Nitrification in Powdered-Activated Carbon-Activated Sludge Process

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Abstract: Powdered activated carbon (PAC) has been added to activated sludge processes over the past 10 years to improve process performance in a variety of ways, including ammonia removal. Improved ammonia removal is a surprising benefit of PAC since it is not adsorbed. Investigators have speculated that PAC adsorbs inhibitory compounds or provides a media for nitrifier growth. To ascertain the mechanism of nitrification enhancement, a series of experiments were performed with adsorbable (aniline, phenol) and nonadsorbable (ethanol) inhibitors. Experimental results show that adsorption of nitrification inhibitors can dramatically improve nitrification rates in unacclimated activated sludge cultures.

Introduction

Previous investigators (2,13,15,23,30) have provided evidence that the addition of powdered-activated carbon (PAC) to nitrifying activated sludge (AS) can improve nitrification rates. Plausible, but unsubstantiated, mechanisms that have been proposed to explain PAC-enhanced nitrification include adsorption of compounds toxic to nitrifiers (13,15,23), enhanced nitrifier growth on the carbon's surface (2,30), and bioregeneration. This research was conducted to substantiate mechanisms of PAC enhancement, and experiments were conducted to evaluate adsorption, attached growth and acclimation mechanisms.

Bioregeneration

Bioregeneration is a term used to describe the synergism which is often observed in powdered-activated carbon-activated sludge (PAC-AS) processes. Various researchers (4–6,11) have noted that in specific cases, PAC-AS processes can remove an organic compound more efficiently than would be expected from either biodegradation or adsorption alone. Proposed theories of bioregeneration require that a compound be adsorbed onto the carbon's surface where microorganisms reside, and that adsorption results in higher substrate concentrations than would be expected in the bulk solution. This increase in concentration stimulates biological growth and replenishes the carbon surface for further adsorption. Once adsorbed, these compounds are in contact with the biomass for a length of time equal to the system's cell retention time. This mechanism's applicability to nitrification is questionable, since adsorption of ammonia at the pH and concentrations found in wastewater is negligible; however, bioregeneration may be important in the acclimation of heterotrophic organisms to certain slowly biodegradable inhibitors of nitrification. Adsorption of

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Note. Discussion open until May 1, 1988. To extend the closing date one month, a written request must be filed with the ASCE Manager of Journals. The manuscript for this paper was submitted for review and possible publication on September 15, 1986. This paper is part of the ***Journal of Environmental Engineering***, Vol. 113, No. 6, December, 1987. ©ASCE, ISSN 0733-9372/87/0006-1285/$01.00. Paper No. 22030.

the inhibitor would increase the time available for heterotrophic acclimation and, ultimately, for the removal of nitrifier inhibition.

Enhanced Nitrifier Surface Growth

Up until 1955, it was generally considered that particulate materials such as calcium carbonate, which was used as a buffer in early culture experiments, were necessary for nitrifier growth. It was postulated that the solid surface in the growth media provided obligate surface sites to which nitrifying organisms adsorbed and multiplied. Although this "obligate surface" theory was later disproved by workers who successfully grew Nitrobacter (12) and Nitrosomonas (9) in clear media, the role of suspended solids in nitrification remains unclear. A stimulatory effect of suspended particles on nitrification rates has been reported by a number of investigators in studies with surface waters and soils. These investigators maintain that the enhancement mechanism involves either the particle's ability to provide a physical support medium for growth of nitrifiers (19,29) or substrate (ammonium ion) concentration at the surface of the particles (22). Conflicting evidence has been reported in which no detectable effects on nitrification rates due to suspended particles were observed (1). Other investigators (12,19) assert that while suspended solids were not essential for nitrifier growth, attachment to particles and enhancement occurred if the solids were present.

As a part of this experimental investigation, a reactor was operated using bentonite clay as a site for nitrifier attachment. Bentonite clay was added to an activated sludge reactor, identical to the reactors used in this study, to match the external surface area provided by the carbon in PAC reactors. Experiments were performed for several compounds, both adsorable and nonadsorbable over a two-year period, testing both acute and chronic inhibition. The results are reported in detail by Ng, et al. (24) and show that adding bentonite clay was not beneficial to nitrification.

Adsorption of Compounds Toxic to Nitrifiers

Many organic compounds are known to inhibit nitrification in pure (31,35,37) and activated sludge cultures (30,34,36). Some of these compounds are biologically resistant to degradation while others are resistant and highly adsorbable by activated carbon. Therefore, it is likely that the presence of activated carbon can protect nitrifiers from adsorbable, inhibitory compounds.

In summary, various mechanisms can be suggested to explain the role of adsorption in PAC-enhanced nitrification. The major purpose of this study is to further define the role of adsorption in PAC-enhanced nitrification, and to access these effects independently of biological acclimation. Emphasis is placed on the adsorption of toxics mechanisms because recent work in one laboratory (24) suggest that this is a dominant mechanism in PAC-enhanced nitrification.

Experimental Methods

A series of batch assay experiments using variable activated carbon doses was performed to study PAC-AS nitrification enhancement in the presence of known nitrification inhibitors with different adsorptive characteristics. Selection of inhibitors for experimentation was based upon an

TABLE 1. Adsorption and Nitrification Inhibitory Characteristics of Compounds Tested in Carbon Dose Experiments

Compound (1)	Freundlich Parameters (2)	Langmuir Parameters (3)	Concentration Required for 75% Inhibition (4)
Aniline	K = 12.2 mg/g n^{-1} = 0.52	Q = 0.065 b = 0.324	7.7 mg/L
Phenol	K = 21.0 mg/g n^{-1} = 0.54	Q = 0.158 b = 0.176	5.6 mg/L
Cyanide	data unavailable	maximum adsorption = 2.0 mg/g at C_o = 20.0 mg/L	0.65 mg/L
Ethyl Alcohol	K = 0 mg/g	maximum adsorption = 20 mg/g at C_o = 1,000 mg/L	2,500 mg/L

[a]Freundlich adsorption data for phenol and ethyl alcohol from Dobbs and Cohen (7).
Other adsorption data for ethyl alcohol from Perrich (27).
Cyanide adsorption data from Hoffman (15).
Other inhibition data from Tomlinson, Boon, and Trotman (35).

intensive survey of all known nitrification-inhibiting compounds and their carbon adsorption properties. Potential compounds were characterized either as adsorbable-inhibitory (AI) or nonadsorbable inhibitory (NAI). Other considerations for compound selection included industrial significance and solubility. Table 1 shows the compounds selected for experimentation. Included are the compound's nitrification inhibition and adsorptive characteristics. With the exception of the adsorption parameters for aniline, which were experimentally determined, data from Table 1 were extracted from the literature and hence are subject to interpretation due to differing sets of conditions under which the values were obtained. Nonetheless, the data do provide an indication of the relative adsorptive and inhibitory properties of the compounds chosen for evaluation. For AI compounds, concentrations were selected to produce significantly more than 75% inhibition. For NAI compounds, inhibitory concentrations tested were chosen to yield approximately 75% inhibition in control assays without PAC addition. This was to ensure that nitrification would continue in any given assay and that any benefit, due to PAC addition, would be detected.

Source of Nitrifying Activated Sludge

Nitrifying mixed liquor for experimentation was drawn from a continuous flow bench scale activated sludge plant fed a synthetic substrate and operating at a mean cell retention time of nine days and a hydraulic retention time of eight hours. The reactor was constructed of 1.25 cm (0.5 in.) plexiglass, with a working volume of 12.2 L in the aeration section and 1.5 L in the solid-liquid separator. Several holes were provided in the lid of the reactor: larger holes for a pH probe and access for maintenance and smaller holes for influent, base addition, and air lines. A port hole on the

side of the aeration section was used to withdraw mixed liquor for experimentation and for control of cell retention time. Air, which was added through diffuser stones located near the bottom of the mixed liquor aeration section, provided oxygen for microbial growth as well as turbulence for mixing. Airflow rates, which ranged from 0.14 to 0.28 m^3/hr., were monitored by rotameters. Reactor pH was maintained, using a saturated solution of sodium bicarbonate, at a range of 7–7.2 by means of a pH control meter (Horizons, Inc., Model 5997-20).

Synthetic Feed Composition

Due to the large quantity of substrate required, a dilution system was used whereby concentrated feed was automatically diluted before being pumped into the reactor. 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 reactor 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 $CaCl_2$-$MgCl_2$ solution was separately pumped into the mixing reservoir to prevent the formation of calcium phosphate precipitates. The concentrate 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. Additional details describing the reactor, substrate dilution system, and synthetic feed are available elsewhere (24,25).

Experimental Procedure

Batch Inhibition Experiments

The general procedure for all experiments consisted of the following steps:

1. PAC (Westvaco Nuchar SA-15) was dried at 150°C for a minimum of three hours and stored in a dessicator until use.
2. Appropriate amounts of PAC were analytically weighed and placed dry into designated empty 500 ml Erylenmeyer flasks.
3. Reactor effluent ammonia-N and nitrate-N concentrations were measured.
4. A measured volume of mixed liquor was withdrawn from the reactor and divided equally into the flasks, resulting in activated carbon dosages of 500, 1,000, 2,000, and 4,000 mg PAC/L of mixed liquor added. For NAI compounds evaluated, only PAC concentrations bracketing the highest (4,000 mg/L) and lowest (500 mg/L) concentrations were tested. In all experiments, a minimum of two flasks were retained as controls and did not receive any PAC.
5. An exogenous source of ammonia-N in the form of a solution of ammonium chloride was pipetted into each flask to bring the NH_4^+-N concentration from less than <0.1 to 40–50 mg-N/L.
6. 1.0 ml of the test compound from a concentrated stock solution was pipetted into the test flasks to give the desired calculated concentration. It should be noted that the changes in volumes brought about by the additions of PAC, ammonia-N, and the inhibitory compound were incorporated into the calculation of the final concentrations used.
7. All flasks were placed under a manifold and aerated throughout the experiment. Air was supplied through disposable, plastic aquarium diffuser stones at a flowrate of 0.1 m^3/hr.
8. One or two minutes after the start of aeration (designated as time = 0 hours), two separate 5–10-ml portions of the mixed liquor were withdrawn from each flask using volumetric pipettes and then added into a 100-ml volumetric flask, half filled with distilled water preserved. The flasks were then diluted to volume, capped, shaken, and stored for the analysis of ammonia and nitrate at the end of the experiment.
9. Step 8 was repeated for time = 2, 4, 6, and 8 hours.
10. Every hour throughout the aeration period, the pH was checked and manually adjusted, if necessary, to the range of 7.2–7.4 using 0.1 N NaOH.

In the final experiment (with 10 mg/L aniline), nitrite-N, and liquid phase inhibitor concentration were determined at various times during the aeration period.

Aniline Adsorption Isotherm

An aniline adsorption isotherm was conducted, because aniline was considered to be an "ideal" inhibitor to study PAC-enhanced nitrification. The effects of aniline on activated sludge nitrification are well documented (18,34), and it is known to be both adsorbable and biodegradable, although the extent of its adsorptive properties have not been well established. Aniline at 100 mg/L was contacted with PAC over a concentration range of 0.1–20 g/L. Sample bottles were agitated for nine hours at room temperature (27–29°C). Samples were analyzed by gas liquid chromatography following centrifugation.

Analytical Methods

Inorganic Nitrogen

Specific ion electrodes for ammonia (Orion Model 95-10) and nitrate (Orion Model 93-07) in conjunction with an Orion Ionanalyzer (Model 407A) were used to directly measure ammonia-N and nitrate-N concentrations in influent, mixed liquor, effluent, and assay samples. The probes were calibrated at least once, using laboratory prepared standards, prior to and during each analytical run. If necessary, ammonia and nitrate samples were preserved with 1M HCl (0.1 ml/0.1 L sample) or 1M boric acid (0.1 ml/0.1 L), respectively. Sample volume analyzed was 100 ml or aliquots diluted to 100 ml. Nitrite-N was determined by a wet chemical technique described in Standard Methods (1975). All nitrite samples were preserved with 4 mg $HgCl_2$/0.1 L sample, filtered (0.45 micron), and diluted with distilled water to cover the applicable range of the method (0.01–1.0 mg nitrite-N/L). Photometric determinations were accomplished using a Bausch and Lomb Spectronic 20 (1 cm light path) at 543 nm. Standard curves were obtained for each analytical run using serially diluted nitrite standards ($NaNO_2^-$).

Determination of Aniline

Liquid phase aniline concentrations for the adsorption isotherm and a single batch experiment were measured by direct aqueous injection using a Varian 6000 gas chromatograph and a Hewlett Packard 3300 integrator. The capillary column used was SP 2100 (Supelco, Inc.) operated isothermally at 110°C. Optimal operational conditions for the analysis were found to be as follows: Injector temperature = 200°C; Detector (FID) temperature = 300°C; Carrier gas = Helium at 2.0 ml/min; Detector make-up gas = 30 ml/min; Air and Hydrogen at 300 and 30 ml/min, respectively; Spitless injection at 1.0 microliter sample size with purge vent opened after 0.9 min. at 100 ml helium/min. Reproducibility for a given injection was found to be within 5% for peak area response and 7% for peak height response. All determinations were based on peak area response.

A preliminary test was conducted to determine whether aniline could be recovered from the liquid phase of mixed liquor and accurately analyzed for by gas chromatography. The nature of the substrates used for reactor feed suggested that there would be little interference in the analysis of aniline by direct aqueous injection. The procedure used for the test was as follows:

1. 1.35 L of mixed liquor (MLSS = 1250 mg/L) was withdrawn from the reactor and divided equally into three stirred flasks.
2. An appropriate amount of an aniline stock solution was quantitatively added into each flask producing calculated aniline concentrations of 1.0, 5.0, and 10.0 mg/L.
3. After mixing the contents of each flask for two minutes, 10 ml of mixed liquor was withdrawn from each flask and centrifuged for three minutes or until a clear supernatant was visible. The resulting supernatant was then pipetted into 7.7 ml glass vials with Teflon lined caps and stored at 4°C until analysis. These steps were necessary to preserve the stability of aniline and were satisfactory for subsequent analysis by gas chromatography (28).

Recovery of aniline from controls averaged 89.8% of theoretical recovery. Recovery ranged from a low of 86% at 1.0 mg/L to 96.4% at 10 mg/L. It is likely that the difference between calculated and measured values were due to either inherent experimental error and/or adsorption of aniline onto the biomass. The latter explanation is reasonable, since all measured values were less than the corresponding calculated values. The largest difference (14%) noted was substantially less than the reported 75% recovery of aniline from wastewaters using the same column and a methylene chloride extraction step (28).

Results and Analysis

Aniline Adsorption Isotherm

The equilibrium data for the adsorption of aniline on PAC fitted both the Freundlich (r^2 = 0.98) and the Langmuir (r^2 = 0.97) adsorption model reasonably well. Results show that approximately 12.2 mg aniline/g PAC will be adsorbed at an equilibrium aniline concentration of 1.0 mg/L. Calculated adsorption parameters from the experimental data are shown in Table 1.

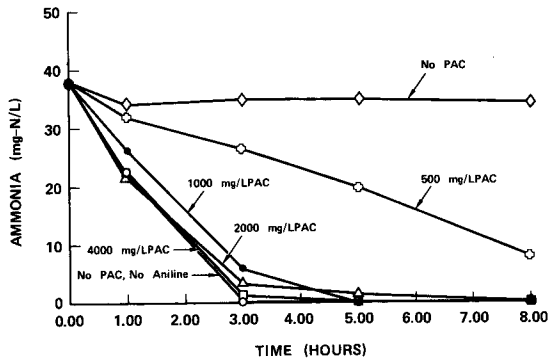

FIG. 1. NH_4^+-N versus Time for Variable Carbon Dose (10 mg/L Aniline 1-85)

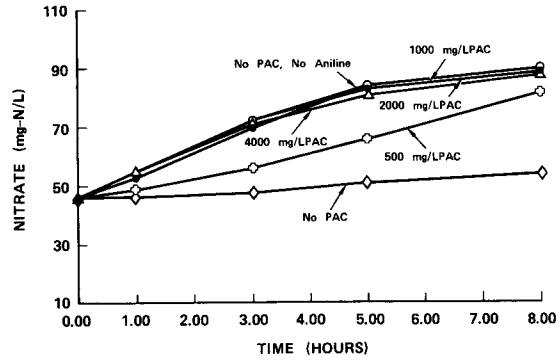

FIG. 2. NO_3^--N versus Time for Variable Carbon Dose (10 mg/L Aniline)

Batch Inhibition Experiments

Ammonia oxidation and nitrate production data generated from three separate experimental runs using 10 mg/L aniline (Figs. 1–2), 0.7 mg/L cyanide (Figs. 3–4) , and 2500 mg/L ethanol (Figs. 5–6) as inhibitors show the effect of PAC concentration on nitrification rates. Data presented in these figures are representative of the nature of data generated from other experimental runs, which are not shown here.

In order to interpret and quantify observed nitrification rates for all experiments, zero-order kinetics were used to estimate nitrification rate constants. Zero-order nitrification kinetics have been observed and used to describe nitrification under various conditions (10,17,20,25,34,36). Reported K_s values for ammonia oxidation in activated sludge typically range from 0.5–2.0 mg-N/L (3,8,32); therefore, for ammonia concentrations used in this study the kinetic expression for ammonia oxidation in a batch assay can be expressed as:

$$\frac{d\,NH_4^+ - N}{dt} = -K \quad \text{..... (1)}$$

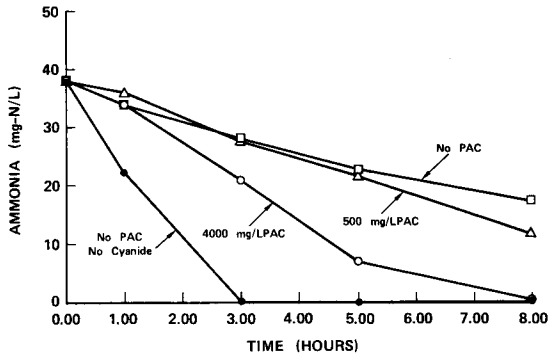

FIG. 3. NH_4^+-N versus Time for Variable Carbon Dose (0.7 mg/L Cyanide)

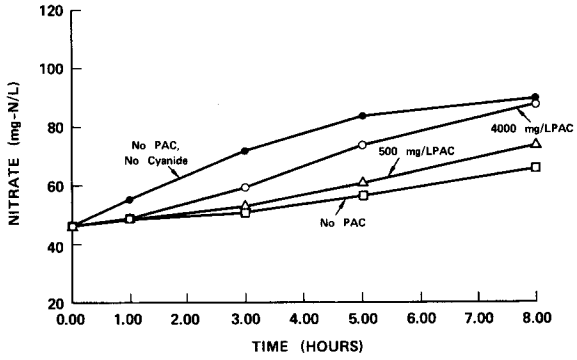

FIG. 4. NO_3^--N versus Time for Variable Carbon Dose (0.7 mg/L Cyanide)

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

$$\frac{d\ NO_3^- - N}{dt} = K \quad \text{..... (2)}$$

The observed zero-order ammonia oxidation and associated nitrate production rate constants K were calculated under nonlimiting substrate conditions by simple linear regression and are presented for all experimental runs in Table 2. Also included in Table 2 are coefficients of determination r^2 which indicates the accuracy of fit between the data and the linear regression equation. The term zero-order here applies to reaction rate with respect to ammonia. The reaction constant K is dependent upon nitrifier biomass concentration. In our early deliberations about experimental design, we considered ways of estimating nitrifier biomass concentration. None of the available methods were sufficiently precise and inexpensive to be useful to us. Therefore we devised an inhibitor constant (24), which is the ratio of reaction rates obtained in experiments to the reaction constant obtained in controls, without inhibitor, but at the same

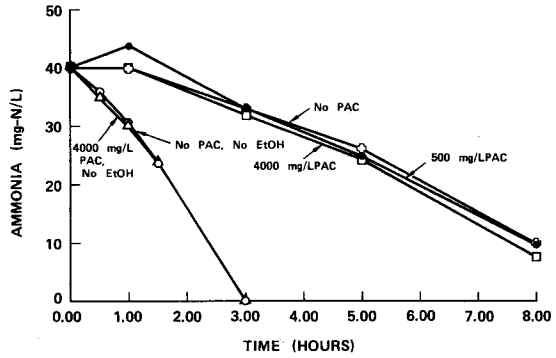

FIG. 5. NH_4^+-N versus Time for Variable Carbon Dose (2500 mg/L Ethanol)

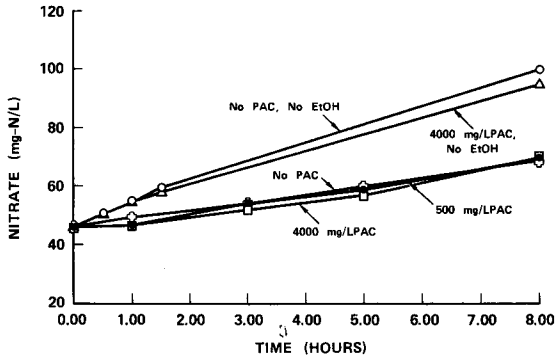

FIG. 6. NO_3^--N versus Time for Variable Carbon Dose (2500 mg/L Ethanol)

biomass concentration. The inhibition constants are independent of biomass concentration.

In general, nitrate production rate constants were observed to range from 60–100% of the corresponding ammonia oxidation rate constants. The discrepancy in rate constants was most evident if ammonia was oxidized relatively rapidly. This suggested an initial lag period for nitrite oxidation since measured nitrate concentrations were all within 14% of expected values (based on reaction stoichiometry and excluding heterotrophic ammonia uptake and endogenous decay) at the end of each experiment. If it had been possible to use continuous experiments, one would expect more agreement between ammonia oxidation and nitrate production rates.

Table 2 shows that for experiments performed using adsorbable inhibitors (i.e., phenol and aniline), PAC addition resulted in enhanced nitrification rates. For nonadsorbable inhibitors (i.e., ethanol and cyanide), little or no significant nitrification enhancement was observed. The results of the experiment with ethanol are in dramatic contrast to experiments using adsorbable inhibitors, where the degree of nitrification enhancement is related to PAC dosage.

TABLE 2. NH_3-N and NO_3-N Reaction Constants and r^2 for Carbon Dose Experiments

Spiked Compound (1)	Type (2)	(3)	control NA[c] (4)	control A[d] (5)	4,000 A[e] (6)	2,000 A[f] (7)	1,000 A[g] (8)	500 A[h] (9)
Aniline	AI[a]	r^2	0.99	0.99	0.97	0.99	0.99	0.99
10 mg/L		$-K(NH_3)$	12.1	0.25	12.0	11.3	10.7	3.6
(1-85)		r^2	0.99	0.99	0.99	0.99	0.99	0.99
		$K(NO_3)$	8.6	0.6	8.3	8.7	8.0	3.4
Phenol	AI	r^2	0.96	0.23	0.96	0.99	0.87	0.2
20 mg/L		$-K(NH_3)$	11.7	0.65	11.75	11.73	4.35	0.78
(1-85)		r^2	0.99	0.7	0.99	0.99	0.95	0.74
		$K(NO_3)$	8.0	0.54	7.2	7.8	3.5	0.79
Cyanide	NAI	r^2	0.99	0.99	0.99	—[i]	—	0.97
0.7 mg/L		$-K(NH_3)$	12.1	2.6	6.3	—	—	4.5
(1-85)		r^2	0.99	0.98	0.99	—	—	0.98
		$K(NO_3)$	8.6	2.44	5.5	—	—	3.5
Cyanide	NAI	r^2	0.99	0.65	0.69	—	—	0.4
1.4 mg/L		$-K(NH_3)$	10.7	−0.67	1.69	—	—	0.7
(2-85)		r^2	0.99	0.74	0.86	—	—	0.6
		$K(NO_3)$	8.84	0.59	2.2	—	—	0.43
Ethanol	NAI	r^2	0.99	0.96	0.97	—	—	0.95
2500 mg/L		$-K(NH_3)$	10.7	3.82	4.14	—	—	4.12
(2-85)		r^2	0.99	0.99	0.96	—	—	0.99
		$K(NO^3)$	8.8	2.82	3.0	—	—	2.98
Aniline	AI	r^2	0.98	0.97	0.97	0.96	0.99	0.97
10 mg/L		$-K(NH_3)$	15.9	3.16	15.0	14.4	14.1	6.1
(2-85)		r^2	0.99	0.98	0.99	0.99	0.97	0.99
		$K(NO_3)$	11.8	2.07	11.3	11.3	11.0	6.1

[a]AI = Adsorbable inhibitor.
[b]NAI = Nonadsorbable inhibitor.
[c]Control NA = Control with no activated carbon or inhibitor added.
[d]Control A = Control with inhibitor added but no activated carbon.
[e]4,000 A = Inhibitor and 4,000 mg/L carbon added.
[f]2,000 A = Inhibitor and 2,000 mg/L carbon added.
[g]1,000 A = Inhibitor and 1,000 mg/L carbon added.
[h]500 A = Inhibitor and 500 mg/L carbon added.
[i]Carbon doses not evaluated in these experimental runs.

In using ethanol, the least adsorbable inhibitor of all compounds evaluated, there was no significant difference among nitrification rates in all test assays. Dissolved oxygen concentration was measured during and after the ethanol experiment. This was done to insure that oxygen limiting conditions were not created through increased heterotrophic ethanol oxidation. All DO levels were measured to be greater than 5 mg/L.

Data (see Table 2) from the experiments involving cyanide showed enhancement due to PAC addition. The degree of enhancement was significantly less than those observed for adsorbable compounds, and suggests that the degree of nitrification enhancement is related to adsorptivity of the inhibitor.

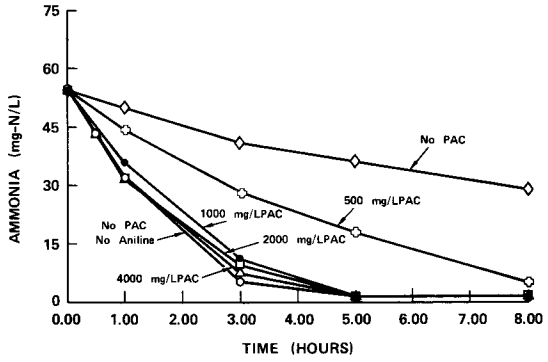

FIG. 7. NH_4^+-N versus Time for Variable Carbon Dose (10 mg/L Aniline 2-85)

In the final batch experiment with 10 mg/L aniline (Figs. 7–10), liquid phase aniline concentrations were measured by gas liquid chromatography at specific sampling periods throughout the experiment. Results show that nitrification inhibition is inversely related to PAC concentration. Since the amount of aniline adsorbed is directly related to PAC concentration, it can be shown that nitrification inhibition is directly related to liquid phase aniline concentration. It appears that for assays with no PAC addition, approximately 2 mg/L of aniline was either metabolized and/or adsorbed onto the biological mass. Figure 10 also indicates that near equilibrium conditions were rapidly established, with 80%–95% of the total adsorption occurring within 30 min.

Using the previously determined adsorption isotherm parameters for aniline, the expected liquid phase aniline concentration at each PAC dosage can be determined and compared to the corresponding measured concentration. The following equation, derived from the Freundlich adsorption model, was used to calculate expected liquid phase aniline concentrations:

$$K_f G \quad \text{..... (3)}$$

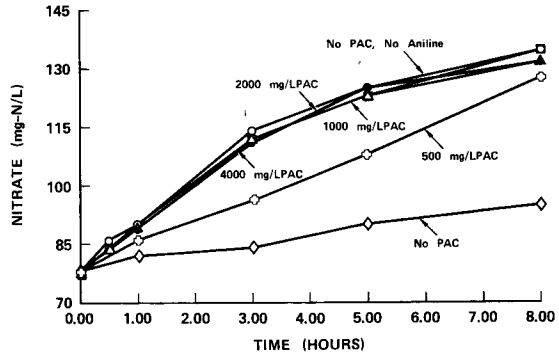

FIG. 8. NO_3^--N versus Time for Variable Carbon Dose (10 mg/L Aniline 2-85)

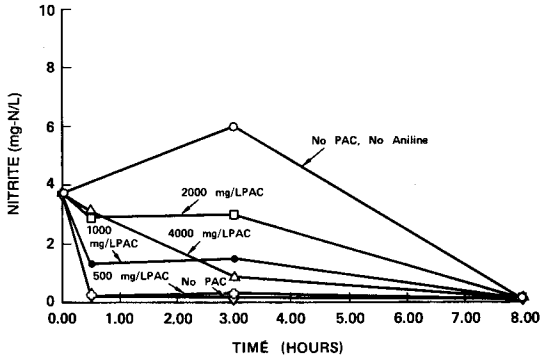

FIG. 9. NO_2^--N versus Time for Variable Carbon Dose (10 mg/L Aniline 2-85)

in which C_i = initial aniline concentration, 10 mg/L; C_f = final equilibrium liquid phase aniline concentration, mg/L; $1/n$ = experimentally determined Freundlich parameter (0.52); K_f = 12.2 mg/g; and G = PAC dose, g/L. The equation is implicit, requiring trial and error to determine the expected liquid phase aniline concentrations. Results are shown in Table 3 for an initial aniline concentration of 10 mg/L.

The detection limit for the gas chromatography method was 0.3 mg aniline/L. The reasons for the difference between expected and measured values are speculative. Different mixing conditions exist between activated sludge cultures and isotherm experiments. Equilibrium conditions may not have been obtained in the 30 minute period used for this experiment. Also there may have been competition for carbon sites. Martin and Iwugo (37) reported that suspended solids, particularly biological solids, could interfere with the adsorption process, both in terms of capacity and rate. They found that organic suspended solids at 500 mg/L or higher concentrations interfered with the adsorption process for single solutes and that adsorption was significantly reduced.

By interpolation of Fig. 10 (to be discussed) for the final aniline experiment on 2-85, it can be estimated that the PAC concentration at

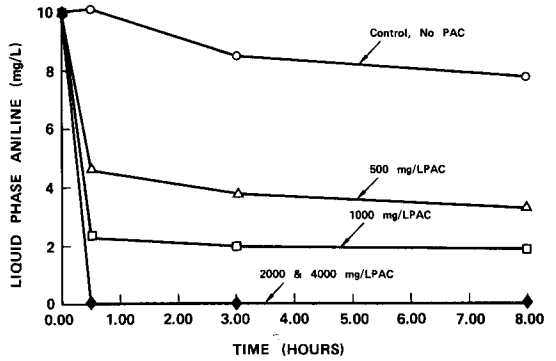

FIG. 10. Liquid Phase Aniline Concentration versus Time (2-85)

TABLE 3. Aniline Predictions

PAC Dose (mg/L) (1)	Expected Liquid Phase Aniline (mg/L) (2)	Measured Aniline (mg/L) (3)
500	1.8	3.9
1,000	0.6	1.9
2,000	0.17	not detected
4,000	0.05	not detected

which 75% nitrification occurred was approximately 80 mg/L PAC. The corresponding liquid phase aniline concentration for this PAC dose, based on the isotherm parameters, is 7.2 mg/L. For comparative purposes, Tomlinson (35) observed, under similar experimental conditions, that the concentration of aniline causing 75% nitrification inhibition in nitrifying activated sludge is 7.7 mg/L. Thus, the foregoing discussion suggests, at least for aniline, that nitrification inhibition is caused by liquid phase inhibitor concentration, as opposed to total inhibitor concentration in the PAC-AS process.

To form a quantitative basis for comparing the degree of nitrification enhancement among different experiments, an inhibition coefficient (I) was calculated to express the degree of inhibition observed at each PAC dosage for each inhibitor tested. I is defined as the ratio of calculated reaction rate constant K in the presence of the added compound to K in the control (i.e., no added compound). Calculated I's for ammonia oxidation rate constants for all experiments are presented in Table 4. Inspection reveals that for nonadsorbable compounds such as cyanide, nitrification enhancement above that in the control assays with no PAC additions was 16 and 30%, respectively, for 0.7 and 1.4 mg CN/L, at the highest PAC dose tested (4,000 mg/L). For ethanol, the least adsorbable of the compounds tested, the degree of enhancement was only 3% at the highest PAC dose tested. In contrast, nitrification enhancements of 75%, 97%, and 94% over the corresponding controls with no PAC addition were observed for aniline, aniline, and phenol, respectively, at 4,000 mg/L PAC. These results provide strong evidence that adsorption is the major mechanism of nitrification enhancement in activated sludges.

Figure 11 shows inhibition constants, based upon ammonia oxidation rate, plotted against PAC dosage for adsorbable and nonadsorbable inhibitors. There is a general relationship, dependent on inhibitor adsorptivity, between the degree of nitrification enhancement and PAC concentration. For adsorbable inhibitors, at the initial concentrations used, the relationship can be characterized by an S-type curve. This indicates that nitrification is marginally enhanced at low PAC doses and that the degree of enhancement increases steadily with increasing PAC dose until a plateau is reached. For nonadsorbable inhibitors, the enhancement/PAC relationship is characterized by a relatively horizontal curve showing little or no enhancement. Thus, it appears that enhancement depends upon the lowering of inhibitor concentration, through adsorption, to some threshold value before nitrification can proceed at reasonable rates. Similar results were obtained for inhibition constants based upon nitrate production.

TABLE 4. Nitrification Inhibition Coefficients, I Based on Ammonia Reaction Constants for Carbon Dose Experiments

Spiked Compound (1)	Type (2)	Adsorption[c] Parameters (3)	Control A (No PAC) (4)	4,000 A mg/L (5)	2,000 A mg/L (6)	1,000 A mg/L (7)	500 A mg/L (8)
Aniline 10 mg/L (2-85)	AI[a]	12.2 mg/g 0.52	0.19	0.94	0.91	0.88	0.38
Aniline 10 mg/L (1-85)	AI	12.2 mg/g 0.52	0.02	0.99	0.93	0.88	0.3
Phenol 20 mg/L (1-85)	AI	21.0 mg/g 0.54	0.06	1.0	1.0	0.37	0.07
Cyanide 1.4 mg/L (2-85)	NAI[b]	2.0 mg/g	0.0	0.158	—[d]	—[d]	0.0
Cyanide 0.7 mg/L (1-85)	NAI	2.0 mg/g	0.22	0.52	—[d]	—[d]	0.37
Ethanol 2,500 mg/L (2-85)	NAI	0.0 mg/g	0.357	0.387	—[d]	—[d]	0.385

[a]AI = Adsorbable nitrification inhibitor.
[b]NAI = Nonadsorbable nitrification inhibitor.
[c]Adsorption parameters are Freunlich parameters K and 1/n for aniline, phenol, and ethanol (based on C_e = 1.0 mg/L); for cyanide, the adsorption parameter represents the maximum adsorption observed at an initial concentration of 20 mg/L.
[d]Carbon doses not evaluated in these experiments.

It is important to note that in these experiments, unacclimated activated sludge and virgin PAC were used. For adsorbable inhibitors, the beneficial effects of PAC were observed almost immediately after the start of the experiments (i.e., 1–2 hr). These observations further support the adsorption of inhibitory compounds for nitrification enhancement. Other theories cannot account for the results since there was insufficient time for the following: (1) Enhanced nitrifier growth on the PAC surface, (2) biological acclimation; or (3) concentration of trace nutrients on the virgin PAC.

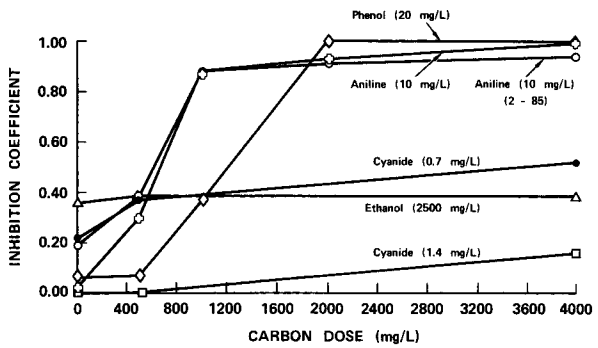

FIG. 11. Inhibition Coefficient, I (NH_4^+-N) versus Powdered Activated Carbon Dosage

Conclusions

Based on the results in this study, the following conclusions are presented:

1. The addition of PAC in the proper amounts can completely nullify the toxic effects of an adsorbable nitrification inhibitor. For adsorbable inhibitors, the addition of PAC resulted in nitrification enhancements of 75%–97%. For relatively nonadsorbable inhibitors, nitrification enhancements of only 3%–30% were observed at the same PAC dosage. These results provide convincing evidence in support of the theory that PAC can adsorb inhibitory compounds, thereby enhancing nitrification rates.
2. Results of nitrification enhancement in this study cannot be accounted for by any of the following mechanisms: (1) Enhanced growth of nitrifiers on the PAC surfaces; (2) increased trace nutrient or substrate concentration on the PAC surfaces; or (3) heterotrophic acclimation and subsequent bioregeneration.
3. There appears to be an optimal dose of PAC required to negate the effects of an inhibitor, given that its concentration and adsorptive properties are known *a priori*.

Acknowledgments

This work was supported in part by NSF Grant CEE 7911792. At the time the research was being performed, the writers were postgraduate engineer and associate professor, respectively, Dept. of Civil Engineering, University of California, Los Angeles, CA 90024.

Appendix I. References

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