

Anaerobic toxic wastes treatment: dilution effects

G.F. Nakhla^{a,*}, M.T. Suidan^b

^a *Department of Civil Engineering, King Fahd University of Petroleum and Minerals,
Dhahran 31261, Saudi Arabia*

^b *Department of Civil and Environmental Engineering, University of Cincinnati, Cincinnati,
OH 45221, USA*

Received 21 January 1994; accepted in revised form 30 December 1995

Abstract

The impact of waste strength on the treatability of toxic wastes such as coal gasification wastewater by the anaerobic GAC reactor operating with periodic GAC replacement was assessed by operating three units treating 30%, 60% and full strength wastewater. At a COD loading of 4.7 kg/m³ d performance was unimpacted by dilution at all the GAC replacement rates investigated in this study to define the minimum adsorptive capacity required to overcome the wastewater toxicity, with all three reactors achieving over 94% COD removal, more than 99.9% phenol removal, 98–99% cresols removal, and virtually complete removal of dimethyl phenols. The full strength wastewater was not treatable at COD loading rates higher than 10 kg/m³ d while the reactors treating the diluted wastewater maintained a COD removal efficiency of about 90% and over 99.5% reduction of phenolic compounds at a loading of 32–34 kg COD/m³ d. At this loading with a biological solids residence time of less than 21 d and hydraulic retention times of 4–8 h, biological activity was not affected at all by the toxicity of the waste.

1. Introduction

Many industrial operations such as coal gasification, oil refining, manufacturing of petrochemicals, pharmaceuticals, and steel mills generate wastes that contain a myriad of toxic organics. The promising technology of converting coals to gaseous fuels is often associated with the production of wastewaters that are highly polluted with phenolics, ammonia, cyanide, thiocyanate and a variety of suspected mutagenic substances. Although the biological treatment of phenolic compounds is favored over physicochemical treatment, the other components of the coal gasification wastewater (CGWW) typically impair the performance of biological treatment processes [1, 2].

* Corresponding author. Fax: 966-3-860-2879.

Furthermore, the settleability of the sludge produced by the aerobic treatment of high strength coal conversion wastewaters is very poor [3].

Given the high concentrations of toxicants in coal gasification wastewater, dilution of the waste has often been a requisite for biological treatment. Luthy et al. [4] treated ammonia stripped wastewater at 33% strength by the activated sludge process and achieved phenol removal efficiencies exceeding 99% and COD removal efficiencies of 84%. Caire et al. [5] reported a 90% reduction in COD from 10% strength CGWW by activated sludge treatment. Janeczek and Lamb [6] have demonstrated the biological treatability of coal gasification wastewater diluted to one-quarter strength. However, the problems of high water consumption and the subsequent large volumes of wastewater, concomitant with dilution have not been addressed in the foregoing investigations.

Anaerobic process have long been known to be prone to inhibition and therefore aerobic processes have dominated the field of toxic wastewater treatment. Recently, however, the amenability of such wastes to anaerobic treatment in granular activated carbon (GAC) reactors has been documented in the literature [6, 7]. Although the GAC serves as a biofilm support its adsorptive capacity for organic toxicants was indispensable for sequestering toxicity and permitting long-term processing of the wastes. Goeddertz et al. [8] have reported on the feasibility of the anaerobic biological activated carbon (AnBAC) process for treatment of a high strength multicomponent inhibitory wastewater. The main constituent of the 28.9–35.5 g COD/l wastewater was phenol accounting for about 80% of the COD with formaldehyde and methanol making up the remaining 20%. Bench-scale columns achieved 95% COD removal at loadings ranging in 0.01–0.06 g COD/g GAC/d while pilot-scale columns treating the full strength wastewater at 0.015–0.02 g COD/g GAC/d realised a 98% reduction of COD. Methane production to COD removed ratios approached the theoretical ones, indicating that the inhibitory wastewater was rendered completely biodegradable.

The capability of the fluidized bed anaerobic GAC reactor, operating with GAC replacement to replenish the adsorptive capacity of the bed, to treat toxic wastewaters containing inhibitory nonbiodegradable components with no adverse impact on biological activity was recently demonstrated [9]. The GAC replacement rate is governed by the adsorptive capacity of the carbon for toxins, their concentrations, and the wastewater application rate, which is a function of the hydraulic retention time (HRT) of the treatment system. Neglecting biomass loss in the effluent, the GAC replacement rate dictates the biological solids residence time (SRT) which is then equal to the inverse of the fraction of the bed replaced daily. Consequently then, SRT and HRT are closely related. The HRT dictates the capital cost of treatment while the GAC replacement cost represents a major component of the operating cost. Furthermore if waste dilution is deemed necessary for treatment, the additional cost of dilution water may be substantial. While this study assesses the impact of dilution on treatment, it is noteworthy that the experimental design focused on the optimization of treatment cost by determining the minimum GAC replacement rate needed to control the toxicity of the waste and the highest treatable loading rate.

2. Materials and methods

2.1. Reactor design

Three identical completely mixed expanded-bed anaerobic GAC reactors (Fig. 1) were employed in this investigation to treat 30%, 60%, and full strength ammonia-stripped CGWW. The anaerobic reactor was constructed of a 134.6 cm long, 0.63 cm thick transparent plastic tube with an outside diameter of 11.4 cm. This 111

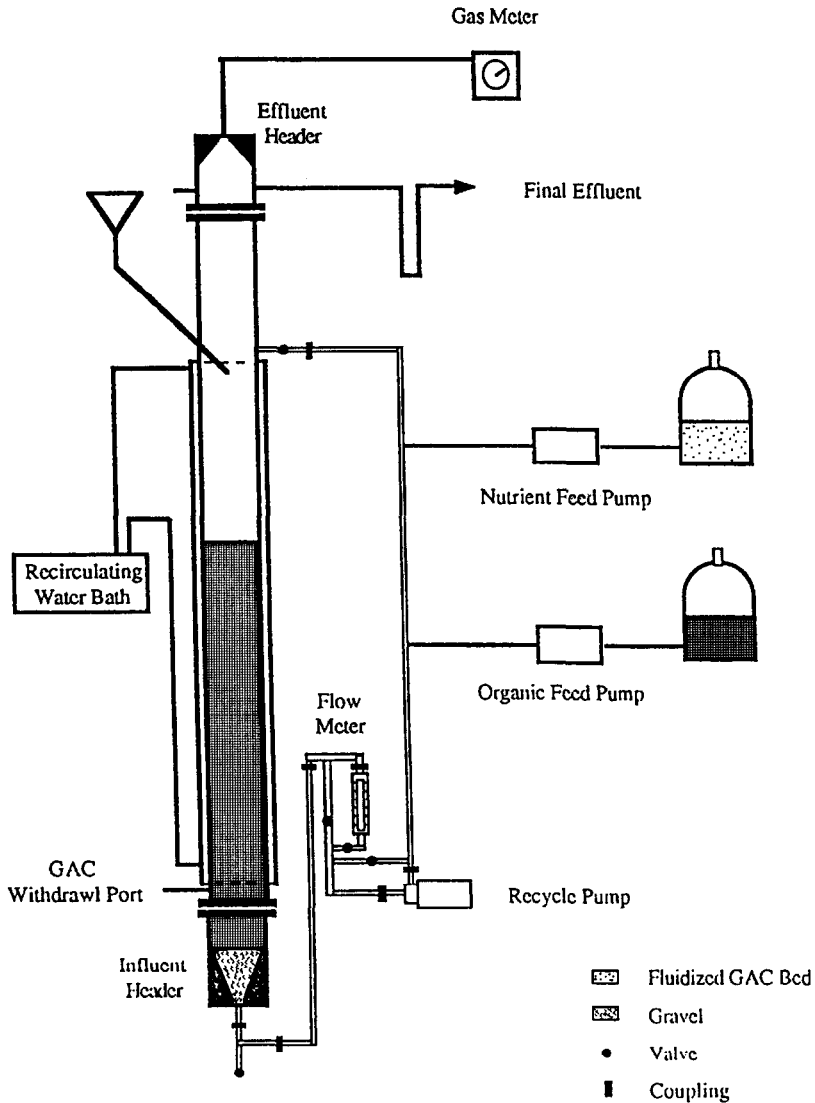


Fig. 1. Schematic of an anaerobic fluidized bed reactor.

columnar reactor was surrounded by a plexiglas jacket for the heated water necessary to maintain a constant temperature of 35 °C within the reactor. Effluent recycle at the rate of 5.0 l/min was employed to achieve completely mixed conditions and provide a bed expansion of 25% to 50%. Each of the reactors was initially charged with 1.5 kg (750 g virgin and 750 g from other reactors operating on CGWW) of 16 × 20 US Mesh Filtrasorb 400 GAC (Calgon Corp., Pittsburgh, PA, USA) resulting in a 3.4 l consolidated bed.

2.2. Operation and control

The composition of the wastewater, obtained from Morgantown Energy Technology Center (METC) in Morgantown, WV, after ammonia stripping is shown in Table 1. The undiluted ammonia-stripped wastewater, fed to each reactor at a flow rate of 0.87 l/d was supplemented with 0.04 l/d of an inorganic nutrient and vitamin mixture whose composition was reported elsewhere [10]. The desired feed dilutions of 30% and 60% strength were obtained by adding dilution water to the nutrient solution at flow rates of 2.12 and 0.61 l/d, respectively. Two types of loading pertain to this technology; the mass loading, defined as mass of COD applied per unit mass of GAC replaced and volumetric loading rate defined as daily mass of COD applied per unit volume of consolidated bed. To convert from mass loading to volumetric loading, the former is multiplied by the daily mass of GAC replaced and subsequently divided by the consolidated bed volume of 3.4 l.

The experimental protocol adopted for the study involved operation of the three anaerobic reactors for two phases; the first aimed at determining the minimum GAC replacement rate needed to overcome toxicity, and the second targeted the maximum COD loading rate that can be treated without failure. The first phase lasted for 413 d during which operation at a constant volumetric COD loading rate of 4.7 kg

Table 1
Chemical characteristics of ammonia-stripped coal gasification wastewater

| Parameter | Concentration ^a | Percent of COD |
|----------------------------------|----------------------------|----------------|
| pH | 8.92 | – |
| Alkalinity, as CaCO ₃ | 3000 | – |
| COD | 18450 | – |
| DOC | 4650 | – |
| NH ₃ -N | 800–1200 | – |
| Phenol | 2150 | 27.73 |
| <i>Ortho</i> -cresol | 220 | 3.00 |
| <i>Meta</i> + <i>para</i> cresol | 710 | 9.70 |
| 2,4-dimethyl phenol | 50 | 0.71 |
| 3,5-dimethyl phenol | 150 | 2.13 |
| 3,4-dimethyl phenol | 50 | 0.71 |
| Percent COD due to phenolics | | 43.98 |

^aAll concentrations are in mg/l except pH.

COD/m³ d, extended from day 0 to 364 while the GAC replacement rate was continuously decreased, in steps of 25 g, from 200 to 75 g/wk. From day 364 to 413, the influent COD loading was increased by 25% while a carbon replacement rate of 75 g/wk was continued. This final replacement rate of 0.58 g GAC/g feed COD was maintained constant throughout the second phase while the wastewater flow rates were increased. However after day 581, the ratio of GAC replaced to COD applied was increased to 0.68 g GAC/g COD in order to avert some observed inhibition of methane production and maintain stable operation.

Daily readings of wastewater and nutrient solution flow rates, gas production, room temperature and effluent pH were recorded. Reactor temperature was maintained at 35 °C ± 2 °C by recirculating water from a temperature-controlled water bath around the reactors and the effluent pH was controlled between 6.8 and 7.3 by the addition of concentrated HCl or 6N NaOH to the feed reservoirs.

2.3. Analytical methods

Weekly samples collected from the reactors were subjected to routine analysis following the procedures of *Standard Methods for the Examination of Water and Wastewater*, 16th Edition (APHA-AWWA-WPCF, Washington, DC, 1985) with the exception of the gas analysis and the analysis for specific organic compounds. Gas analyses were performed on a Fisher Model 1200 Gas Partitioner (Fisher Scientific Co., Chicago, IL). Analysis for specific organic compounds were conducted on 0.45 µm filtered aqueous samples. These samples were extracted with ether into acid, base, and neutral fractions, and subsequently dried and concentrated according to the procedures given by Luthy et al. [4]. The three solvent phases were analyzed via gas chromatographic separation on a Hewlett Packard model 5840 A gas chromatograph equipped with a flame ionization detector (FID) using a 25 m flexible fused silica OV-101 capillary column. The temperature was programmed to increase from 90 ° to 200 °C at 4 °C per minute with a three-minute hold at 90 °C.

3. Results and discussion

3.1. General performance

The reactors treating 30%, 60%, and full strength coal gasification wastewater are denoted henceforth as Reactors 1, 2, and 3, respectively. The temporal variation of influent and effluent COD from reactors 1–3 is illustrated in Fig. 2(a)–(c). Despite the apparent flatness of the total and soluble effluent COD curves, two trends are readily discernible. The soluble effluent COD in all three reactors was observed to increase with decreasing carbon replacement rates and this will be discussed at length later. The other pattern is the continuous increase in insoluble COD throughout the two phases of the study. This phenomenon is more pronounced in Reactors 1 and 2 than in Reactor 3. Since both organic and hydraulic loadings to the reactors were maintained constant in Phase I, the increased biomass shearing is attributed to the reduction in

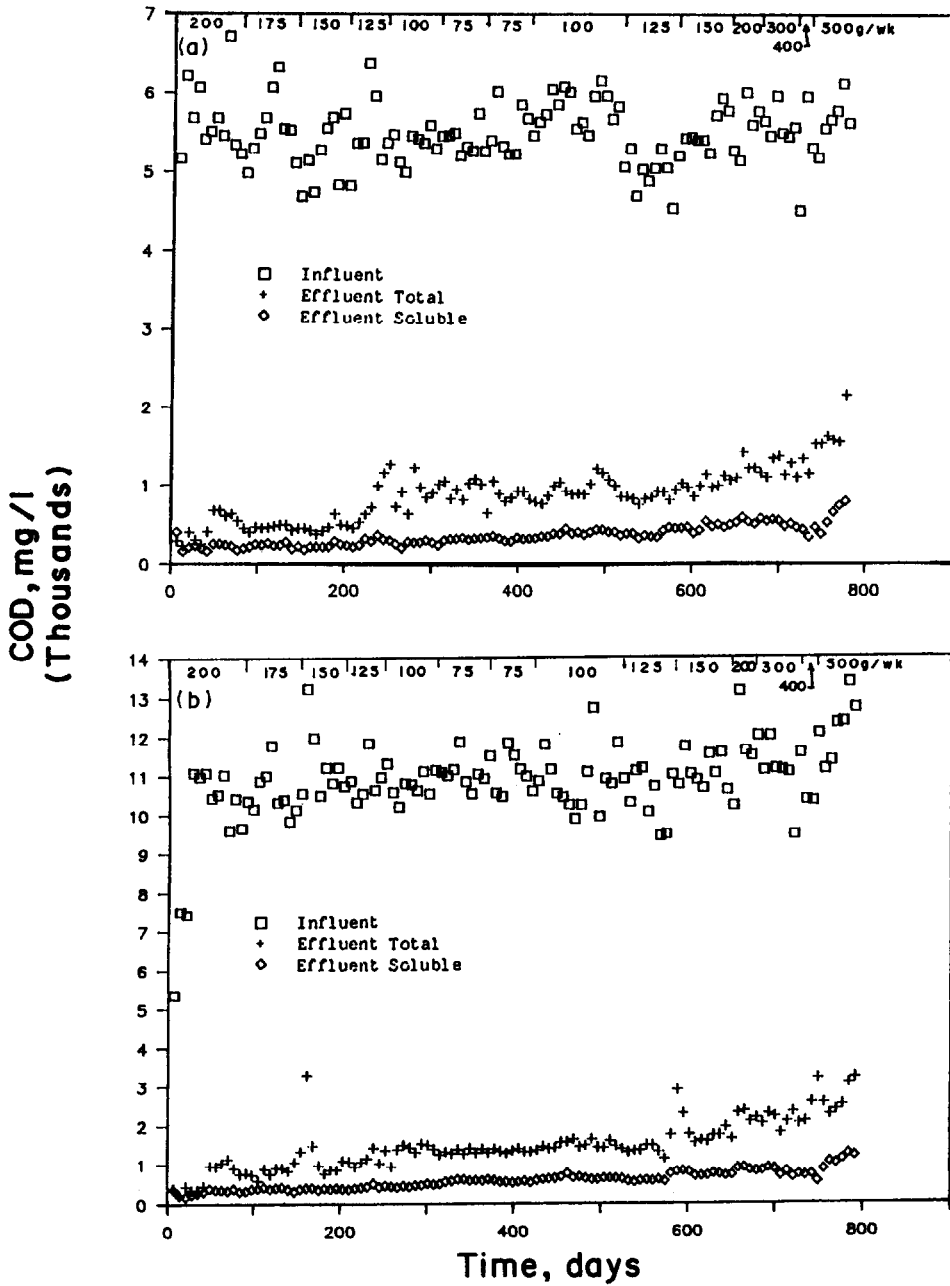


Fig. 2. Temporal variation of influent and effluent COD in (a) Reactor 1, (b) Reactor 2, and (c) Reactor 3.

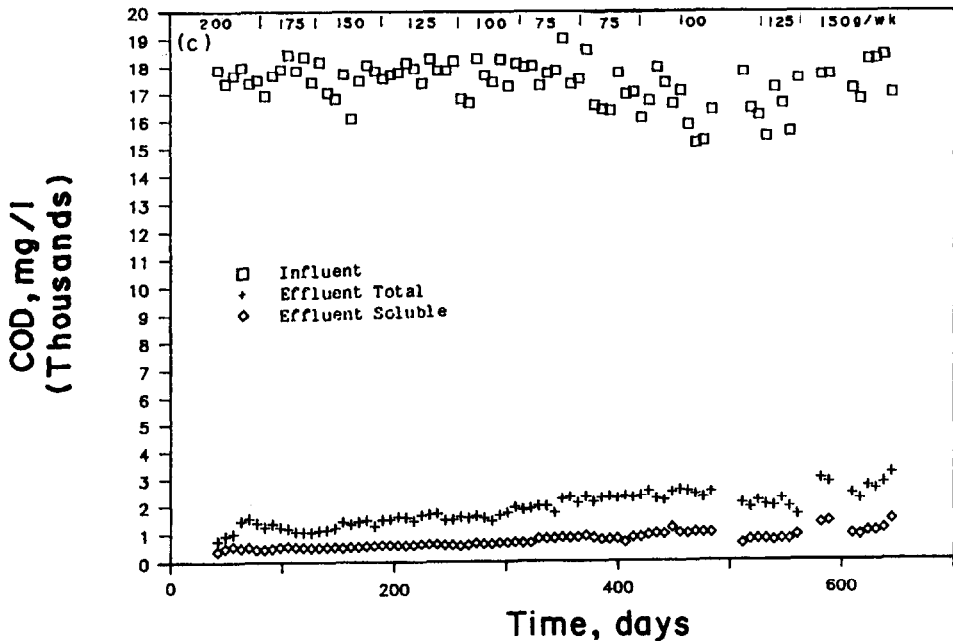


Fig. 2. Continued.

carbon replacement rate and the ensuing decrease of fresh surface area available for microbial attachment. In Phase II, hydrodynamic shear increased due to the higher organic and hydraulic loading rates implemented. The resulting biomass detachment offset the increase of fresh microbial attachment area induced in the system as a result of increasing GAC replacement rates.

The steady-state soluble effluent COD concentration from the three reactors during Phase I is shown as a function of the GAC mean residence time and the COD mass loading in Fig. 3(a). It is apparent that all reactors removed more than 95% of the influent COD reducing the concentration from about 5500 to 300 mg/l in Reactor 1. Reactors 2 and 3 performed similarly reducing the influent COD concentration from 11 000 to less than 600 mg/l, and from 18 000 to less than 800 mg/l, respectively. These removal efficiencies concur with those observed by Janeczek and Lamb [6] during the treatment of underground CGWW by the powdered activated carbon/activated sludge process. However two points in connection with this comparison must be emphasized. Janeczek and Lamb [6] treated only 25% strength wastewater as opposed to the full strength waste processed in this study and the high removal efficiencies were realized at a PAC dose of 0.9 g COD/g PAC versus 1.5 g COD/g GAC here.

Fig. 3(a) depicts an increase in the soluble effluent COD with increasing GAC mean residence time and COD mass loadings. Increasing effluent concentrations with the GAC mean residence time, which ignoring biomass loss by shearing is equal to the

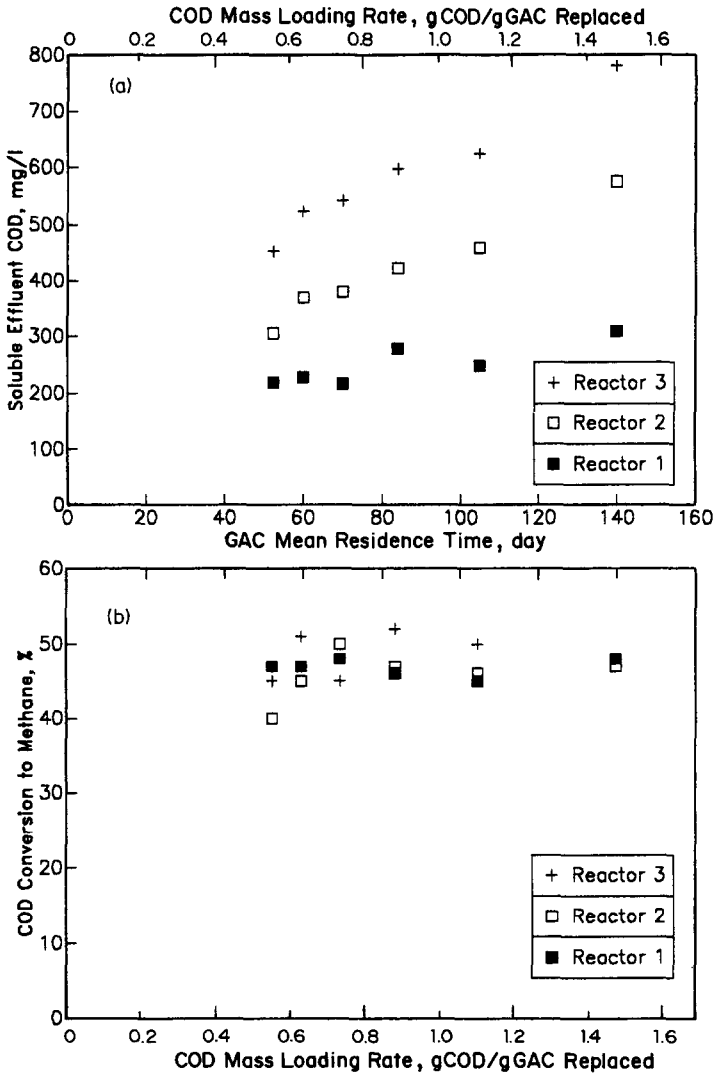


Fig. 3. Variation of effluent soluble COD (a) and COD conversion to methane (b) with GAC mean residence time and COD mass loading in Phase I.

biological SRT is not consistent with the kinetics of substrate utilisation by continuous microbial cultures. The increase in effluent COD with increasing COD mass loadings is primarily attributed to the reduction in the adsorptive capacity of the bed due to decreasing GAC replacement rates. The steadiness of the COD conversion rate to methane around the 50% level for most of the first phase (Fig. 3(b)) strongly confirms that the observed increase in effluent COD was mostly due to the breakthrough of nonbiodegradable adsorbable toxins.

It is important to note that during the second phase of the work, which was undertaken to assess the impact of the COD volumetric loading rate and hence the HRT on system performance, the ratio of wastewater flow (COD applied) to mass of GAC replaced was maintained constant while both the wastewater flow and the GAC replacement rate varied accordingly. Consequently the SRT decreased while the loading increased continuously during Phase II which was started on day 365 by stepping up the COD loading rate by 25% while maintaining a GAC replacement rate of 75 g/wk. Observing no deterioration in performance, subsequent loadings were increased from 1.5 g COD/g GAC replaced at the end of Phase I to 1.85 g COD/g GAC replaced. However after day 581, the original COD mass loading of 1.48 g COD/g GAC replaced was adopted to avert some observed inhibition of methane production and maintain stable operation. This loading rate was continued until the termination of the study.

This phase was characterized by a sharp increase in effluent COD concentrations from all units as depicted in Fig. 4(a). The magnitudes of the increase varied from one reactor to the other with Reactor 1 showing the least and Reactor 3 the greatest increase. Effluent COD concentrations from Reactors 1 and 2 rose by over 100% of the highest levels of Phase I while Reactor 3 showed only a modest 45% increase due to its inability to sustain high COD volumetric loading rates. According to the kinetics of biological substrate removal by continuous cultures, the reduction in SRT associated with the increase of the GAC replacement rate compounded with decreasing HRT reduces removal efficiency, hence increasing the concentration of biodegradable organics persisting in the reactor effluent. However, the percentage COD conversion to methane illustrated in Fig. 4(b) clearly indicates that biological activity was not significantly impacted by the reduction in SRT. Thus, the observed increase in effluent COD is not solely attributable to a reduction in biological conversion and it appears that the increase in the liquid phase concentrations of adsorbable biodegradable compounds has resulted in the displacement of some less adsorbable nonbiodegradable organics from the reactors GAC as evidenced by the relatively higher effluent concentrations of cresols and dimethylphenols during Phase II (Tables 2–4).

3.2. *Treatability of full strength CGWW*

The most salient feature of the second phase of the study that can be inferred from Fig. 4 is the failure of the reactor treating the full strength CGWW at a COD volumetric loading of 9.5 kg COD/m³ d attested by a COD conversion to methane of only 36% and the continued operation of the two reactors treating the diluted wastewater at an average loading of 33 kg COD/m³ d. In fact Reactor 3 exhibited unstable operation at the 9.5 kg COD/m³ d loading and the COD conversion to methane varied from as low as 20% to about 52%. This suggests that at high loadings, dilution not only produces the best effluent but also provides operational stability.

Between days 490 and 504, at a time when the COD volumetric loading rate was 7 kg COD/m³ d, Reactor 3 was undergoing a period of poor performance indicated by a 40% COD conversion to methane and a significant increase in COD retention

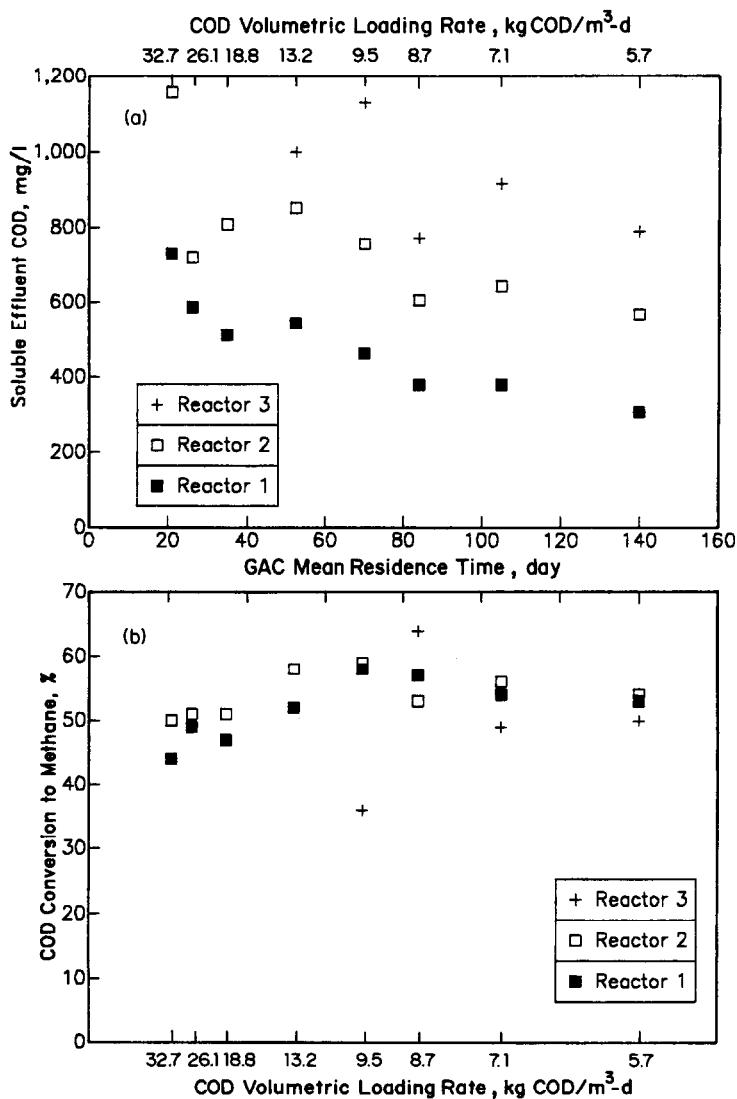


Fig. 4. Variation of effluent soluble COD (a) and COD conversion to methane (b) with GAC mean resident time and COD volumetric loading.

(Fig. 5(c)). During the period extending from day 518 to day 560 at a COD volumetric loading rate of 8 kg COD/m³d methane productivity increased sharply and COD conversion level soared to 64%. This conversion is much higher than the average conversion throughout its operation. This phenomenon, accompanied by a steady decrease of COD retained (Fig. 5(c)) suggests that biodegradable substances that have been previously retained during the preceding period of poor performance were

Table 2
Effluent phenolic compounds concentrations^a – Reactor 1

| Mass loading g COD/g GAC | Volumetric loading kg COD/m ³ d | Phenol | Cresols | | Dimethyl phenols | | |
|-----------------------------|---|--------|----------|--------------|------------------|------|------|
| | | | <i>o</i> | <i>m + p</i> | 2,4 | 3,5 | 3,4 |
| 0.585 | 4.9 | 0.010 | 0.19 | 0.01 | ND | ND | ND |
| 0.634 | 4.7 | ND | 0.14 | 0.01 | ND | ND | ND |
| 0.714 | 4.5 | 0.013 | 0.12 | 0.02 | ND | ND | ND |
| 0.912 | 4.8 | 0.005 | 0.15 | 0.02 | ND | ND | ND |
| 1.113 | 4.7 | 0.004 | 0.39 | 0.07 | ND | ND | ND |
| 1.484 | 4.7 | 0.072 | 2.30 | 0.57 | 1.62 | 1.34 | ND |
| 1.778 | 5.6 | 0.045 | 0.29 | 0.23 | 0.07 | 0.10 | ND |
| 1.698 | 7.1 | 0.089 | 6.11 | 0.61 | 0.96 | 1.37 | 1.27 |
| 1.673 | 8.8 | 0.062 | 0.03 | 0.05 | 0.08 | 0.31 | ND |
| 1.511 | 9.5 | 0.027 | 1.24 | 0.37 | 0.13 | 0.30 | ND |
| 1.560 | 13.1 | 0.315 | 0.32 | 0.08 | ND | ND | ND |
| 1.470 | 18.5 | 0.018 | 0.08 | 0.10 | ND | 0.11 | ND |
| 1.522 | 25.6 | 0.314 | 0.77 | 0.14 | ND | ND | ND |
| 1.506 | 31.6 | 0.039 | 0.03 | 0.02 | ND | ND | ND |

^a All concentrations are expressed as percent of the influent concentration.

Table 3
Effluent phenolic compounds concentrations^a – Reactor 2

| Mass loading g COD/g GAC repl. | Volumetric loading kg COD/m ³ d | Phenol | Cresols | | Dimethyl phenols | | |
|-----------------------------------|---|--------|----------|--------------|------------------|------|------|
| | | | <i>o</i> | <i>m + p</i> | 2,4 | 3,5 | 3,4 |
| 0.587 | 4.9 | 0.0001 | 0.13 | 0.03 | ND | ND | ND |
| 0.658 | 4.8 | 0.0001 | 0.10 | 0.03 | ND | ND | ND |
| 0.735 | 4.6 | 0.011 | 0.06 | 0.01 | ND | ND | ND |
| 0.899 | 4.7 | 0.010 | 0.13 | 0.01 | ND | ND | ND |
| 1.144 | 4.8 | 0.073 | 0.24 | 0.05 | ND | ND | ND |
| 1.482 | 4.7 | 0.088 | 1.14 | 0.48 | 0.22 | 0.20 | ND |
| 1.862 | 5.9 | 0.040 | 1.04 | 0.18 | 0.71 | 0.33 | 0.24 |
| 1.732 | 7.3 | 0.030 | 5.05 | 0.72 | 0.87 | 0.71 | 0.78 |
| 1.632 | 8.6 | 0.050 | 0.29 | 0.13 | 0.11 | 0.44 | ND |
| 1.461 | 9.2 | 0.020 | 0.46 | 0.40 | 0.46 | 0.49 | 0.31 |
| 1.580 | 13.3 | 0.020 | 1.44 | 0.23 | 0.33 | 0.28 | 0.57 |
| 1.520 | 19.1 | 0.190 | 4.66 | 1.25 | 1.14 | 1.34 | 0.61 |
| 1.585 | 26.6 | 0.010 | 0.72 | 0.09 | ND | ND | ND |
| 1.606 | 33.7 | 0.020 | 0.02 | 0.01 | ND | ND | ND |

^a All concentrations are expressed as percent of the influent concentration.

desorbing from the carbon and utilized by the microorganisms. However, failure of the biological system which is crucial to the continued successful treatment of toxic wastes by the fluidized-bed GAC reactor, resulted upon increasing the loading to 9.5 kg COD/m³ d on day 507 as reflected by the drop in COD conversion to methane

Table 4
Effluent phenolic compounds concentrations^a – Reactor 3

| Mass loading g COD/g GAC repl. | Volumetric loading kg COD/m ³ d | Phenol | Cresols | | Dimethyl phenols | | |
|-----------------------------------|---|--------|----------|--------------|------------------|------|------|
| | | | <i>o</i> | <i>m + p</i> | 2,4 | 3,5 | 3,4 |
| 0.572 | 4.8 | 0.016 | 0.19 | 0.11 | ND | ND | ND |
| 0.666 | 4.9 | 0.002 | 0.07 | 0.23 | ND | ND | ND |
| 0.742 | 4.7 | 0.002 | 0.08 | 0.01 | ND | ND | ND |
| 0.916 | 4.8 | 0.002 | 0.16 | 0.00 | ND | ND | ND |
| 1.144 | 4.8 | 0.007 | 0.11 | 0.09 | ND | ND | ND |
| 1.484 | 4.7 | 0.007 | 0.87 | 0.18 | 0.32 | 0.22 | 0.28 |
| 1.764 | 5.6 | 0.011 | 0.01 | 0.08 | 0.04 | 0.04 | ND |
| 1.647 | 6.9 | 0.389 | 3.82 | 0.59 | 1.37 | 0.95 | 0.61 |
| 1.628 | 8.6 | 0.006 | ND | ND | ND | ND | ND |
| 1.553 | 9.8 | 0.366 | 1.21 | 0.35 | 0.30 | 0.25 | 0.33 |

^a All concentrations are expressed as percent of the influent concentration.

to about 23% and then to only 17% on day 588 with the soluble effluent COD exceeding 3000 mg/l. Goeddertz et al. [8], *vide ut supra*, also observed that higher organic loading rates of phenolics were treatable with dilution with the organic loading increasing by almost threefold when the influent concentration was halved.

On the other hand, Reactors 1 and 2 continued to perform satisfactorily maintaining about 50% COD conversion to methane and (respectively) affecting 88% and 91% COD removal efficiency at the end of the study when a COD volumetric loading of 32–34 kg/m³ d corresponding to a loading of 0.071–0.076 g COD/g GAC/d was sustained. It is noteworthy that at this loading the HRT was only 4 h in Reactor 1 and 8 h in Reactor 2 and the SRT was 21 d. Similar findings have been reported for a high strength phenolic wastewater [8]. In that study, COD removals of 95% were achieved at loadings ranging in 0.01–0.06 g COD/g GAC at hydraulic detention times ranging from 9 to 112 h. Thus despite the toxicity of this wastewater, the GAC reactor operated with carbon replacement, appears to achieve comparable performance to the uninhibited AnBAC at 25% higher loading rates.

The relationship between the COD retained by the GAC in the three reactors calculated by a COD material balance around the unit is depicted as a function of operating time in Fig. 5. The COD retained is due to adsorbed compounds and attached biomass. However, since the bacterial yield in anaerobic systems is generally very low, most of the COD retained is in the form of adsorbed compounds. Fig. 5 shows that the COD retained decreased mildly at first and increased steadily thereafter to peak on day 413 before subsiding. The initial decrease in COD retention is due to the biodegradation of previously adsorbed compounds. This phenomenon of 'bioregeneration' is typical in such systems. Initially the population of microorganisms is insufficient to degrade the substrate while the carbon is still fresh. Thus the primary removal mechanism during start-up is adsorption. As operation continues, a healthy microbial population is established and the GAC adsorption capacity is partially

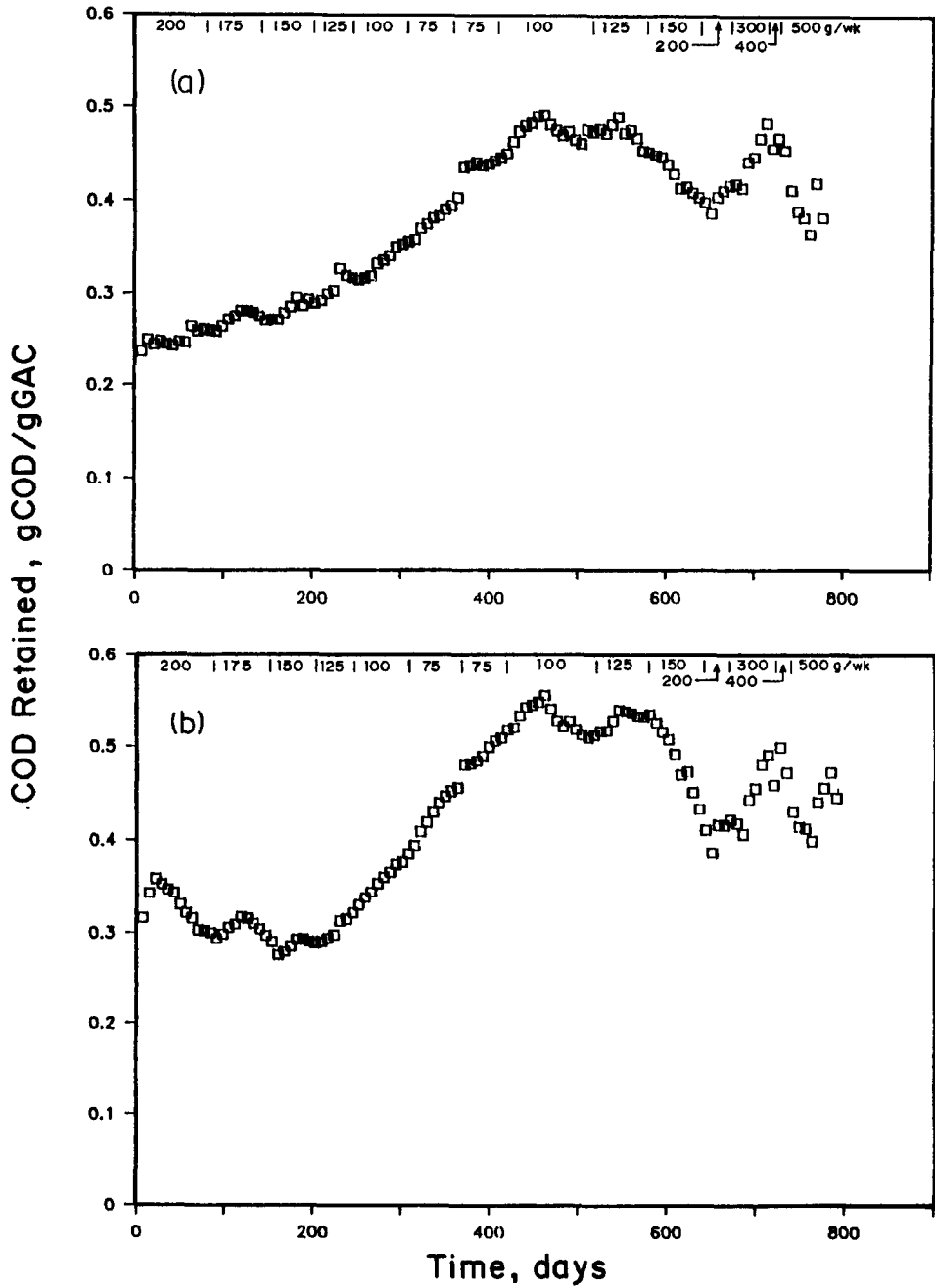


Fig. 5. Temporal variation of COD accumulation in (a) Reactor 1, (b) Reactor 2, and (c) Reactor 3.

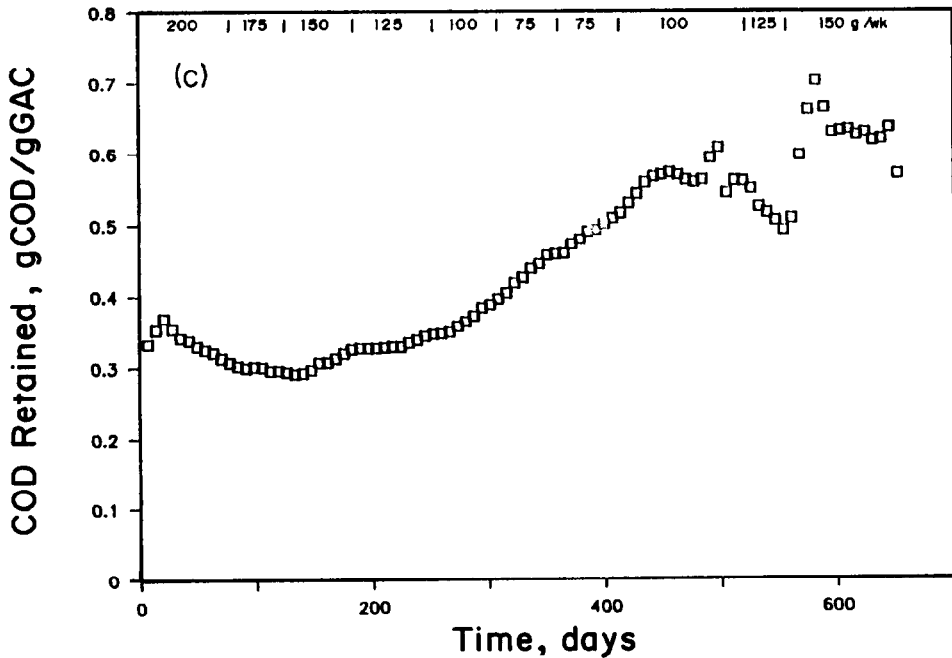


Fig. 5. Continued.

exhausted, the concentration of COD in solution is decreased by the active population of microorganisms and the previously adsorbed COD desorbs and is metabolized. For most of the second phase of the study, the COD retention decreased due to increasing GAC replacement rates. However, after day 690, as apparent from Fig. 5(a) and (b), the COD retention started to increase concurrently with the increase in effluent concentration of phenolics (Tables 2 and 3). The reduction in biological activity, albeit relatively small, compounded with the application of very high COD volumetric loading rates elevated the effluent phenolics concentrations, thus increasing the amounts of phenolics retained by the GAC.

It is conceivable that the failure of the reactor treating the full strength wastewater may be associated with the accumulation of toxins on the reactor GAC. The reactor first showed signs of stress at a COD loading rate of $7 \text{ kg COD/m}^3 \text{ d}$ and a COD accumulation of 0.62 g/g GAC . The reactor failed at a COD loading rate of $9.5 \text{ kg COD/m}^3 \text{ d}$ and a COD accumulation of 0.6 g/g GAC . However, after recovery (not discussed here) the reactor failed at a COD accumulation and loading rate of 0.42 g/g GAC and $10 \text{ kg COD/m}^3 \text{ d}$, respectively. It is therefore believed that failure was more closely related to the loading than to the accumulation and that a COD volumetric loading rate in the range of 9.5 to $10 \text{ kg COD/m}^3 \text{ d}$ clearly defines the limit of full strength treatability of CGWW by the fluidized-bed GAC reactor technology.

3.3. Removal of specific organics

The influent and effluent from the reactors were analyzed for phenol, cresols, and dimethylphenols. Tables 2–4 show the effluent phenolic compounds as a percentage of the influent for Reactors 1–3, respectively. During Phase I, the three reactors achieved better than 99.9% removal of phenol, over 99.5% removal of cresols and virtually complete removal of dimethylphenols. In the second phase, somewhat higher concentrations of all phenolic compounds particularly dimethyl phenols were detected in all effluents. Despite this increase, effluent phenol levels above 20 mg/l were detected in Reactor 3 only during periods of failure. Similarly *o*-cresol levels during failure were between 5 and 10% of the influent and therefore effluent concentrations of 11–22 mg/l reflected system stress during which effluent dimethyl phenols jumped to over 3 mg/l. The increase in the concentration of readily biodegradable phenolics such as phenol and *m*- and *p*-cresol during Phase II is obviated by the reduction in SRT associated with increasing volumetric loadings. But the jump in effluent concentrations of the more recalcitrant phenolics such as *o*-cresol and dimethyl phenols, despite maintaining the adsorptive capacity of the system as reflected by the steady COD mass loading is rather confounding. This drastic increase is explained however by the increased competition for adsorption sites from the biodegradable adsorbable constituents. The noteworthy finding of this study is that over 99% removal of all phenolics in the CGWW can be achieved by treating the diluted waste at COD volumetric loading rates as high as 34 kg COD/m³ d.

4. Summary and conclusions

Based on the findings of this study the following conclusions can be drawn:

- At a loading of 4.7 kg COD/m³ d and a GAC replacement rate of 0.58 g GAC/g COD applied dilution did not appear to offer any appreciable advantages, and all reactors achieved better than 94% COD removal, over 99.9% removal of phenol, 98–99% cresol removal and virtually complete removal of dimethyl phenols, while converting about 50% of the influent COD to methane gas.

- The full strength wastewater is not treatable by the GAC reactor at loadings in excess of 10 kg COD/m³ d. Dilute CGWW wastewater was inadversely treatable at a COD loading rate as high as 34 kg/m³ d and HRTs ranging between 4 and 8 h as reflected by COD removal efficiencies between 88 and 91%. Operation at this loading rate, resulted in a biological SRT of 21 days but the reactors continued to stabilize all the biodegradable waste constituents as reflected by a COD to methane conversion efficiency of about 50%. However, the effluent concentrations of the phenolic compounds generally increased with the increase in COD volumetric loading rates.

- The effluent soluble COD from the three reactors increased steadily in this study; the increase in the two phases was mostly accounted for by the breakthrough of toxic non biodegradable adsorbable compounds.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the Morgantown Energy Technology Center of the US Department of Energy in conducting the research reported herein, under Grant No. DE-AC21-80MC14713.

References

- [1] J. Ganczarczyk and D. Elion, Extended aeration of coke-plant effluents, in: Proc. 33rd Purdue Industrial Waste Conf., Purdue University, Indiana, 1978, pp. 895–902.
- [2] W.A. Sack and W.R. Bokey, Biological treatment of coal gasification wastewater, in: Proc. 33rd Purdue Industrial Waste Conf., Purdue University, Indiana, 1978, pp. 278–285.
- [3] D.D. Jones, Biological treatment of high strength coke-plant wastewater, in: Proc. 36th Purdue Industrial Waste Conf., Purdue University, Indiana, 1982, pp. 561–570.
- [4] R.G. Luthy, D.J. Sekel and J.T. Tallon, Biological treatment of synthetic fuel wastewater, *J. Environ. Eng., ASCE*, 106 (1980) 609–629.
- [5] T.P. Caire, D.F. Lawler and M.J. Humerick, Biological treatability of underground coal gasification wastewater, in: Proc. 38th Purdue Industrial Waste Conf., Purdue University, Indiana, 1984, pp. 519–526.
- [6] J. Janeczek and J.C. Lamb, Treatability of a coal gasification wastewater using the powdered activated carbon/activated sludge process, in: Proc. 37th Purdue Industrial Waste Conf., Purdue University, Indiana, 1983, pp. 497–505.
- [7] M.T. Suidan, C.E. Strubler, S.W. Kao and J.T. Pfeffer, Treatment of coal gasification wastewater with anaerobic filter technology, *J. Water Pollut. Control Fed.*, 55 (1983) 1263–1270.
- [8] J.G. Goeddertz, A.S. Weber and W. Ying, Startup and operation of an anaerobic biological activated carbon (AnBAC) process for treatment of a high strength multicomponent inhibitory wastewater, *Environ. Prog.*, 9 (1990) 110–117.
- [9] G.F. Nakhla, M.T. Suidan and J.T. Pfeffer, Operational control of an anaerobic GAC reactor treating hazardous wastes, *Water Sci. Technol.*, 21 (1989) 167–173.
- [10] M.T. Suidan, G.L. Siekerka, S.W. Kao and J.T. Pfeffer, Anaerobic filters for the treatment of coal gasification wastewater, *Bioengineering and Biotechnology*, 25 (1983) 1581–1596.