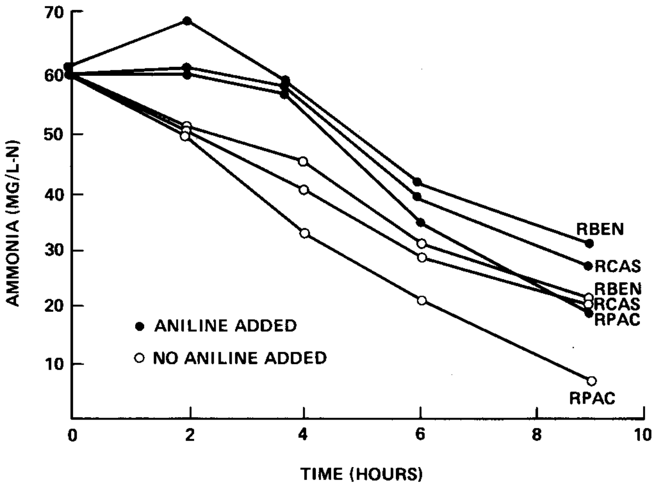

Figure 6—Batch inhibition experiment with 10 mg/L aniline, refinery wastewater-fed reactors.

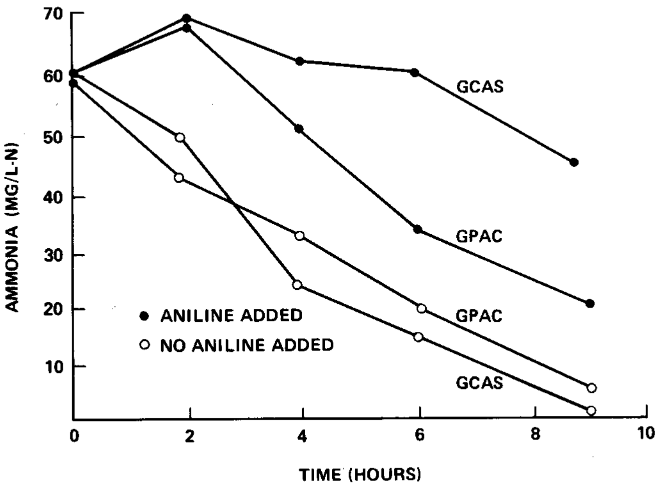

Figure 7—Batch experiment with 10 mg/L aniline, glucose-fed reactors.

For this reason the ammonia oxidation data, which was considered to be more reliable than the nitrate production data, were selected for further analysis.

Table 7 presents the ammonia oxidation rate constants using an inhibition coefficient, I. Defined as the ratio of K in the test assay, (in presence of the added compound) to K in the control assay, I can be used to facilitate comparisons among the different reactor types and the degrees of nitrification inhibition observed. An I value of 1.0, or less than 1.0 would indicate, respectively, no inhibition, or an inhibitory effect on nitrification, caused by the added compound. Inspection of Table 7 reveals that the addition of acrylonitrile (non-adsorbable) and toluene (adsorbable), which are both known to be non-inhibitory to nitrifiers, did not significantly affect the nitrification rate. With the exception of two cases (toluene in the RW bentonite reactor, I = 1.29 and acrylonitrile in the RW control reactor, I = 0.85), all values are close to unity. Duplicate assays on the same reactor type in two separate experimental runs (aniline and toluene) indicated that the variability of I within a given experimental run is 7% or less.

Table 7 shows that for adsorbable, inhibitory compounds such as aniline or phenol, the benefits of PAC addition were pronounced for unacclimated activated sludges (glucose-fed reactors). In two cases out of three, the PAC-AS assays handled a shock load of the inhibitory compound more readily than the corresponding non-PAC assays. In the case where the non-PAC outperformed the PAC assays, as indicated by I values, the differences were not statistically significant, and will be discussed later. The differences among the RW reactors subjected to adsorbable inhibitors were less pronounced than that between the glucose reactors. This is attributed to microbial acclimation to the wastewater. The microorganisms in the RW reactors were routinely exposed to a variety of inhibitory compounds for an extended period of time (4 to 6 months). Any beneficial effects, caused by the addition of either PAC or bentonite at the dosage used (50 mg/L feed), was not sufficient to provide any further improvement beyond the benefits of acclimation. It should be noted however, that in the initial batch experiment conducted (with 10 mg/L aniline), the PAC-AS assay outperformed the corresponding non-PAC and bentonite-AS assays. It is conceivable that the RW reactors at this early stage of experimentation were not yet fully acclimated to the wastewater. This then would provide for a more sensitive experiment for the detection of any beneficial effect of the added PAC. A similar experiment with 10 mg/L aniline, conducted 100 days later, showed no significant nitrification enhancement for either PAC or bentonite addition in the RW assays.

Further evidence for microbial acclimation in the RW reactors is provided in all experimental runs with cyanide. Table 7 shows that while cyanide, a non-adsorbable inhibitor, had detrimental effects on all measured nitrification rates, inhibition was much more severe in the unacclimated reactors. The results with spiked cyanide are inconclusive with respect to any observable benefits of added PAC or bentonite.

The results of covariance analysis on ammonia oxidation rate data for all batch experiments are presented in Table 8. The analysis was used to provide for a more rigorous method of judging any benefit of PAC or bentonite addition, based on a pre-established statistical criteria. In this study, the null hypothesis (that is, no difference between the test and control assays) is tested, and either accepted or rejected according to a prescribed level of probability, using the F statistic, defined as follows:

$$F = \frac{\sigma^2(\text{between})}{\sigma^2(\text{within})}. \quad (5)$$

The results of the statistical analysis confirm the generalizations drawn from Table 5 of inhibition coefficients, I. No difference in nitrification rates are observed for non-inhibitory compounds regardless of adsorptive characteristics. The statistical results for cyanide, a non-adsorbable inhibitor, show no definite advantage in adding either PAC or bentonite. Table 8 reveals that the control AS nitrified as well or better than AS supplemented either with PAC or bentonite. For adsorbable inhibitors, the benefit of PAC addition is demonstrated in unacclimated assays. For RW assays, the benefits of PAC are statistically significant only in the earliest experimental run. This may have resulted because the RW reactors were not yet fully acclimated.

Continuous experiments. The results of the continuous experiments are plotted in Figures 8 through 13. In the initial experiments, each RW reactor was subjected to a simultaneous pulse and step addition of 30 mg/L aniline and a pulse of 75 mg NH_4^+-N/L reactor. Figure 8 shows surprising results, in that nitrification was completely inhibited in the PAC supplemented reactor, whereas the control and bentonite supplemented reactor resumed nitrification to completion following a lag period of 6 (control) to 15 hours (bentonite). Further evidence for the complete inhibition of nitrification in the PAC reactors is provided by concurrent observations of negligible caustic uptake (Figure 9) and a continuous decrease in reactor nitrate concentration (Figure 10). Based on prior batch experimental results, the reason(s) for the lack of nitrification in the PAC unit were perplexing and it was decided (on the 75th hour of the experiment) to add 1000 mg/L PAC in the inhibited reactor. Figures 8 through 10 show that the response to the added PAC was dramatic with an immediate resumption of nitrification, caustic uptake and nitrate production. Although Figure 9 indicates a short lag in caustic uptake, it was not indicative of true consumption, because the aniline spike had raised the reactor pH from 7.0 to 8.3. The caustic pump was set to actuate when the pH dropped below 7.0; therefore the lag noted in Figure 9 actually represents the period of time in which the reactor pH dropped from 8.3 to below 7.0. Following the experiment, daily reactor effluent sam-

Table 6—Ammonia oxidation constants, *K*, and regression coefficients, r^2.

Spiked compound	Type		GPAC	GPACC	GCAS	GCASC	RPAC	RPACC	RCAS	RCASC	RBEN	RBENC
Acrylonitrile, 10 mg/L	NANI	r^2	0.92	0.98	0.92	0.98	0.90	0.94	0.85	0.94	0.85	0.96
		K	3.47	3.33	3.35	3.28	2.39	2.49	1.25	1.48	1.07	1.13
Aniline, 10 mg/L	AI	r^2	0.90	0.92	0.52	0.98	0.90	0.98	0.92	0.98	0.79	0.98
		K	5.12	6.98	1.87	5.92	4.76	5.47	4.17	4.82	3.77	4.14
	Duplicate test	r^2	0.96	0.98								
		K	4.82	6.98								
Aniline, 10 mg/L	AI	r^2	0.77	0.009	0.44	0.34	0.94	0.92	0.88	0.96	0.66	0.90
		K	0.9	0.03	−0.39	−0.269	1.44	1.83	0.84	1.75	0.49	1.42
Cyanide, 1 mg/L	NAI	r^2	0.74	0.71	0.52	0.97	0.05	0.96	0.03	0.70	0.54	0.78
		K	−0.76	0.58	−0.60	1.18	0.19	2.11	−0.14	0.58	−0.70	−0.68
Cyanide, 3 mg/L	NAI	r^2	0.66	0.98	0.98	0.94	0.94	0.87	0.94	0.86	0.98	0.96
		K	0.66	2.9	1.39	3.76	1.25	2.46	1.3	2.15	0.752	1.78
Cyanide, 3 mg/L	NAI	r^2	0.02	0.98	0.24	0.94	0.61	0.92	0.77	0.90	0.79	0.88
		K	−0.16	4.51	0.72	3.88	2.17	4.86	1.33	2.37	1.77	2.5
Phenol, 10 mg/L	AI	r^2	0.48	0.90	0.87	0.88	0.92	0.88	0.98	0.98	0.94	0.92
		K	1.26	2.89	2.69	3.65	2.46	2.51	1.84	1.83	1.82	1.77
Phenol, 20 mg/L	AI	r^2	0.98	0.98	0.45	0.94	0.98	0.94	0.98	0.83	0.98	0.92
		K	4.36	5.42	1.59	4.42	3.28	3.46	2.65	2.44	2.03	2.1
Toluene, 10 mg/L	ANI	r^2	0.98	0.98	0.98	0.98	0.96	0.90	0.92	0.90	0.94	0.87
		K	5.38	5.44	5.24	5.19	4.22	4.02	3.15	3.13	4.24	3.29
	Duplicate test	r^2					0.94	0.98				
		K					3.88	4.05				

NANI = non-absorbable, non-inhibitory compound
AI = absorbable, inhibitory compound
NAI = non-absorbable, inhibitory compound
ANI = absorbable, non-inhibitory compound
K = ammonia oxidation rate constant, mg-N/L-h
r^2 = linear regression correlation coefficient
GPAC = glucose carbon reactor supplemented with PAC GCAS = glucose control AS
RPAC = refinery fed reactor supplemented with PAC
RCAS = refinery fed reactor control AS
RBEN = refinery fed reactor supplemented with bentonite
Appended C denotes corresponding control

Table 7—Nitrification inhibition coefficients, I.

Spiked compound	Type	GPAC	GCAS	RPAC	RCAS	RBEN
Acrylonitrile, 10 mg/L	NANI	1.04	1.02	0.96	0.85	0.95
Aniline, 10 mg/L	AI	[a]	[a]	0.787	0.48	0.345
Aniline, 10 mg/L	AI	0.733, 0.691	0.316	0.87	0.87	0.91
Cyanide, 1 mg/L	NAI	0.15[b]	0.183[b]	0.26[b]	0.24[b]	0.18[b]
Cyanide, 3 mg/L	NAI	0.228	0.369	0.508	0.607	0.422
Cyanide, 3 mg/L	NAI	0.153[b]	0.186	0.446	0.56	0.708
Phenol, 10 mg/L	AI	0.435	0.736	0.98	1.0	1.02
Phenol, 20 mg/L	AI	0.804	0.36	0.95	1.09	0.97
Toluene, 10 mg/L	ANI	0.99	1.0	1.05, 0.96	1.0	1.29

[a] The reactors were not nitrifying before the experiment. Therefore valid comparisons could not be made.

[b] Because ammonia concentration was greater at the end of the test period than at the start for the test flasks, K(test) + 1/K(control) + 1 was used to calculate I.

ples indicated that nitrification proceeded in all reactors at efficiencies exceeding 99% (with 30 mg/L aniline in RW feed) for the next 3 weeks until the second continuous experiment commenced.

It is difficult to interpret the results of the initial continuous experiment, given that aniline is an adsorbable inhibitor and that the PAC-AS was the only reactor type severely inhibited. One plausible explanation for the observed results is desorption. Desorption involves the displacement of a previously adsorbed compound by another whose adsorption affinity is greater. It is possible that such a compound existed in the RW and when displaced by aniline into the liquid phase, caused the observed inhibition. The PAC may have sequestered this potential inhibitor from the microorganisms in the bulk solution, and if acclimation to the compound was possible, it was effectively prevented by reduced exposure. Desorption of the compound may have allowed an opportunity for the microorganisms to slowly acclimate for a short period of time (75 hours) until the virgin PAC was added. For this explanation to be feasible, the unknown compound of interest must be both a powerful inhibitor of nitrification and less adsorbable than aniline at the concentration used.

In the second continuous experiment (Figures 11–13), the RW reactors were subjected to a step increase of aniline concentration from 30 to 60 mg/L feed and a pulse addition of 60 mg aniline/L reactor. It should be noted that all reactor operating conditions were similar to that of the initial experiment except that the PAC-AS reactor was now running at a mixed-liquor PAC concentration of 4000 mg/L. This was because of the additional 1000 mg/L PAC spiked in the initial experiment. The daily PAC dose (66 mg/L feed) was adjusted accordingly to maintain the PAC reactor concentration.

Figure 11 shows that all reactors responded similarly with respect to ammonia oxidation with no apparent advantage of either PAC or bentonite addition. Ammonia oxidation was typically inhibited for 15 hours before the effects of aniline dissipated. This observation is consistent with the results of Joel and Grady[33] who suggested that heterotrophic aniline degradation and nitrification was sequential with nitrification commencing as soon as aniline was reduced to a non-inhibitory concentration. Concurrent SOC data further supports this theory. Figure 12 shows that the filtered mixed-liquor SOC in each reactor increased approximately 30–35 mg/L 3 hours after the experiment began (an aniline concentration of 60 mg/L corresponds to approximately 48 mg/L SOC). This suggests that the maximum capacity of the heterotrophs to metabolize aniline had been reached. After approximately 16 hours, the initial increase in SOC was reduced by more than 50% in all reactors, which corresponded to the time nitrification resumed. Whether this decrease in SOC was primarily caused by microbial degradation

Table 8—Regression results (F statistics) for ammonia data (test versus control assays).

Reactor type	Acrylonitrile, 10 mg/L NANI	Aniline, 10 mg/L AI	Aniline, 10 mg/L AI	Cyanide, 1 mg/L NAI	Cyanide, 3 mg/L NAI	Cyanide, 3 mg/L NAI	Phenol, 10 mg/L AI	Phenol, 20 mg/L AI	Toluene, 20 mg/L ANI
Glucose PAC	0.07/0.866 (no)	[a]	2.23/0.186 (no)	16.25/0.007 (yes)	45.3/0.005 (yes)	32.24/0.001 (yes)	3.2/0.123 (no)	2.13/0.195 (no)	0.01/0.934 (no)
Glucose control	0.01/0.913 (no)	[a]	13.82/0.01 (yes)	25.1/0.002 (yes)	5.69/0.054 (no)	12.23/0.129 (yes)	0.04/0.85 (no)	6.02/0.0495 (yes)	0.02/0.88 (no)
Refinery PAC	0.03/0.866 (no)	1.64/0.237 (no)	0.42/0.541 (no)	14.65/0.009 (yes)	4.4/0.081 (no)	4.23/0.085 (no)	0.16/0.705 (no)	0.08/0.781 (no)	0.05/0.837 (no)
Refinery control	0.39/0.55 (no)	15.74/0.004 (yes)	0.68/0.44 (no)	0.86/0.39 (no)	3.12/0.126 (no)	2.31/0.179 (no)	0.0/0.99 (no)	0.08/0.786 (no)	0.0/0.988 (no)
Refinery bentonite	0.05/0.828 (no)	10.2/0.013 (yes)	0.1/0.77 (no)	10.76/0.17 (yes)	26.8/0.002 (yes)	1.1/0.336 (no)	0.01/0.922 (no)	0.02/0.884 (no)	0.92/0.375 (no)

[a] The reactors were not nitrifying before the experiment, therefore, valid comparisons could not be made.

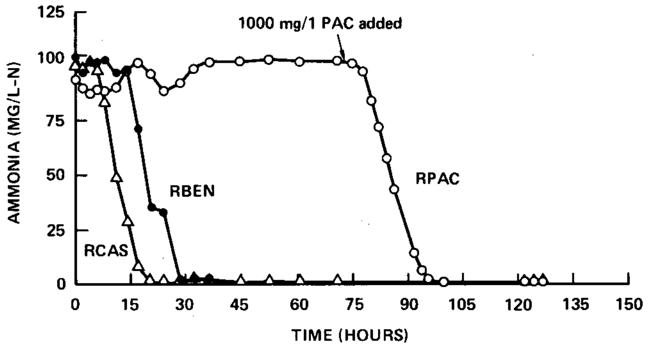

Figure 8—First chronic experiment: ammonia versus time.

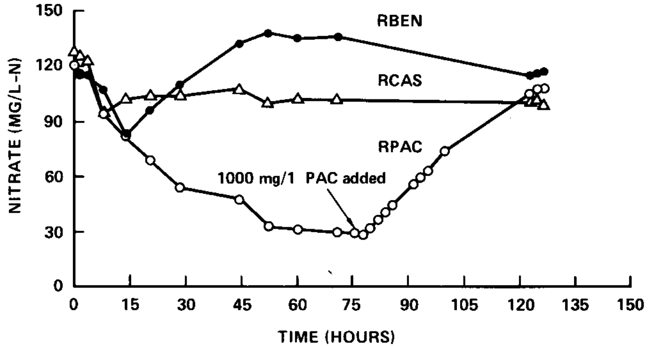

Figure 10—First chronic experiment: nitrate versus time.

or by the washout of aniline (hydraulic retention time = 24 hours), or a combination thereof is unknown; however, it appears that as soon as the aniline reaches some threshold concentration, nitrification can begin.

Figure 12 also suggests that at a PAC reactor concentration of 4000 mg/L little of the aniline is adsorbed from the liquid phase. This is evident from the differences noted among the increases in SOC in each reactor. If the reactor SOC increases were caused wholly by the addition of aniline, it would appear that the PAC reactor adsorbed no more than 5 mg/L SOC (6.5 mg/L aniline). This, in turn, would suggest that the adsorptive capacity of the PAC in the reactor had been effectively exhausted under prior steady-state conditions. Thus, for the PAC dose, aniline concentration, and wastewater feed used in this steady-state experiment, heterotrophic acclimation in nitrifying activated sludge seems to be more important in mediating the inhibitory effects than the PAC addition.

Data on nitrite oxidation and nitrate production (Figure 13) shows that *Nitrobacter* activity was inhibited. Prior batch experiments and the initial continuous experiment with aniline demonstrated only ammonia oxidation inhibition; however, it is apparent that at higher aniline concentrations, Nitrobacter metabolism can be severely affected. Figure 13 also shows that nitrite oxidation and nitrate production recovered most rapidly in the bentonite and PAC reactors. This logically suggests that, between the nitrifying genera, *Nitrobacter* would be more apt to be associated with surface growth or attachment. Although this theory could account for some of the discrepancies reported in the literature regarding the role of suspended solid on nitrification,[34–36] much more research is needed to substantiate this hypothesis. Following the second continuous experiment, daily effluent samples indicated that all reactors consistently achieved nitrification efficiencies exceeding 99% in the presence of 60 mg aniline/L RW feed.

Additional observations. Several relevant observations were noted with respect to reactor operation and performance. Throughout the duration of this study, the PAC supplemented reactor consistently demonstrated the greatest stability among the RW-fed reactors. The differences between batches of RW received provided an opportunity to compare the stability of all reactor types. The PAC reactor was observed to be the most stable in terms of foam suppression and sludge settleability. In contrast to the PAC reactor, the control and bentonite reactors often suffered from settling problems (high sludge blankets) and generally did not demonstrate consistent or desirable settling characteristics. With almost every new batch of wastewater, the control, and especially the bentonite supplemented reactor, experienced foaming problems. Typically, it would require one week of stable operation with the new batch of wastewater before foaming problems would subside. No foaming was ever noted in the PAC reactors.

Increased nitrification efficiencies were also evident, particularly during the initial reactor start-up period. These observations are best supported by Figures 14 and 15 which are cumulative probability plots for effluent ammonia concentration for each reactor type studied. Figure 15 shows that the addition of PAC made no significant difference in nitrification in the GA-fed reactor. However, the addition of PAC to the RW reactor

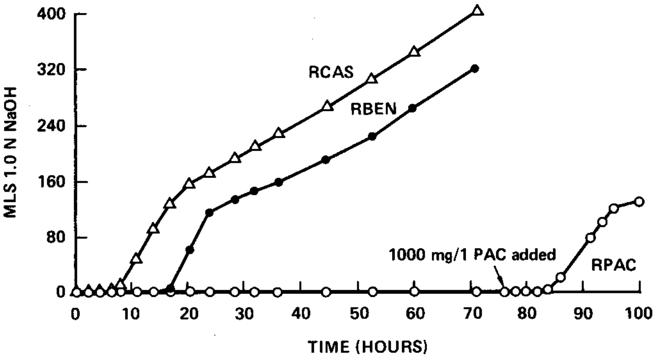

Figure 9—First chronic experiment: caustic uptake versus time.

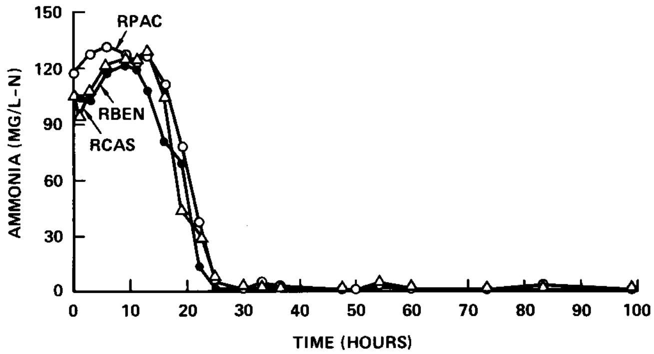

Figure 11—Second chronic experiment: ammonia versus time.

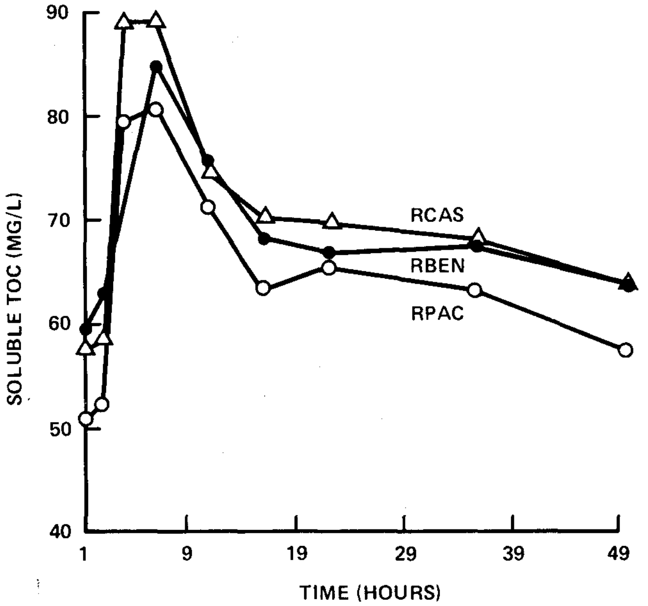

Figure 12—Second chronic experiment: soluble organic carbon versus time.

resulted in significantly more nitrification over the control and bentonite supplemented reactors. These benefits were observed almost exclusively during the start-up period when reactor upsets were common. Following the start-up period (approximately 4 months), all refinery reactors achieved excellent nitrification and reactor effluent samples were taken less frequently.

SUMMARY AND CONCLUSIONS

Based on the results reported herein, the findings and conclusions of this study can be summarized as follows:

- In the batch inhibition experiments, nitrification enhancement caused by PAC addition was demonstrated in unacclimated activated sludge cultures in the presence of adsorbable inhibitors. Enhancement caused by the addition of either PAC or bentonite was not observed in any experiments involving a non-adsorbable inhibitor. These findings provide evidence that adsorption of inhibitory compounds is a more important mechanism for nitrification enhancement than enhanced nitrifier growth on the surface of suspended solids.

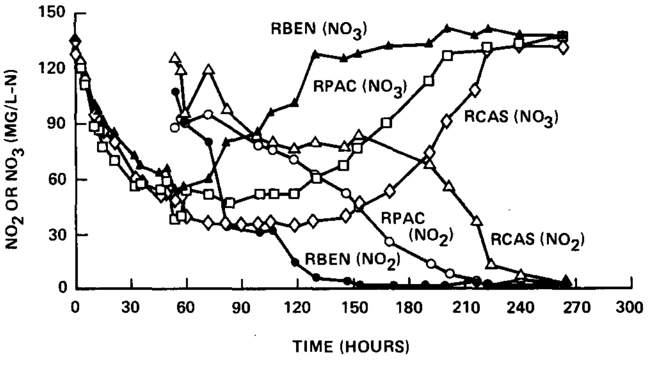

Figure 13—Second chronic experiment: NO_2^- or NO_3^- versus time.

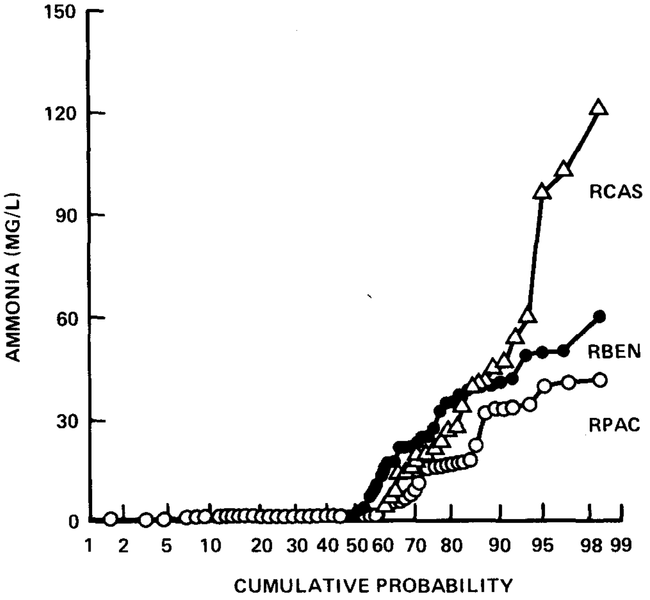

Figure 14—Cumulative effluent ammonia-N probability for refinery reactors.

- For acclimated activated sludges, nitrification enhancement was much more difficult to demonstrate, presumably because at the low dosages used (50 mg/L influent), the benefits of microbial acclimation were much more pronounced and perhaps obscured any benefits the added carbon could produce.
- The continuous experiments showed that acclimated nitrifying activated sludges are capable of completely recovering from a shock loading of high inhibitor concentrations. At the dosages used (50–66.6 mg/L influent), the addition of either PAC or bentonite provided no significant enhancement of nitrification rates.

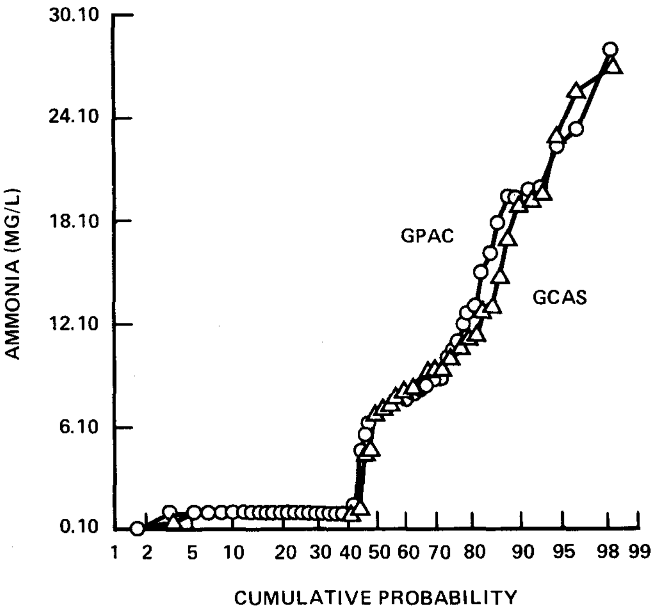

Figure 15—Cumulative effluent ammonia-N probability for glucose reactors.

- The initial continuous experiment provided evidence that the addition of PAC to activated sludge can indirectly inhibit nitrification by virtue of desorption of a previously adsorbed inhibitor. In this same experiment, it was shown that an adequate dose of virgin PAC can dramatically arrest the inhibition and completely restore nitrification. The second continuous experiment demonstrated that at a high concentration of aniline (60 mg/L), *Nitrobacter* activity was inhibited. Previous studies had implicated aniline as an inhibitor to ammonia oxidation. This experiment also suggested that *Nitrobacter* sp. may have an affinity for attachment or growth on suspended solids.
- Over the course of the experiments, it became apparent that an important factor for continued high efficiency nitrification was heterotrophic acclimation ability. It is proposed that providing a highly equalized influent wastewater could provide approximately the same benefits to nitrification as PAC addition at the dose evaluated (50–66.6 mg/L influent).

ACKNOWLEDGMENTS

Credits. This work was supported in part by Standard Oil Co. (Ohio), and in part by the National Science Foundation, under grant no. CEE 7911792.

Authors. Adam Ng is a biochemical engineer in the Energy and Environmental Systems Division of Argonne National Laboratory. Michael K. Stenstrom is professor of civil engineering, Civil Engineering Department, UCLA, Los Angeles, Calif. David R. Marrs is a senior project engineer, Woodward-Clyde Consultants, Walnut Creek, Calif. During the time of this research the authors were, respectively, post graduate engineer, Civil Engineering Department, UCLA, professor, Civil Engineering Department, UCLA, and project leader, the Standard Oil Co. (Ohio). Correspondence should be sent to Michael Stenstrom, Civil Engineering Department, School of Engineering and Applied Science, Los Angeles, CA 90024.

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