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Adsorption of biologically inhibitory compounds as a process control mechanism in biological reactors

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Abstract

An innovative reactor design that decouples biological removal mechanisms from physical removal mechanisms has demonstrated promise for the treatment of wastewaters containing high concentrations of inhibitory compounds. Inhibition and toxicity prevent treatment of such wastewaters in conventional biological reactors. The reactor design consists of a high-rate biological reactor with a granular activated carbon (GAC) adsorber inserted into the recycle line of the biological reactor. Partial replacement of GAC from the GAC adsorber provides a mechanism for controlling the concentration of inhibitory compounds in the biological reactor. As a process control parameter, GAC replacement can be used to maintain the concentration of inhibitory compounds in a range optimal for growth and acclimation. GAC replacement is also varied in response to changes in the influent loading and can be used to provide rapid recovery from shock loadings. Agreement between isotherm studies and experimental data from pilot-scale systems was observed when the average GAC particle residence was greater than 3.75 days. Isotherm studies may be used to design the GAC adsorber and predict optimal operating conditions. The concept of using an adsorption process to optimize biological removal provides an environmentally sound treatment alternative for many high-strength wastewaters.

1. Introduction

Many hazardous wastewaters contain high concentrations of biologically inhibitory compounds that prevent the application of biological treatment. The majority of the components in a complex wastewater may be easily biodegraded if the inhibitory compounds are removed by physical adsorption. Activated carbon has been used to suppress the concentration of inhibitory compounds in the PACT™ process [1] (Fig. 1). However, this process has no process control mechanism for adsorption, large volumes of hazardous sludge may be produced, and volatile compounds can be

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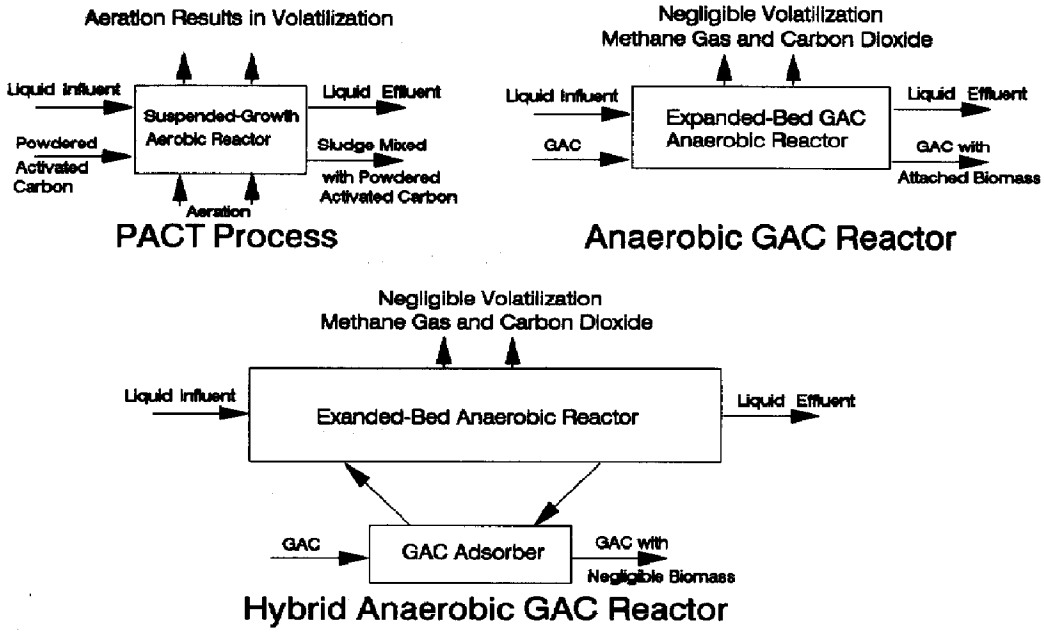

Fig. 1. Activated carbon biological reactors. The PACT™ system is an aerobic suspended-growth biological reactor with PAC addition. The system provides no direct control over adsorption. The GAC reactor provides partial control over adsorption while the hybrid GAC reactor utilizes GAC adsorption as a process control parameter.

stripped into the exhaust air, thus requiring further air treatment. The anaerobic expanded-bed granular activated carbon reactor (GAC reactor) (Fig. 1) has demonstrated promise for the treatment of hazardous wastewaters including hazardous landfill leachate, oil refining wastewater, and resin processing wastewater [2–4]. The combined biological and physical removal mechanisms suppress the concentration of inhibitory compounds and the large adsorptive capacity in the reactor makes the reactor resilient to changes in operation and wastewater composition. Since the process is anaerobic, sludge production is minimized and volatilization is negligible. Periodic GAC replacement is often necessary to replenish adsorptive capacity, however, biomass attached to the GAC is also removed. Thus, GAC replacement is limited as a process control mechanism since a high GAC replacement rate will result in reduced biological removal efficiency.

A hybrid GAC reactor designed to separate biological removal mechanisms from physical removal mechanisms utilizes GAC replacement as a process control parameter capable of optimizing biological removal. The hybrid GAC reactor design consists of a GAC adsorber inserted into the recycle line of an expanded-bed biological reactor (Fig. 1). In the hybrid GAC reactor system, GAC replacement from the GAC adsorber does not remove significant biomass and physical removal by adsorption may be controlled by the GAC replacement rate and the rate of the flow through the adsorber. The goal of physical removal is to suppress the concentration of adsorbable inhibitory compounds to allow for both the biodegradation of easily adsorbable compounds and for the biodegradation of the inhibitory/refractory compounds.

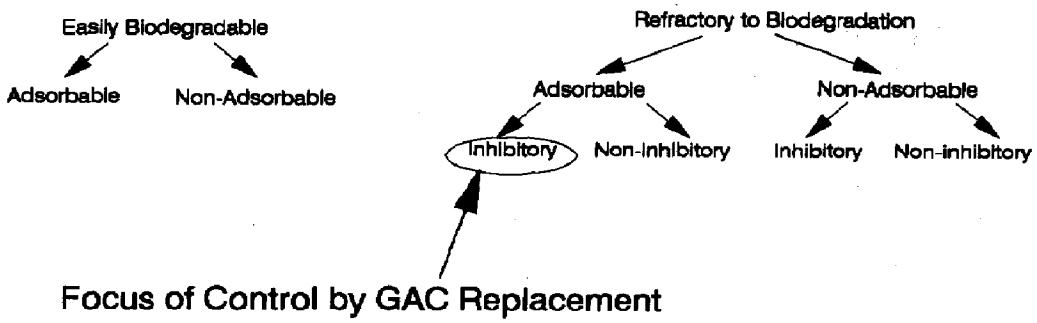

Fig. 2. Three-tier classification system. Wastewaters are complex mixtures whose components may be classified by biodegradability, inhibitory effect, and adsorptivity. The primary removal mechanism in an activated carbon biological reactor will be determined by this classification. The goal of GAC replacement is to control the concentration of inhibitory adsorbable compounds.

In Fig. 2, a three-tier classification system is used to illustrate the behavior of a complex mixture of compounds in an activated carbon/biological reactor. Compounds are classified based upon their biodegradability, adsorption characteristics assuming reversible adsorption, and their inhibitory effect on biodegradation. Easily biodegradable compounds will be removed primarily by biodegradation and are generally non-inhibitory. Adsorbable biodegradable compounds will be partially removed by adsorption and will compete for adsorption sites with refractory adsorbable compounds. Adsorbable refractory compounds may be removed by adsorption while weakly adsorbed compounds will not be efficiently removed. Weakly adsorbed refractory compounds are most often inorganic compounds such as metals that will require pre- or post-treatment. Inhibitory refractory compounds will have a negative impact on the biodegradation of both easily biodegradable substances and refractory compounds. When these inhibitory compounds are organics that are readily adsorbed, as is the case for many wastewaters, treatment in a GAC reactor is possible. In this paper, results from pilot tests comparing a GAC reactor with two hybrid GAC reactor systems are presented. The reactors were fed a synthetic wastewater composed of acetate and 3-ethylphenol (3-ep). Acetate represents a non-adsorbable, easily biodegradable compound while 3-ep represents a refractory/inhibitory compound that is strongly adsorbed. All removal mechanisms were independently characterized by batch tests. The goal of this study is to combine steady-state and batch test results to determine general operational control strategies while using GAC replacement for process control.

2. Materials and methods

2.1. Experimental apparatus and operation

The experimental apparatus used in this study consisted of three jacketed, expanded-bed anaerobic reactors identical to the reactors described by Fox et al. [5]

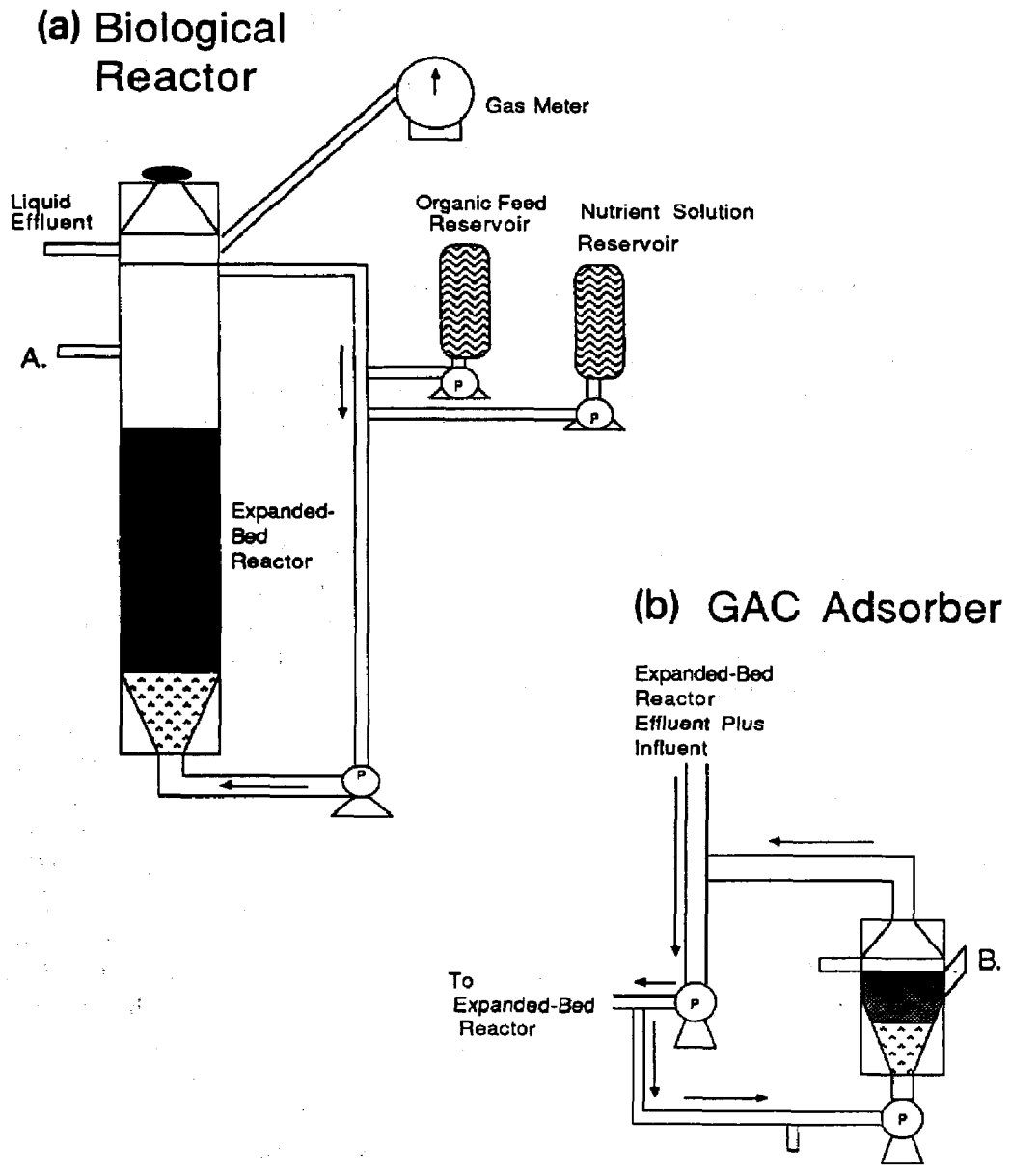

Fig. 3. (a) Expanded-bed biological reactor. GAC was the attachment medium in the GAC reactor and hybrid GAC reactor while sand was the attachment medium in the hybrid sand reactor. (b) The expanded-bed GAC adsorber was inserted into the recycle line of the hybrid reactors.

(Fig. 3a). An expanded-bed GAC adsorber was attached to the recycle line of the expanded-bed biological reactors to form a hybrid sand reactor and a hybrid GAC reactor (Fig. 3b). Bed-expansion was maintained by recycle and characteristics of the reactors studied are summarized in Table 1. The temperature was maintained at $35 \pm 2\,^{\circ}C$ throughout the reactor systems. GAC was replaced from the appropriate port as described by Fox et al. [6].

The three reactors were charged with identical seeds and brought to steady-state at an influent acetate concentration of 5 g/l. The influent acetate concentration was

Table 1
Characteristics of reactors studied

	GAC reactor	Hybrid GAC reactor		Hybrid sand reactor	
		Biological reactor	GAC adsorber	Biological reactor	GAC adsorber
Medium	GAC	GAC	GAC	Sand	GAC
Diameter (mm)	0.7	0.7	0.7	0.35	0.7
U.S. Mesh	(20 × 30)	(20 × 30)	(20 × 30)	(30 × 40)	(20 × 30)
Weight of medium (g)	1500	1350	150	6100	150
Reactor volume (l)	11	11	1	11	1
Expanded-bed volume (l)	5	4.5	0.7	5	0.7
Recycle flow (l/d)	4000	4000	3500	4000	3500

Table 2
Steady-state 3-ethylphenol loadings

Steady state	Influent 3-ep mg/l, g/day		Influent 3-ep loading on GAC replaced g 3-ep/g GAC	Average GAC residence time (days)	Actual 3-ep loading on GAC replaced g 3-ep/g GAC
GAC reactor					
Start-up	0	0			
GRSS1	500	5	0.167	50	0.167
GRSS2	833	8.33	0.167	30	0.113
GRSS3	1250	12.5	0.167	20	0.153
GRSS4	2500	25	0.167	10	0.166
GRSS5	1500	15	0.200	20	0.186
GRSS6	1875	18.75	0.250	20	0.235
GRSS7	2500	25	0.333	20	0.333
Terminate	2500	25	0		
Hybrid GAC reactor					
Start-up	0	0			
HGRSS1.a	500	5	0.167	5	0.167
HGRSS1.b	500	5	0.200	6	0.133
HGRSS2	833	8.33	0.208	3.75	0.095
HGRSS3	1250	12.5	0.208	2.5	0.100
HGRSS4	2500	25	0.208	1.25	0.116
HGRSS5	1500	15	0.250	2.5	0.065
HGRSS6	1875	18.75	0.313	2.5	0.087
HGRSS7	2500	25	0.416	2.5	0.117
Terminate	2500	25			
Hybrid sand reactor					
Start-up	0	0			
HSRSS1.a	500	5	0.167	5	0.167
HSRSS1.b	500	5	0.200	6	0.121
Terminate	1250	12.5	0.2–0.5	2.5–6	

Flow rate = 10 l/d, HRT = 1 day, influent acetate concentration = 5000 mg/l. The average time period of operation for each of the steady-states is three to four times the average GAC residence time for the GAC reactor.

maintained at 5 g/l henceforth and 3-ethylphenol (3-ep) was introduced to the reactors. During the first phase of the study, steady-state operation was observed while the influent 3-ep concentration and the GAC replacement rate were increased in corresponding step-wise increments (Table 2; SS1–SS4). Therefore, the loading rate of 3-ep per g GAC replaced (influent 3-ep in g per g GAC replaced) was relatively constant. The hybrid sand reactor was operated only during the first two steady-states. During the remainder of the steady-state study, the GAC replacement rate was maintained constant while the influent 3-ep concentration was increased (Table 2; SS5–SS7) which increased the influent loading of 3-ep per g GAC replaced. At the end of the study, GAC replacement was terminated to study biodegradation alone.

2.2. Analytical methods

Liquid, gas, and media samples were collected on a weekly or biweekly basis. Gas samples were analyzed with a gas partitioner using certified calibration standards. Liquid samples were preserved by acidification and filtered with 0.45 μm membrane filters. The analytical techniques are summarized in Table 3. Independent batch tests were used to characterize acetate utilization rates, 3-ep utilization rates, and 3-ep adsorption which are the removal mechanisms in the reactor systems.

Table 3
Analytical methods

Analysis	Method	Comments
COD	Standard methods [7]	
pH	Standard methods [7]	
Volatile fatty acids	Gas chromatography (direct aqueous injection)	2 mm ID, 92 cm glass column packed with 0.3% Carbowax and 0.1% H_3PO_4; injection port = 150 °C, FID = 200 °C, oven = 100 °C, GC = HP5730
3-Ethylphenol	UV spectrophotometry	Scan 300–230 nm with PE Lambda III; background correction by wavelength programming
	Gas chromatography (ether extract)	Periodically done to verify UV; 2 mm i.d., 183 cm glass column packed with SP-2100 on 80/100 Supelco; injection port = 200 °C, FID = 200 °C, oven = 135 °C, GC = HP5880
3-Ethylphenol (adsorbed on GAC)	Soxhlet extraction gas chromatography	20–30 min in methanol and 3–4 days in methylene chloride
Acetate utilization	Batch tests [8]	Done in serum bottles and with rate entire reactor for verification
3-ep utilization	Fed-batch technique [9]	Used 20 × 30 F-400 GAC at 35 °C; anaerobic conditions in 160 ml serum bottles
adsorption isotherms	Point-bottle technique	

3. Results and discussion

3.1. Results

During start-up with acetate as the sole C source, all three reactors exhibited similar acetate utilizing potential and the same methanogenic culture. When 3-ep was introduced to the reactors, GAC replacement was implemented to control the effluent concentration of 3-ep. GAC replacement removed biomass from the GAC reactor, while the effect of GAC replacement on biomass removal from the hybrid reactors was negligible since GAC was replaced only from the GAC adsorber [6].

During SS1–SS4, the removal of biomass as a consequence of GAC replacement resulted in dramatic differences in the biodegradation of 3-ep. As biomass was removed from the GAC reactor, the 3-ep utilizing organisms washed out and 3-ep biodegradation became negligible. The slow-growing 3-ep utilizing organisms had an apparent critical sludge age of ten days, which demonstrated the need for the long sludge ages in the hybrid reactors which averaged near 100 days. Indeed, the hybrid GAC reactor responded to increases in the influent 3-ep loading with corresponding increases in the influent 3-ep biodegradation rate (Fig. 4). The performance of the hybrid sand reactor was almost identical to the hybrid GAC reactor for the period studied indicating that GAC was not necessary as an attachment medium in the biological reactor.

The primary removal mechanism for 3-ep in the GAC reactor was adsorption and, consequently, the effluent 3-ep concentration was controlled only by GAC adsorption. Since the loading rate of 3-ep per g GAC replaced was constant during SS1–SS4

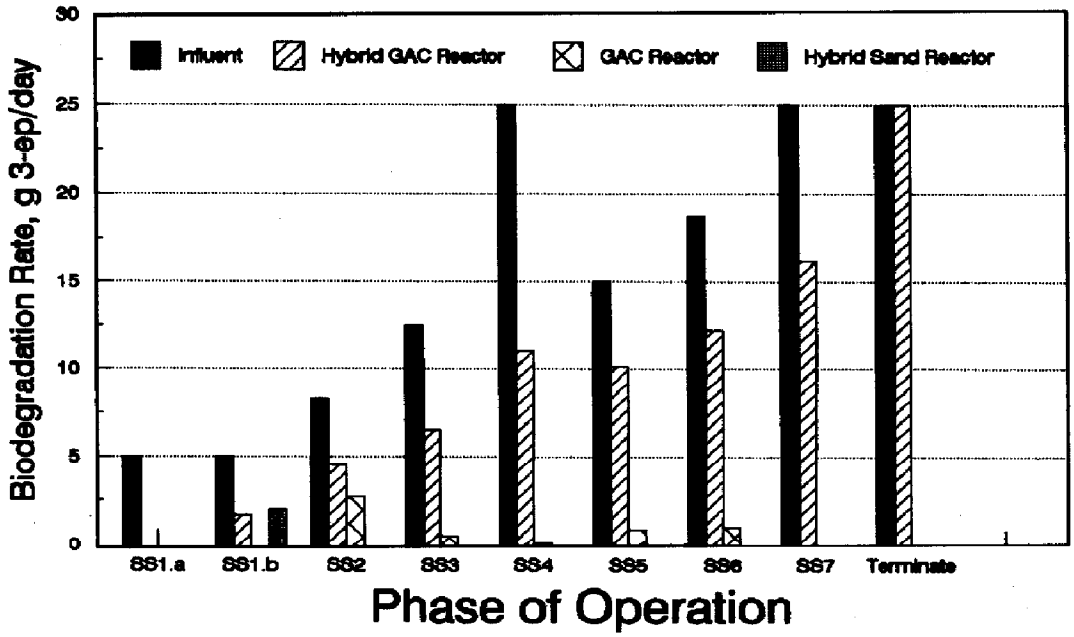

Fig. 4. Biodegradation of 3-ep in the reactors studied. The hybrid sand reactor was only operated during SS1.a and SS1.b.

(Table 2), when 3-ep biodegradation was negligible, the actual loading of 3-ep on the GAC was constant and the effluent 3-ep concentration was controlled in the range of 10–14 mg/l. GAC replacement provided greater than 97% removal of 3-ep irregardless of the biodegradation rate and acetate removal was not affected by non-inhibitory 3-ep concentrations as evidenced by greater than 99% acetate removal efficiencies. During SS5–SS7, the influent 3-ep loading was increased while the GAC replacement rate was maintained constant, therefore the effluent 3-ep concentration increased. Concentrations of 3-ep less than 100 mg/l did not significantly affect acetate utilization. During SS7, effluent 3-ep concentrations greater than 200 mg/l resulted in 'threshold' type inhibition of acetate utilization and the acetate removal efficiency rapidly decreased to less than 60%.

After acclimation, biodegradation of 3-ep in the hybrid GAC reactor removed 40–60% of the influent 3-ep. The hybrid GAC reactor responded to increases in the influent 3-ep loading with corresponding increases in the 3-ep biodegradation rate. Therefore, the mass of 3-ep adsorbed per gram GAC replaced was relatively constant and the effluent 3-ep concentration did not exceed 8 mg/l. In the hybrid GAC reactor, no inhibition was observed and greater than 99% removal efficiencies for both acetate and 3-ep were maintained since a stable population of 3-ep utilizers had developed.

After sufficient steady-state data were collected to observe the effects of GAC replacement and inhibition, GAC replacement was terminated with step-wise decreases in the GAC replacement rate from the reactors. The hybrid GAC reactor responded by biodegrading over 99% of the influent 3-ep without a decrease in effluent quality. By eliminating the physical removal mechanism of adsorption, the 3-ep previously removed by adsorption was available for biodegradation. This experiment demonstrated that GAC replacement was necessary during start-up to establish a population of 3-ep utilizers and that GAC replacement can be eliminated as biodegradation becomes the primary removal mechanism. Such a control strategy is impossible in the GAC reactor since a population of 3-ep utilizing organisms could not be established. Prior to decreasing GAC replacement in the hybrid sand reactor, 40% of the influent 3-ep was biodegraded during SS1.b indicating that a population of 3-ep utilizing organisms was established. The influent 3-ep loading was increased from 5 to 12.5 g 3-ep/day while the GAC replacement rate was initially increased to 60 g GAC/day, and then decreased to 25 g GAC/day. The reactor responded by tripling the rate of 3-ep biodegradation since more 3-ep was available for biodegradation while GAC replacement controlled the effluent 3-ep concentration below the inhibitory level. Operational problems with the experimental apparatus prevented completion of the experiment.

4. Discussion

In the GAC reactor, the use of GAC replacement to control the 3-ep concentration removed biomass from the system and prevented the biological removal of 3-ep [6]. Since biodegradation of 3-ep was negligible, analysis of the data may be used to develop an operational control strategy for the case in which an inhibitory compound

is not biodegraded. For this case, the goal of using GAC replacement is to prevent the inhibitory effect of the adsorbable inhibitory compound, 3-ep, on the utilization of the easily biodegradable compound, acetate. Serum bottle batch tests that measured acetate utilization as a function of the bulk 3-ep concentration were performed with a methanogenic culture from the GAC reactor and the results are presented in Fig. 5. Threshold type inhibition was observed at 3-ep concentrations greater than 150–200 mg/l in both the serum bottle batch tests and during continuous operation of the reactor. Concentrations of inhibitor below the threshold level exert negligible inhibition while extreme inhibition is observed for inhibitor concentrations greater than the threshold level.

Luong [10] successfully applied a parabolic model to many different data sets to describe threshold inhibition.

$$V\frac{dS}{dt} = \frac{[1 - (I/K_i)^a]kXS}{K_s + S} \tag{1}$$

where S is the substrate concentration (mg/l), I is the inhibitor concentration (mg/l), kX is the maximum substrate utilization rate (mg/d), K_s is the Monod half-velocity constant (mg/l), and K_i is the inhibition constant (mg/l). The term $[1 - (I/K_i)^a]$ of Eq. (1) is the inhibition term that modifies the Monod kinetic expression [11]. The parabolic model predicts growth and will cease at inhibitor concentrations greater than K_i and also predicts that low concentrations of inhibitor will exert little inhibition. Although the mechanistic competitive inhibition model was used to successfully describe the effects of 3-ep on acetate utilization for 3-ep concentrations less than 160 mg/l [8], an empirical model such as the parabolic model is necessary to describe inhibitory effects over a complete range of concentrations. Since threshold

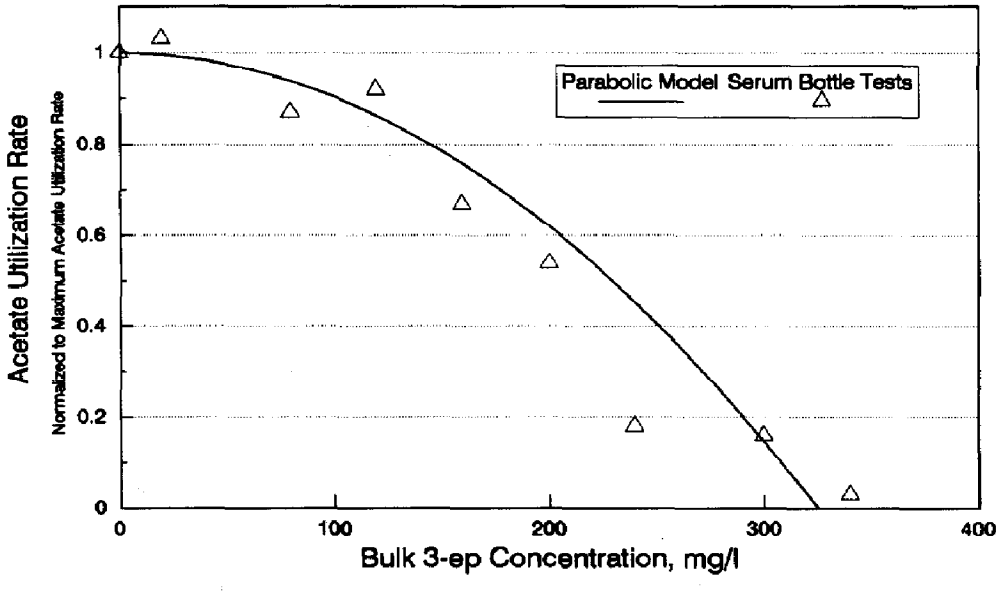

Fig. 5. Inhibitory effect of 3-ep on acetate utilization and a 'threshold' inhibition model fit.

inhibition is a ubiquitous phenomenon, in developing a more general process control strategy, the parabolic model should provide a better prediction than mechanistic inhibition models.

For the effects of 3-ep on acetate utilization, the parabolic model with a value of K_i of 326 mg/l and a value of $a = 2.3$ fits the serum bottle batch test data (Fig. 5). The model fits observed inhibitory effects including negligible inhibition for 3-ep concentrations less than 100 mg/l and almost complete inhibition for 3-ep concentrations greater than 250 mg/l. Thus, the goal of GAC replacement for process control would be to maintain an effluent 3-ep concentration near 100 mg/l. Similar process control strategies were developed for treating complex wastewaters such as coal gasification wastewater [12] where the goal of GAC replacement was to maintain the total effluent cresol concentration below a threshold inhibitory level of 100 mg/l. Although with complex wastewaters predicting the exact GAC replacement rate will be difficult and will likely require a pilot study, the GAC replacement rate for simpler mixtures may be accurately predicted. This is because near equilibrium adsorption occurs in the GAC reactors due to long average GAC residence times (Table 2) and isotherm studies on the inhibitory compounds may be used to predict physical removal within a GAC reactor. In Fig. 6, isotherm results for 3-ep are presented alongside data points from the reactors representing the measured effluent 3-ep concentrations and the corresponding adsorbed mass of 3-ep per gram GAC. Data points from the GAC reactor are coincident with isotherm values indicating that average GAC residence times of ten days or more were sufficient to establish equilibrium adsorption.

The adsorption of 3-ep on GAC was fit to a Freundlich isotherm model using linear regression where I is the liquid 3-ep concentration (mg/l), q is the adsorbed phase

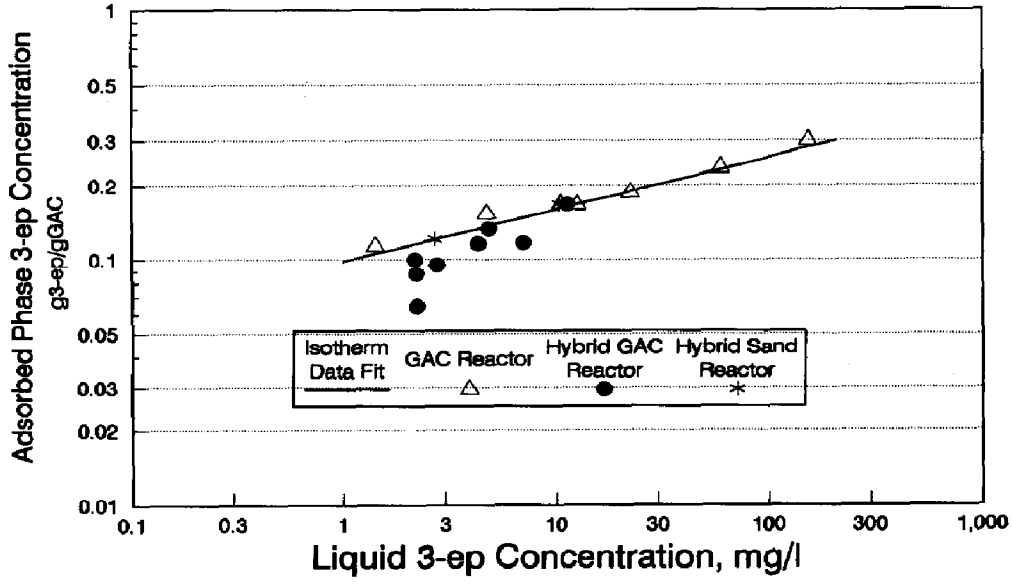

Fig. 6. Isotherm for equilibrium adsorption of 3-ep on GAC and steady-state data from reactors. Average GAC residence times greater than 3.75 days resulted in near equilibrium adsorption within the reactors.

concentration of 3-ep (mg^3 ep/g GAC), and k_f is the Freundlich adsorptive capacity (mg^3 ep/g GAC):

$$q = k_f I^n = 99.0\, I^{0.208} \tag{2}$$

At steady-state in the GAC reactor, 3-ep biodegradation is negligible and the rate of GAC replacement necessary to maintain a given effluent concentration may be calculated by a mass balance on 3-ep as follows:

$$Q(I_{in} - I) = q(M) = 99.0\, I^{0.208}(M) \tag{3}$$

where Q is the influent flow rate (l/day), I_{in} is the influent 3-ep concentration (mg/l) and M is the GAC replacement rate (g GAC/day). Rearranging Eq. 3 to solve for M yields:

$$M = 0.00101\, Q(I_{in} - I)/I^{0.208} \tag{4}$$

Eq. 4 represents a simple method for calculating the GAC replacement rate. As an example, during GRSS5, the GAC reactor was operated with $Q = 10$ l/d and $I_{in} = 15\,000$ mg/l. If the desired 3-ep concentration was 100 mg/l, a GAC replacement rate of 58 g GAC/day would maintain the 3-ep concentration below the inhibitory level. More complex scenarios for GAC reactors that include the effects of multicomponent adsorption have been analyzed by Nakhla et al. [13].

The goal of GAC replacement in the hybrid GAC reactors is to stimulate the biodegradation of inhibitory compounds and, thereby, eliminate the need for GAC replacement. In this case, the concentration of inhibitory compound must be maintained at a concentration to stimulate biodegradation of the inhibitory compound while not exerting significant inhibition on the easily biodegradable substrates. In general, these concentrations of inhibitory compounds will be below the threshold inhibition level. However, this situation is much more complicated than the threshold inhibition case since the inhibitory compounds are being removed by both biodegradation and adsorption. Also, low GAC residence times in the GAC adsorber resulted in deviations from equilibrium adsorption as evidenced in Fig. 6. Average GAC residence times of less than 3.75 days were not sufficient to establish equilibrium adsorption, thus, the consideration of adsorption kinetics might be necessary at low GAC residence times.

The kinetics of 3-ep biodegradation were analyzed using a fed-batch technique which demonstrated that 3-ep was an inhibitory substrate [9]. The Haldane model [11] was used to describe the substrate inhibition kinetics as follows:

$$V\frac{dI}{dt} = \frac{kXI}{K_s + I + I^2/K_{ih}} \tag{5}$$

Non-linear regression was used to search for K_{ih}, the Haldane inhibition constant, and K_s by normalizing all data to the maximum 3-ep utilization rate, kX [9]. The best-fit values of K_s and K_{ih} were determined to be 5 mg 3-ep/l and 143 mg 3-ep/l, respectively. The kinetics of 3-ep utilization are plotted in Fig. 7. The maximum 3-ep

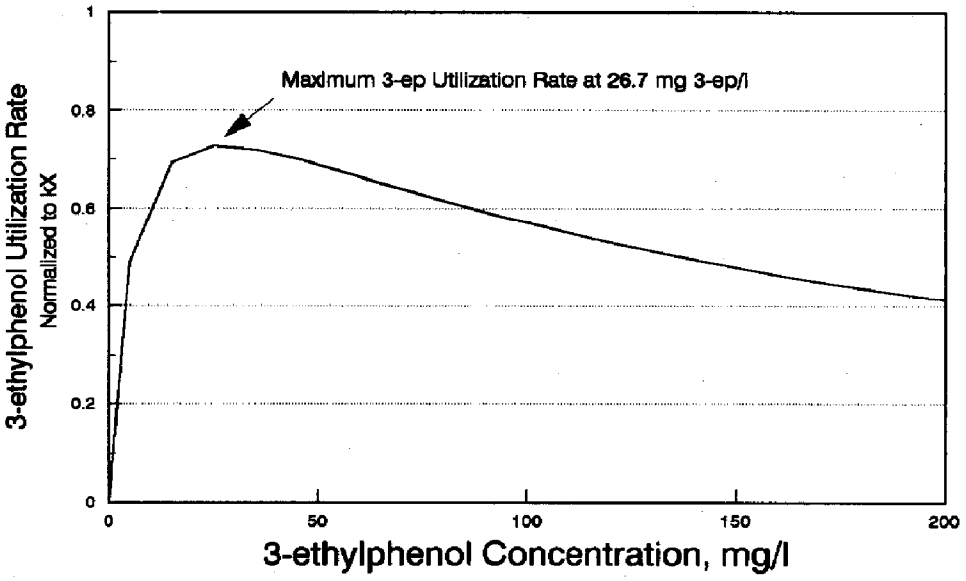

Fig. 7. Haldane model fit to describe substrate inhibition kinetics of 3-ep utilization.

utilization rate occurs at a concentration of inhibitory substrate given by [14]:

$$I_{(dI/dt)max} = (K_s K_{ih})^{1/2} \tag{6}$$

Thus, the maximum 3-ep utilization rate and corresponding maximum growth rate of 3-ep utilizing organisms occurs at a 3-ep concentration of 26.8 mg/l (Fig. 7).

GAC replacement may be used to stimulate biodegradation by maintaining a concentration of inhibitory substrate near the maximum substrate utilization rate. Higher concentrations of inhibitory substrate will result in inhibition while lower concentrations of substrate will limit the growth rate, and thereby, limit the biodegradation removal efficiency. However, acclimation to low concentrations of inhibitory substrates is often necessary to initiate a population of inhibitory substrate-utilizing organisms. An optimal start-up strategy would be to use GAC replacement to expose the microorganisms to low concentrations of inhibitory compounds during an acclimation period. Following acclimation, GAC replacement should be reduced to increase the concentration of inhibitory substrate to a level near $(K_s K_{ih})^{1/2}$ which will provide the maximum growth rate. This process control strategy will stimulate the accumulation of inhibitory substrate-utilizing organisms and reduce reactor start-up time. After the inhibitory substrate-utilizing organisms have accumulated in the biological reactor, GAC replacement will not be necessary and the microorganisms will continue to reduce the concentration of inhibitory substrate until pseudo-steady-state operation is achieved.

For 3-ethylphenol biodegradation in the hybrid GAC reactor, the process control strategy discussed above was partially implemented. An acclimation period of 50 days during HGRSS1.a initiated a population of 3-ep utilizers while a 3-ep concentration near 12 mg/l was maintained. During the remainder of steady-state operation, GAC replacement rates were above the optimal level and the combined biological and

physical removal of 3-ep maintained the concentration of 3-ep near 5 mg/l, which was far below the optimum growth concentration of 26.8 mg 3-ep/l. However, the experimental period was over 800 days which was sufficient time to establish a large population of 3-ep utilizers under sub-optimal conditions. Therefore, termination of GAC replacement resulted in only a minor increase in the effluent 3-ep concentration from 5 to 8 mg/l, which was sufficient to stimulate virtually complete biodegradation of the influent 3-ep (Fig. 4).

During the operation of the hybrid sand reactor, an attempt at demonstrating the optimal control strategy was made. The acclimation period during HSRSS1.a was almost identical to the acclimation period of the hybrid GAC reactor and 3-ep utilizers were allowed to accumulate during HSRSS1.b. The influent 3-ep loading was then increased in an attempt to increase the effluent 3-ep concentration to the optimal level. An increase in the 3-ep concentration from 2 to 12 mg/l increased the rate of 3-ep utilization over three-fold which was consistent with the Haldane kinetic expression. Mechanical problems prevented completion of the experiment and continuation of experiment might have demonstrated how GAC replacement can be used to optimize the growth of inhibitory-substrate utilizers.

The optimal control strategy for developing a population of inhibitory-substrate utilizers is similar to fed-batch control strategies applied in biotechnological processes that utilize inhibitory substrates. Most fed-batch control strategies are based on increasing the loading rate of inhibitory substrate to maintain a constant concentration of inhibitory substrate. For the treatment of wastewaters in hybrid GAC reactors, varying the loading for process control is not practical due to the complexity of the mixture which includes many easily biodegradable substrates. If a constant loading of wastewater is maintained, an explicit fed-batch control strategy may be developed when the biodegradation kinetics of the inhibitory substrate and the adsorption of the inhibitory substrate have been characterized. Assuming equilibrium adsorption and Haldane kinetics, the optimal rate of GAC replacement may be calculated from a pseudo-steady-state mass balance:

$$Q(I_{in} - I) = q(M) + \frac{kXI}{K_s + I + I^2/K_{ih}} \tag{7}$$

As the inhibitory substrate-utilizers grow, kX will increase and I will decrease, therefore, M must be decreased to maintain I near the optimal concentration.

A heuristic method to calculate the optimal GAC replacement rate may be based on measured values of I. Measured values of I could be used to calculate kX, a measure of the activity of the inhibitory-substrate utilizers. Then, the new value of kX can be used to estimate the new GAC replacement rate, M, that will increase or decrease I to the optimal concentration $(K_sK_{ih})^{1/2}$.

$$M = \frac{2QI_{in}K_s(K_sK_{ih})^{-n} + (QI_{in} - 2QK_s - kX)(K_sK_{ih})^{1/2-n} - Q(K_sK_{ih})^{1-n}}{k_f[2K_s + (K_sK_{ih})^{1/2}]} \tag{8}$$

Eq. 8 may be used to calculate the optimal GAC replacement based on the value of kX. This heuristic approach to optimizing GAC replacement is illustrated in Fig. 8.

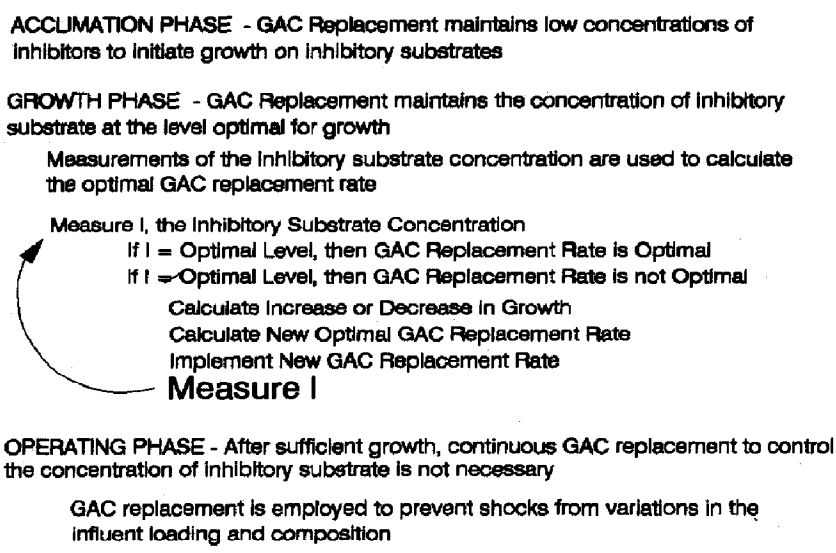

Fig. 8. Heuristic approach to optimizing GAC replacement in a hybrid reactor system.

The method uses measured values of I to estimate the actual increase in growth and adjusts the GAC replacement rate accordingly. Since variations in the influent loading are incorporated into the calculation, the GAC replacement rate will also compensate for variable loading. A deficiency of the method is the assumption of equilibrium adsorption, however, design of the GAC adsorber to provide average GAC residence times greater than 3.75 days will allow for near equilibrium conditions.

After a population of inhibitory-substrate utilizing organisms has been established, biodegradation will be the primary removal mechanism and GAC replacement will no longer be necessary. This was demonstrated in the hybrid GAC reactor when termination of GAC replacement did not adversely affect 3-ep removal. The GAC adsorber may then serve to compensate for variations in the influent loading or to recover the biological reactor from a toxic shock. After terminating GAC replacement, the hybrid GAC reactor was subjected to step increases in the influent loading rate by increasing the influent concentration of influent 3-ep and influent acetate from 2.5 g/l and 5 g/l to 7.5 g/l and 15 g/l, respectively. GAC replacement during the first two increased loadings prevented adverse effects on biological removal. During the third increase in influent loading, GAC replacement was not implemented and the reactor was allowed to approach failure. When the effluent 3-ep concentration increased to more than 200 mg/l and reactor failure was imminent, the reactor was recovered from severely inhibited conditions by replacing GAC from the GAC adsorber. Subsequent recovery of the reactor was rapid and removal efficiencies in excess of 98% were observed in less than 24 hours. The variable loading experiment demonstrated how GAC replacement may be used for process control to both protect the reactor from failure and provide high removal efficiencies during extreme variations in loading.

Table 4
Wastewaters treated with anaerobic GAC reactors

Coal gasification wastewater [9]
Refinery sour water stripper bottoms [3]
Hazardous landfill leachate [2]
Thermoplastic resin strong liquor [4]
Metal cutting fluids [15]
Paint stripping wastewater [16]
Trichloroethane wastewater [17]
Mixture of chlorinated phenols [2]
Mixture of six VOC priority pollutants [2]
Mixture of six semi-volatile priority pollutants [2]

5. Conclusions and recommendations

The GAC reactor has successfully treated many real wastewaters and several synthetic wastewaters as listed in Table 4. These wastewaters were mixtures that contained high concentrations of inhibitory compounds. Due to increased process control, the hybrid GAC reactor has demonstrated potential to provide more efficient and economical treatment than the GAC reactor. The hybrid GAC reactor is capable of efficiently biodegrading many inhibitory/refractory compounds that must be removed by adsorption in the GAC reactor.

GAC replacement strategies for both the GAC reactor and the hybrid GAC reactor were developed in this paper. Near equilibrium adsorption was observed during continuous operation of the reactors, therefore, isotherm studies were sufficient to predict adsorption phenomena. For the GAC reactor, the GAC replacement rate should maintain a concentration of inhibitor below the threshold inhibition level. In the hybrid GAC reactor, increased process control may be used to obtain efficient biodegradation of inhibitory compounds. GAC replacement is used to: (1) acclimate the microorganisms to low concentrations of inhibitory compounds; (2) optimize the growth of microorganisms capable of utilizing the inhibitory compounds; (3) compensate for variations in the influent loading.

The concept of combining a GAC adsorber with a biological reactor could also be applied to other fixed-film biological reactors that can tolerate moderate recycle rates. Therefore, the efficiency of fixed-film biological reactors might be enhanced by retrofitting with a GAC adsorber. Also, other adsorbers might be combined with biological reactors for specific applications. The process control strategies presented in this paper would apply to a number of different reactor configurations.

6. Nomenclature

a	Exponent for parabolic inhibition (dimensionless)
I	Inhibitor concentration (M/l^3)

I_{in} Influent inhibitor concentration (M/l^3)
k_f Freundlich adsorptive capacity (M/M)
K_i Inhibition constant (M/l^3)
K_{ih} Haldane inhibition constant (M/l^3)
K_s Monod half-velocity constant (M/l^3)
kX Maximum substrate utilization rate (M/time)
M GAC replacement rate (M/time)
n Freundlich exponent
Q Influent flow rate (l^3/time)
S Substrate concentration (M/l^3)

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