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APPLICATION OF A GRANULAR ACTIVATED CARBON–BIOLOGICAL FLUIDISED BED FOR THE TREATMENT OF LANDFILL LEACHATES CONTAINING HIGH CONCENTRATIONS OF AMMONIA

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ABSTRACT

The Envirex granular activated carbon biological fluidized bed (GAC-BFB) process was used to treat landfill leachate containing organic material with typical COD values in the range 800 to 2,700 mg/l, but with high concentrations of ammonia in the range 220 to 800 mg/l. Prior to treatment the leachate was softened by raising the pH to 9.0 using lime in order to remove any contaminating heavy metals. Two identical pilot-plant GAC-BFB's were used in series to treat the softened leachate. The first of these was intended to achieve carbonaceous removal whilst the second was used for ammonia removal by nitrification. During the first four months of operation at a loading rate of 1.56 kg ammonia-N/m^3 d, the reactors removed 70% of the ammonia, 60% of COD and achieved a complete removal of BOD. After optimising the reactor operating regime, it proved possible to achieve greater than 90% removal of ammonia at a loading rate of 0.71 kg N/m^3 d; however the COD removal remained unchanged. In order to compare the ammonia removal efficiency of the GAC-BFB system, two conventional activated sludge reactors were operated in parallel at hydraulic retention times of 24 and 36 hours (equivalent to ammonia loadings of 0.72 and 0.48 kg ammonia-N/m^3 d) and with a sludge age of 20 days. These reactors were not able to nitrify and although a BOD removal of 90% was achieved the COD removal was poor at 20%. Thus the GAC-BFB system offers a highly effective option for the biological removal of ammonia from high ammonia leachates, with the additional advantage of a good COD removal. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Biodegradation; biological nitrification; fluidized bed; granular activated carbon; high strength ammonia; landfill leachate.

INTRODUCTION

The leachates generated from landfill sites are highly contaminated with a wide range of chemical contaminants, and also show a characteristic change in their composition as they age. Leachates generated from recently emplaced wastes are termed young leachates and have high concentrations of organic compounds, a low pH value and high ammonia concentrations. This organic material is readily biodegradable and as the leachate ages its concentration reduces such that an older leachate has a relatively low, but non-biodegradable organic fraction with a high strength ammonia fraction. In addition leachates will also contain high concentrations of heavy metals, toxic organics, chlorides, sulphates and a high alkalinity (HMSO, 1995).

As a result of the high concentration of contaminants present in a leachate they represent a major environmental hazard if not properly treated prior to discharge to a watercourse. A wide range of treatment options have been utilised for treating a leachate with varying degrees of success. Whereas biological processes are able to remove the readily biodegradable organic fraction, less biodegradable material passes through untreated. In addition it is difficult to achieve biological nitrification due to the large amount of inhibitory material present in the leachate. By contrast physico-chemical treatment options are able to strip ammonia from a leachate but do not achieve a significant degree of organic removal (Fletcher and Ashbee, 1994).

The use of a GAC-BFB process combines both a physico-chemical mechanism with a biological one to offer the potential for both organic and ammonia removal within a single process. The granular activated carbon offers a medium which is able to both adsorb organic material and ammonia, as well as providing a surface to which microorganisms can attach and grow. Thus the organisms are in intimate contact with their substrate and this offers an ideal environment for enhanced biodegradation. As the adsorbed material is biodegraded it releases active sites on the carbon which allows further adsorption of substrate. Thus a steady-state is established of adsorption and biodegradation (Iwami *et al.*, 1992).

It was the aim of this study therefore, to evaluate and optimise the performance of a GAC-BFB system in treating an old leachate containing a large non-biodegradable organic fraction, together with a high concentration of ammonia.

MATERIALS AND METHODS

Reactor system. The GAC-BFB system used in this study was designed by Envirex Inc. and consisted of two fluidized bed reactors in series; the first intended for carbonaceous removal and the second for nitrification. Both reactors had the same dimensions of: active bed height, 1.2 m; diameter, 4 cm and an effective bed volume of: 1,500 cm^3. A schematic diagram of this apparatus is shown in Fig. 1.

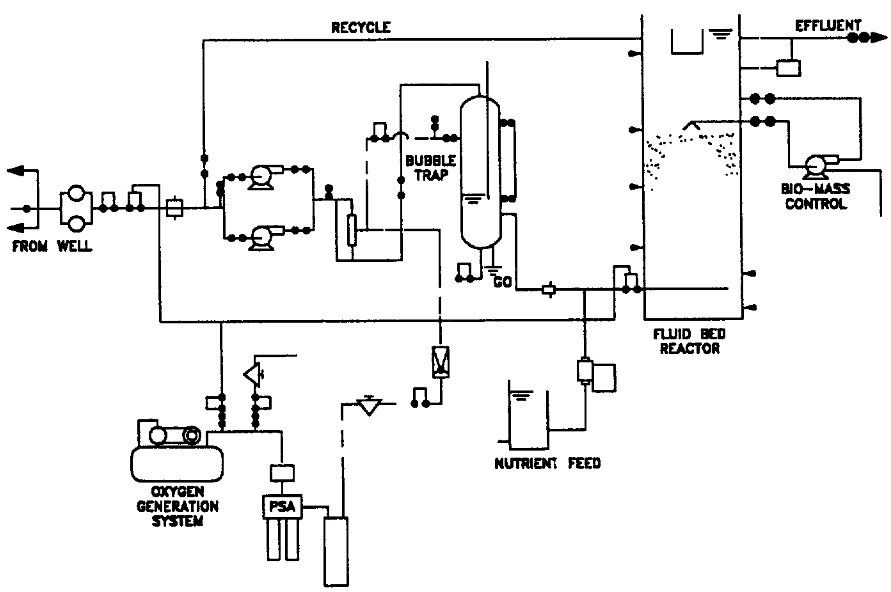

Figure 1. Schematic diagram of the Envirex GAC-BFB apparatus used in this study.

The leachate was softened prior to treatment by raising the pH of the raw leachate to around 9.0 by the addition of lime. It was then left for two hours to settle, and decanted from the lime sludge before being fed to the first reactor. This pre-treatment step was found to be very important in removing the toxic and heavy metals that could inhibit biological growth around the GAC. At this stage the leachate was also supplemented with phosphorus in the form of K_2HPO_4 at a final concentration of 2 mg P/l in order to maintain the nutrient balance necessary for biological treatment. The variations in leachate composition over the duration of this study are outlined in Table 1.

Table 1. The characteristics of the leachate used over the duration of this study

Determinand	**Raw Leachate**		**Lime Dosed Leachate**	
(mg/L)	**Range**	**Average**	**Range**	**Average**
COD	1,740 - 4,850	2,450	800 - 2,700	2,100
BOD	94 - 440	185	55 - 160	110
Ammonia-N	350 - 830	744	220 - 800	720
Alkalinity	3,648 - 4,705	4,275	1,682 - 4,275	2,805
Suspended solids	95 - 1850	380	54 - 180	113

The lime softened leachate was then fed to the reactor where it was combined with the highly oxygenated recycle flow from the flow buffer vessel. The combined influent and oxygenated recycle were pumped via a fluidization pump into the base of the reactor to maintain the desired fluidization; this was set at 0.74 l/min for both reactors. The effluent from the first reactor then acted as a feed to the second reactor

Two pilot-scale activated sludge reactors of volume 1.8 l were also operated on the same feedstock. These were assembled and operated as described in OECD (1972).

Experimental procedure. Approximately 500 g of granular activated carbon was added to each reactor and they were seeded with 4 l of return activated sludge from the Knostrop effluent treatment plant in Leeds. The two reactors were then operated at an almost constant room temperature of 20°C. Due to the high oxygen demand necessary for the biodegradation of the COD and ammonia, pure oxygen was utilised in order to achieve the required oxygen transfer. This was supplied to the reactors through an oxygen vessel which injected the oxygen to the oxygen dissolution loop, through a bubble contactor which saturates the recycled flow with oxygen. The effluent dissolved oxygen was always maintained above 5.0 mg/l to ensure that the system was not oxygen deficient.

The pH within the reactors was monitored daily and maintained within the range of 6.5 to 7.0 during the first few months of operation and then increased up to a value of 7.0 to 7.5. Alkalinity was measured regularly to ensure enough residual alkalinity for nitrification to proceed and also to provide a good buffering capacity against a pH drop. When necessary, soda ash or sodium bicarbonate was added to the second rig. All analyses were performed on composite samples of effluent for: BOD, COD, ammonia, nitrite, chloride, alkalinity, sulphate and suspended solids.

Analytical methods. COD tests were carried out using the closed reflux method after adding sulfamic acid to eliminate the interference of the nitrites. Ammonia was determined using the distillation method, and the sulphates were analysed spectrophotometrically. A Dionex was used to measure nitrites and nitrates after spiking the samples with a known concentration of standard solution to prevent the high chloride peak from interfering with the nitrite peak. However, chlorides were determined by titration. All tests were carried out as outlined in *Standard Methods for the Examination of Water and Wastewater, 19th Edition* and using the quality control procedures documented therein (APHA, 1995).

RESULTS AND DISCUSSION

After reactor start-up with fresh granular activated carbon and an activated sludge seed, the reactors were operated with a first-stage feed rate of 4 l/d, and a feed rate to the second stage of 3l/d. The pH in both reactors was maintained between 6.5 to 7.0 and over a 3 month period removal rates of 60% for the organic carbon and 70% for the ammonia were achieved across the two reactors. The presence of nitrate and nitrite in the effluent confirmed that removal of ammonia was by nitrification (Table 2).

Table 2. Performanceof the two-stage system during reactor start-up*

Determinand	Influent	Reactor 1	Reactor 2	Combined Removal (%)
COD (mg/L)	1970	1147	911	-
COD load (kg/m^{3}d)	-	5.22	2.3	-
COD removal (%)	-	42	21	54
Ammonia-N (mg/L)	590	257	179	-
Ammonia load (kg/m^3 d)	-	1.56	0.51	-
Ammonia removal (%)	-	56	28	70
Nitrate (mg/L)	0.00	483	513	-

* The results represent the average of 12 assays taken over a 70 day period when the reactor was operating at a steady-state

Despite the establishment of a population of nitrifying organisms in both reactors, there was no significant increase in the nitrification rate over time. The poor nitrification efficiency in the second stage reactor (28% removal compared to 55% removal in the first reactor) was a cause for concern as the intended role of this reactor was to achieve biological ammonia removal. It was thought that the poor nitrification may have been due to a combination of : i) a pH lower than the optimum for nitrification; ii) an excessively high ammonia loading rate; and, iii) a low organic carbon loading to the second stage which prevented growth of heterotrophic bacteria. These are thought necessary to provide suitable attachment sites for the nitrifying bacteria (Cheng and Chen, 1994).

In order to evaluate the above, a number of phased changes were made to the reactor operating conditions. Initially the direction of flow of the two reactors was changed, thus operating the second stage as a first stage and operating the first stage as a second stage, a regime analogous to that of alternate double filtration. The aim of this was to exploit the high heterotrophic biomass that had accumulated in the first reactor and which had demonstrated the ability to nitrify. Then the feed rate of the first stage was decreased from 4 l/d to 2 l/d, thus decreasing the ammonia loading rate from an average of 1.56 kg ammonia-N /m^3 d to an average of 0.71 kg ammonia-N./m^3 d. Finally the pH in both reactors was increased to operate in the range 7.0 to 7.5.

Table 3 Performance of the two-stage system after modification to the reactor operating conditions*

Determinand	Influent	Reactor 1	Reactor 2	Combined Removal (%)
COD (mg/L)	2116	1250	958	-
COD load (kg/m^{3}d)	-	2.82	1.66	-
COD removal (%)	-	40	22	55
Ammonia-N (mg/L)	535	153	37	-
Ammonia load (kg/m^3 d)	-	0.71	0.51	-
Ammonia removal (%)	-	69	73	93
Nitrate (mg/L)	0.00	346	575	-

* The results represent the average of 6 assays taken over a 22 day period when the reactor was operating at a steady-state

After a new steady-state was established, nitrification improved drastically with ammonia removal rates of 93% being achieved, which produced an effluent ammonia of 37 mg/l. However, the COD removal rate did not change significantly, remaining at about 55% and an effluent quality of 900 mg COD/l could not be bettered (Table 3). This suggests that this represents the non-biodegradable COD fraction of the leachate and to confirm this a number of samples taken from reactor 2 were analysed for BOD; in all cases their BOD was <2 mg/l.

The alkalinity requirements for nitrification in the GAC-BFB reactor were very low with an average of 1.5 mg bicarbonate alkalinity/L required to remove 1 mg ammonia-N/lGenerally an alkalinity requirement of between 6 to 7.2 mg/l is necessary (Barnes and Bliss, 1983) and the low requirement in the GAC-BFB system may indicate that some denitrification is occurring with a concommitant claw back of alalinity. Nitrogen mass-balances have not yet been performed around the reactor and so this cannot be confirmed.

In order to calculate the amount of biodegradation occuring in the GAC-BFB reactor a mass-balance was constructed around the reactor based on the assumption that soluble COD is removed either by biodegradation or by adsorption to the carbon surface. With the latter mechanism desorption of the adsorbed carbon renders some of it particulate and this leaves the process as suspended solids. The soluble, desorbed COD is picked up during analysis of the reactor soluble COD. The average COD in the filtered effluent from the first reactor was 1,200 mg/l whilst the COD of the unfiltered sample was 1,500 mg/l, thus 300 mg/l of COD was present as particulate material. With an average influent COD of 3,800 mg/l the effluent soluble and particulate COD accounted for 30% and 7% of the total. The remaining 63% was completely lost from the system and this represents the COD removal by biodegradation.

The two activated sludge units were operated in parallel for a period of 60 days treating an identical, lime-softened leachate to that treated in the GAC-BFB unit. These reactors reached steady-state after 20 days and achieved a consistent removal efficiency from then on. They demonstrated a good BOD removal but this was not mirrored by the COD removal efficiency, which was low at 20%. This confirms the observation that much of the organic material in the leachate is very recalcitrant, but also demonstrates that the GAC-BFB system is removing a lot of this recalcitrant material. At no point during operation of the activated sludge units was nitrification observed (Table 4), despite close control of the reactor pH and dissolved oxygen. With a temperature of 20°C, adequate alkalinity and a sludge age of >20 days, full nitrification could be expected and thus it seems likely that the leachate contained inhibitory material.

Table 4. Performance of the activated sludge plants treating lime softened leachate

Parameter	Reactor 1	Reactor 2
Hydraulic retention time (h)	36	24
BOD Removal (%)	84	81
Effluent BOD (mg/L)	17	20
COD Removal (%)	20	17
Effluent COD (mg/L)	1626	1687
Effluent Nitrate (mg N/L)	0.5	2.3
Effluent Nitrite (mg-N/L)	0.9	2.4

The GAC-BFB reactor demonstrated a low removal efficiency for suspended solids and an equilibrium is reached between the suspended solids entering the reactor and those leaving (Figure 2). Thus where suspended solids are an important consented parameter it is necessary to provide additional solids removal, and this can best be achieved by use of a sand filter. Current research in these laboratories is centred on varying the operating regime of the system to introduce a backwash phase, in a similar manner to a BAF system. This will allow solids to be removed from the media in a much reduced volume, thus they can be recirculated to the head of the plant for removal in the lime dosing system.

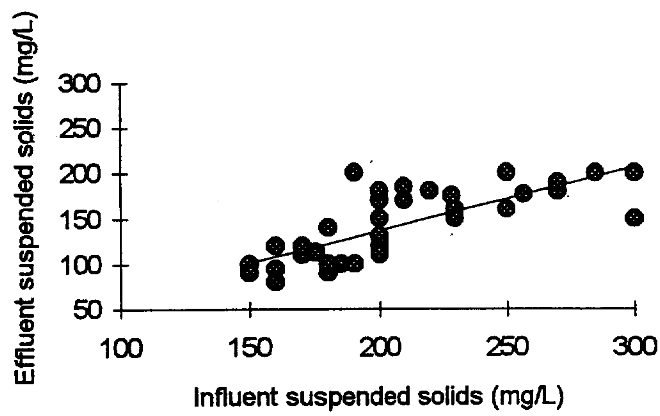

Figure 2. The steady-state established between influent and effluent solids concentration.

CONCLUSIONS

The GAC-BFB reactor system has proved to be a very effective process for the removal of high concentrations of ammonia from a difficult waste which proved inhibitory to nitrification in a conventional activated sludge process.

It was also able to completely remove all the biodegradable organic material from this waste, together with a large fraction of the recalcitrant COD.

When a conventional activated sludge process was operated at similar ammonia loading rates this was not able to nitrify and demonstrated a much reduced COD removal efficiency. The activated sludge process still did not demonstrate nitrification even at much reduced ammonia loadings and thus the GFC-BFB process should find many applications for ammonia removal from wastewaters which are difficult to nitrify.

Solids removal was not achieved in the GFC-BFB system and therefore additional solids removal facilities will be required with this process. However this can be achieved easily by means of a conventional sand filter system.

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