International Journal of Engineering and Technology, Vol. 7, No.1, 2010, pp. 12-20

BIOFILMS IN WATER AND WASTEWATER TREATMENTS

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ABSTRACT

Biofilm reactors are increasingly used to treat industrial effluents with difficult components, this type of process has been applied to wastewaters containing various types of pollutants, such as those containing chlorinated organics. These have not been effectively removed by conventional activated sludge types of processes due to their recalcitrance. Biofilm reactors have biomass active even at very low concentrations of the target organics, rendering the reactor more efficient for removing trace toxic compounds in wastewaters. Biofilm processes, having high biomass concentrations, have also been found to be less sensitive to the presence of toxic and inhibitory materials, and more resistant to shock loadings than the dispersed growth systems. Such characteristics are essential where floor space is becoming expensive and yet there is great need to treat and polish effluents before reuse. With increasing pollution of rivers by trace industrial and household chemicals and pharmaceuticals, and greater demands for water, the difference between effluent polishing and water treatment is diminishing. With increasing knowledge of health effects of trace pollutants, a more effective yet affordable water treatment system than the conventional system has to be investigated. The conventional water treatment system of coagulation, settling and filtration, removes mainly suspended solids; trace and recalcitrant organics would pass through the system. Greater use of groundwater and stricter drinking water limits, such as the new EU Drinking Water Directive (EU DWD), has established the use of biofilm processes in water treatment, such as in northern Italy. Results of on-going research on use of biofilm processes for water and wastewater treatment are reported here. These are uses of biofilm columns for river water treatment and rainwater polishing, and use of biofilm columns for removal of chloroorganics and heavy metals. In all these studies the biofilm columns have been found very effective for treatment of river waters for removal of organics and nutrients, and treatment of wastewaters, for removal of chloroorganics and heavy metals. Metabolite analysis indicated biodegradation of PCP reductive dechlorination had occurred in the reactor, showing that biofilms offered both oxidative and reductive conditions. Besides these special characteristics, no chemicals were employed in both water and wastewater biofilm treatments. Thus no chemical sludge was generated, besides lowering treatment costs due to chemicals. Biofilm processes as used here have potential to be further developed into cheaper, environmentally friendlier processes for treating water and wastewaters containing organics and heavy metals.

INTRODUCTION

Biofilm processes were initially employed for wastewater treatment about a decade ago, i.e. it is a much more recent process than the activated sludge type of process. Those employed for industrial wastewater treatment comprise various reactor configurations, such as fixed bed, moving bed, fluidised bed, recycled bed and upflow anaerobic sludge blanket. These processes operate at relatively short hydraulic retention times (HRT) (often less than 20 hours) and high organic loadings, thus reducing reactor size, floor area requirement (foot print) and capital costs. Important features of these processes which make them cost effective for industrial wastewater treatment are: low operating and maintenance costs, low excess sludge production and odourless operation.

With increasing knowledge of health effects of trace pollutants, a more effective yet affordable water treatment system than the conventional system has to be investigated. The conventional water treatment system of coagulation, settling and filtration, removes mainly suspended solids; trace and recalcitrant organics would mostly pass through the system. Greater use of groundwater and stricter drinking water limits, such as the new EU Drinking Water Directive (EU DWD or the 98/93/EC), have established the use of biofilm processes in large scale water treatment plants, such as in northern Italy (Sorlini et al, 2007). Research work on use of biofilm reactors for water treatment has started increasing only very recently, partly driven by increasing levels of recalcitrant organics in river waters as urbanization stretches to previously rural areas used as river catchments. Recently discovered dangers of micropollutants, such as those with oestrogenic effects, has brought biofilm water treatment processes to the fore as a possible means of removing these trace micropollutants. As previously mentioned biofilm processes are advantageous in that the biomass is active even at very low concentrations of target organic chemicals. In Europe, the recently introduced new EU Drinking Water

Directive (EU DWD or the 98/93/EC) with very low allowable limits of heavy metals, etc, has driven the use of biofilm water treatment units in order to meet the directive. With the above capabilities of biofilms in view, researches on use of biofilms for wastewater and water treatments in Universiti Kebangsaan Malaysia (UKM) have been on-going since the late 1990s. Some results of those studies are reported here.

Biofilm Formation

Initial microbial attachment invariably occurs in the crevices of support media where attached biomass is protected from fluid shear. A variety of media have been employed for biofilm support such as sand, granular activated carbon (GAC) and plastic media of various shapes. Granular media has very high specific surface area reaching 1000-1500 m_2/m_3. GAC is a good bacterial immobilization matrix as it is very adsorptive and has a very high surface-to-volume ratio, due to its large number of internal pores and rough surface textures (Weber *et al.*, 1979; Christiansen and Characklis, 1990). The biofilm process involving GAC is characterised by a combination of physical and biological removal mechanisms that is adsorption onto GAC and biological degradation by microorganisms grown on GAC. The use of small porous fluidised media enables the reactor to retain a high biomass concentration and thereby to operate at a significantly reduced HRT, so that a required degree of treatment can be achieved in a much smaller reactor volume. Alves et al (2002) discovered that the surface characteristics of the support (porosity, roughness and electrical charge) are very important in the early stages of biofilm formation. Surface characteristics, such as unit surface area, porosity and, especially, surface roughness, have been found to influence biofilm formation and concentration. However, during continuous operation, the performance and stability of the reactor depends on the structure of biofilm formed around the support. Hence, parameters such as biofilm thickness, biofilm density and shape and the overall density of the particles covered with biofilm should be controlled to obtain a stable reactor operation (Alves et al 2002).The support media eventually becomes covered with biofilm and the high surface areas afforded by the media results in a biomass concentration approximately an order of magnitude greater than that maintained in a suspended growth system (Sokol, 2001), with the biofilm structure strongly influenced by the substrate concentration (Wimpenny and Colasanti, 1997).

Biofilm Processes

Biofilm processes have also been studied for effluent polishing (Abd.Rahman et al, 2005), effluent polishing performance was enhanced when the bed media was an adsorbent, such as activated carbon. Both adsorption and biodegradation came into play, and recalcitrant organics were retained for longer time via adsorption before biodegradation occured. Biofilms with sufficient thickness, offer both aerobic and anoxic reaction states, thereby enhancing biodegradation possibilities. Simultaneous adsorption and biodegradation by microorganism attached onto GAC have also been found effective for advanced drinking water treatment (Woo *et al.*, 1997). Biofilm reactors have biomass active even at very low concentrations of the target organics, rendering the reactor more efficient for removing trace toxic compounds in wastewaters. Biofilm processes, having high biomass concentrations, have also been found to be less sensitive to the presence of toxic and inhibitory materials, and more resistant to shock loadings than the dispersed growth systems. Such characteristics are essential where floor space is becoming expensive and yet there is great need to treat and polish effluents before reuse (Abd.Rahman et al, 2003). With increasing pollution of rivers by trace industrial and household chemicals and pharmaceuticals, and greater demands for water, the difference between effluent polishing and water treatment is diminishing. Biofilm processes can be designed to handle both waters and wastewaters.

METHODOLOGY

In studies on biofilm water treatment processes for river water treatment and rainwater polishing, biofilter columns were applied. River water biofilm treatment was carried out using a water treatment pilot plant located by the Langat River, which runs beside the UKM campus. This is one of the major rivers of Malaysia, with a large basin draining several townships with large housing areas, commercial centres and industrial estates (Cheras, Sri Kembangan, Kajang, etc), and it is a source of potable water for the region. During extended dry periods, closure of any of its water treatment plants, usually due to elevated levels of ammonia, leads to hardships and significant income losses due to factory closures (Abdul-Rahman, 1999). In the study, raw water from Langat River was pretreated using a rapid sand filter before being fed into the biofilter column in upflow mode. Several flowrates were studied over several years, giving HRTs ranging from 4 to 16 hours. In the application of biofilm for rainwater polishing, rainwater was treated via an upflow biofilm column before being polished in a down-flow sand bed, simulating a slow sandfilter. The study, which ran for about two years, was carried out using a pilot unit located in a housing area in Bangi, Selangor, Malaysia. Rainwater from roofs may be contaminated by organics from bird droppings, leaves, airborne pollutants such as sulphur and nitrogen based acidic pollutants, suspended solids from dusts and smokes, coarse solids from leaves, etc, and heavy metals from dusts and rusts. To remove coarse solids, roof runoff water in this study was passed through a coarse screen before going into a storage tank located on ground level. From the storage tank rainwater was continuously fed into the biofilm column reactor.

A biofilm activated carbon column reactor (BACCOR) was used to treat wastewater containing pentachlorophenol (PCP-Na) at various HRTs or empty bed contact time (EBCT) with studies of metabolites to investigate possible biodegradation of PCP by the biofilm developed on the GAC. The BACCOR column was made of Plexi-Glass (1m long, 5.5 cm internal diameter), packed with 60 cm height of coconut-shell based GAC (at about 360g/L). The BACCOR was operated at EBCTs ranging from 0.75 – 2 hrs and PCP concentrations ranging from 10 – 100 mg/L.

Sample Analysis

For all analysis of dissolved constituents, water samples were filtered through 0.45 μm membrane filter before being analysed for nitrogen nutrients using a Hach spectrophotometer, and for COD using the Hach COD reactor followed by the Hach spectrophotometer. Suspended solids (SS) concentrations were measured gravimetrically or by using the Hach spectrophotometer. For biomass concentration analysis, the amount of attached biomass on biofilm media was measured via the sodium hydroxide solubilisation method (Koch et al., 1991). Metal concentrations were analyzed using Atomic Absorption Spectroscopy (AAS).

For the wastewater treatment, samples were taken at inlet and outlet of BACCOR at least once a week, and analysed for PCP-Na using the 4-aminoantipyrene method. Extraction of chlorophenol from the GAC medium and BACCOR effluent was carried out as described hereafter. GAC of 8 g(wet weight) obtained from sampling port of reactor on 435th day of the experiment and dried at room temperature. It was then placed into Soxhlet extractor and 300 mL of dichloromethane was added. Extraction was continued for 6 hours at 50°C and cycle rate of 10 times/h. Then the dichloromethane phase was collected and concentrated to 100 mL by distillation at 50°C. Liquid-liquid extraction was used for extraction of chlorophenol from the effluent of BACCOR. The sample was filtred and 500 mL of filtrate was poured into a separation funnel of 1 L volume. pH was adjusted to 2 with HCl. 50 mL of dichloromethane was added and shaken for 15 minutes. The dichloromethane phase was collected. The dichloromethane phase extracts were then analysed using mass spectrometer after dehydration with anhydrous sodium sulphate. The temperature condition was 30-350°C and the temperature gradient was150°C/min.

RESULTS AND DISCUSSIONS

In the biofilm river water study, the biofilm column was able to run without experiencing clogging, even though it was run without backwashing during the entire study period of about two years. It can be assumed that the rapid sand prefilter had acted as the coagulation-flocculation stage in a conventional water treatment plant (WTP),but without any chemical requirement. The expanded bed biofilm process was able to maintain a steady bed condition with biomass concentrations at 3,000 to 5,000 mg/L without requiring backwashing. Water quality results obtained are shown in **Fig. 1** to **Fig. 4**. Notable points of the results are that even at HRT of only 4 hours, the biofilm column was still able to lower the NH_3-N content by over 80%, to NH_3-N values of almost zero even when the inlet values were about 3 mg/L. Elevated values of NH_3-N were encountered in the Langat river water due to discharges from sewage treatment plants, agricultural areas and industries. This is very significant considering that elevated values NH_3-N in this river had caused WTPs on it to be closed on several occasions to avoid problems associated with chloroamines, causing hardship to consumers and large economic losses to industries. The biofilm reactor was also able to significantly lower the COD values; this is also an important result as presence of dissolved organics could lead to formation of chloroorganics during chlorination at water treatment plants (WTPs) downstream, as well as bacterial growths in the distribution system, resulting in many consequences, ranging from post treatment contamination, increased corrosion, more rapid loss of residual chlorine, and so on.

In the second study, on biofilm polishing of rainwater, the multimedia biofilter was operated for about two years. The results as shown in **Fig. 5** to **Fig. 7** demonstrate that removal of the most critical pollutants in rainwater, iron (Fe^{2+}) due to rusts, sulphate due to acidic sulphurous gases, and N-nutrients due to bird droppings, can be maintained for extensive periods without replenishment of the carbon media. The biofilm column in this study was able to remove up to 76% of Fe^{2+}, giving an average concentration in the treated water of 0.01 mg/L or 10 ug/L, which satisfies even the requirement of the new drinking water directive. Metals removed accumulate in the biofilm layer. Microbial metal accumulation has received much attention in recent years, due to the potential use of microorganisms for treatment of metal polluted water or wastewater streams (Zouboulis et al., 2004). Several studies have shown biological processes as having potential for heavy metal removal (Bux et al., 1994). In a biofilm processes, dissolved organic materials and nutrients are directly absorbed from bulk phase into biofilms by means of concentration gradient, whereas dissolved heavy metals are generally adsorbed onto biofilm surfaces as a result of interactions between metal ions and the negatively charged microbial surfaces, gradually reducing the aqueous metal concentrations (Jang et al., 2001). In an expanded bed reactor, the interaction between biofilm and heavy metals results in adsorption of heavy metals onto biofilms, and gradually reducing the aqueous metal concentrations.

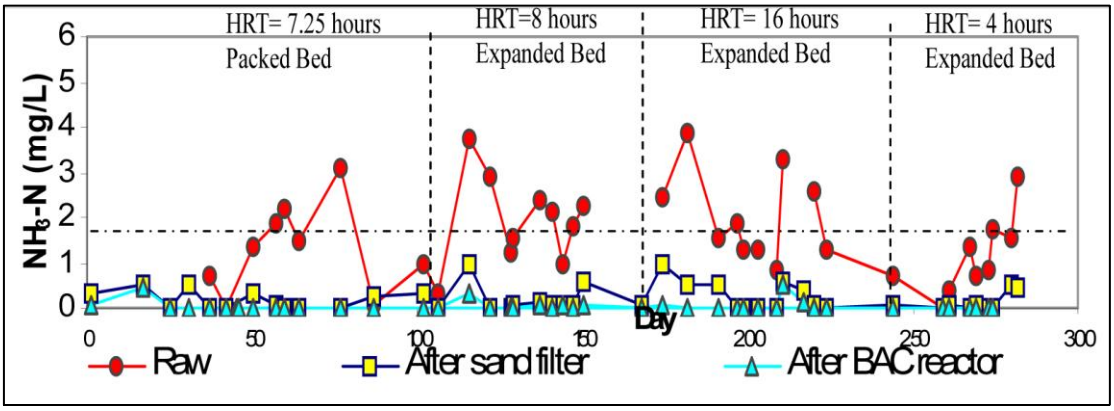

Fig. 1: River water treatment: NH3-N in raw water, after sand filter and BAC biofilm column

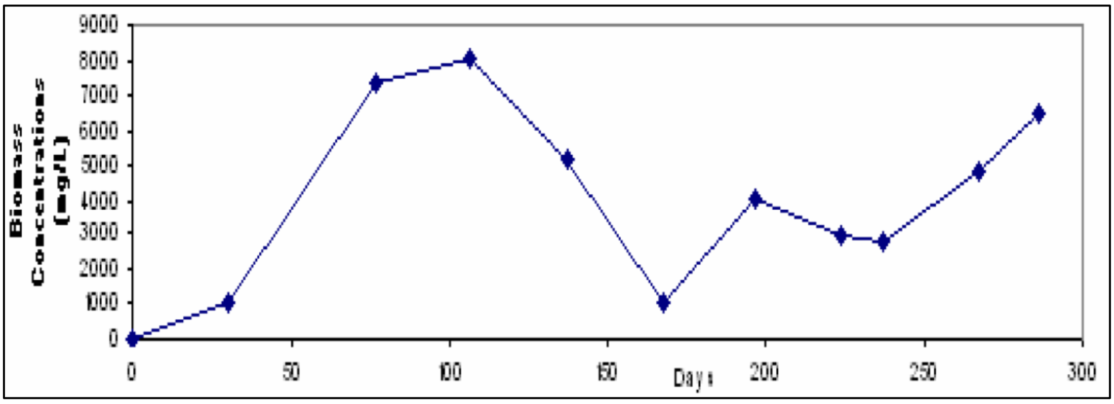

Fig. 2: River water treatment: Biomass concentrations in biofilm reactor

Fig. 3: River water treatment: COD in raw water, after sand filter and biofilm column

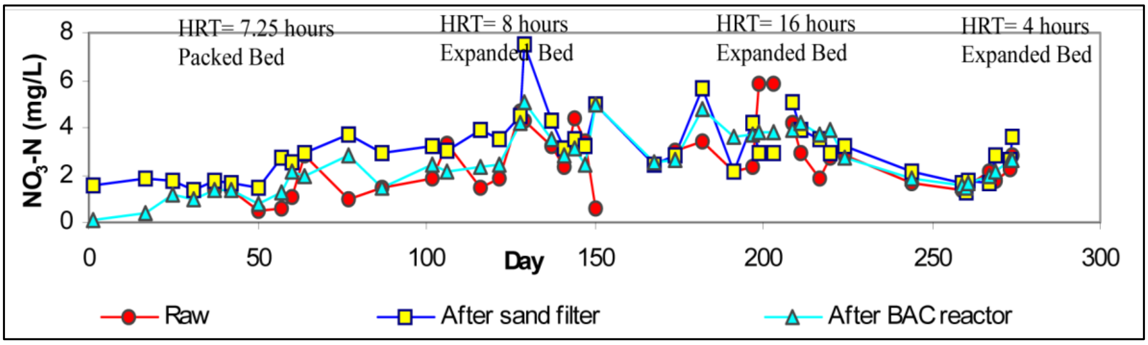

Fig. 4: River water treatment: NO_3-N in raw water, after sand filter and biofilm column

Monitoring carried out during this study gave the average COD in rainwater in the study area at about 7.3 mg/L; the biofilm polishing unit lowered the COD to an average COD concentration of 2.6 mg/L. Overall the COD reduction is in the range of 37 to 93% (Fig. 5). The average concentration of SO_4^{2-} in the treated water is 0.8 mg/L, after removal of 15 - 59% (Fig. 6). The figure also shows steady removal of ammonium nitrogen, giving an average concentration of ammonia (NH_4^+) in treated water at 0.02 mg/L. Percentage reduction of NH_4^+ was 17 - 45%, while that for Nitrate (NO_3^-) was 49 - 83% (Fig. 7). Such good removal of nitrate is desirable as in rainwater most nitrogen nutrients would be in the oxidised nitrate form, as shown by Fig. 6 and Fig 7**.**

PCP-Na removal by BACCOR during the study is shown in Figure 8. The phenols in effluent were found below 0.8 mg/L and average 95% removal rate was achieved at 2 hours EBCT. In Run 2 where the EBCT was 4 hours, the PCP-Na concentration was increased to 50mg/L, the effluent PCP was still maintained at below 1 mg/L. An average of more than 97.6% removal had been achieved at 4 hours EBCT. In Run 3, where the EBCT was reduced to 45 minutes, average 96.2% of removal was achieved which is only slightly lower than that for 4 hours EBCT. In run 4, the EBCT was increased back to 2 hours, the removal rate was 96.8%. In Run 5, where the PCP was spiked into river water, the phenols in effluent were still maintained at under 0.9 mg/L , regardless of the complexity of the river water. Average removal was 93.4% with 2 hours EBCT. In run 6, the EBCT was reduced to 1 hour, 94% of removal was achieved which is even better than in Run 5.

Figure 9 shows the biomass as MLSS in the reactor changing with operating time. The highest biomass measured was 9,400 mg/L; however this high biomass concentration was causing blockage to the reactor and backwash was needed. Backwash was conducted at an average of once every six weeks. The biomass concentration was maintained at 2000 to 7000 mg/L throughout this study.

Chromatograms obtained by MS analysis of extracts from the GAC medium and effluents are shown in Figure 10. PCP (MW=266), Tetrachlorophenol (TeCP, MW=232), and chlorophenol (CP, MW=128) were clearly detected in extract of the GAC medium in the reactor. PCP amount was higher compared with other chlorophenols in extract of the GAC medium indicates that lower chlorinated phenols are more easily degraded by microorganisms grown on the GAC medium. Traces of TeCP and CP were detected in extracts of effluent of the reactor. These indicate that reductive dechlorination of PCP occurred in GAC in the reactor and dechlorinated phenols were adsorbed to the GAC.

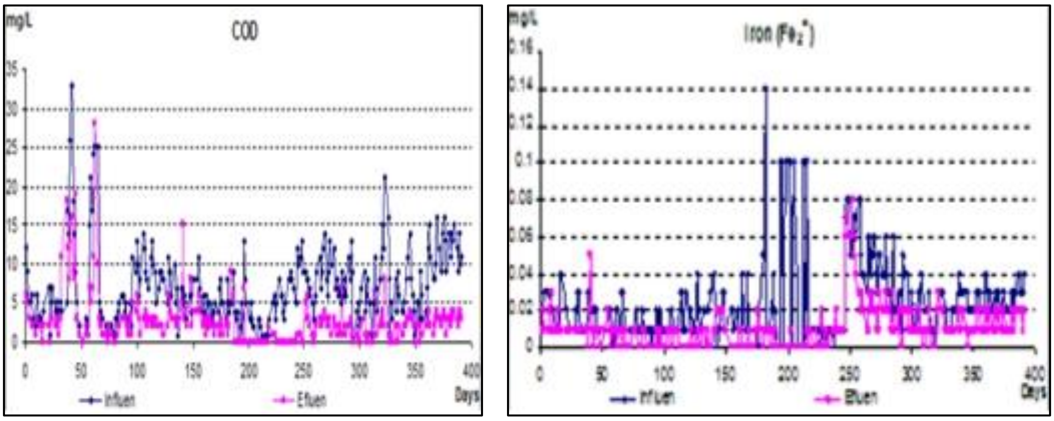

Figure 5: COD and Iron Fe^{2+} concentrations at inlet and outlet of biofilm polishing column

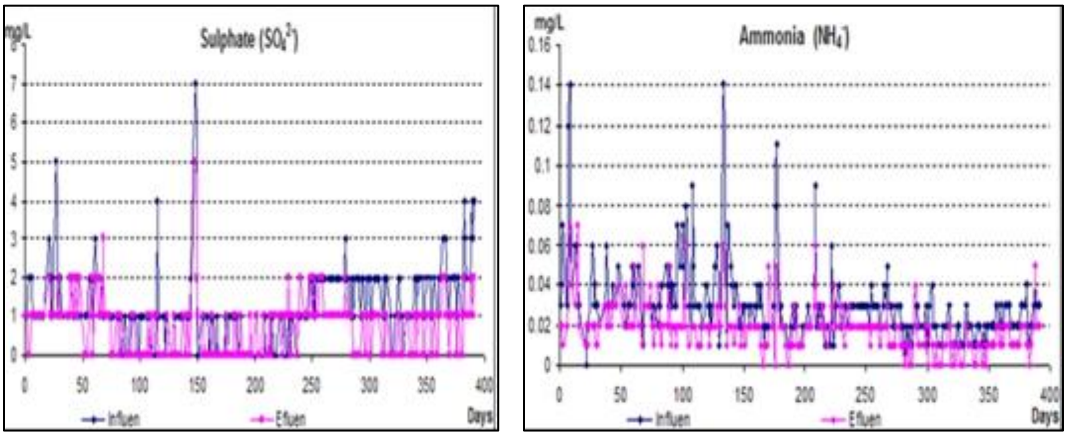

Figure 6: Sulphate and NH4+ concentrations at inlet and outlet of biofilm polishing column

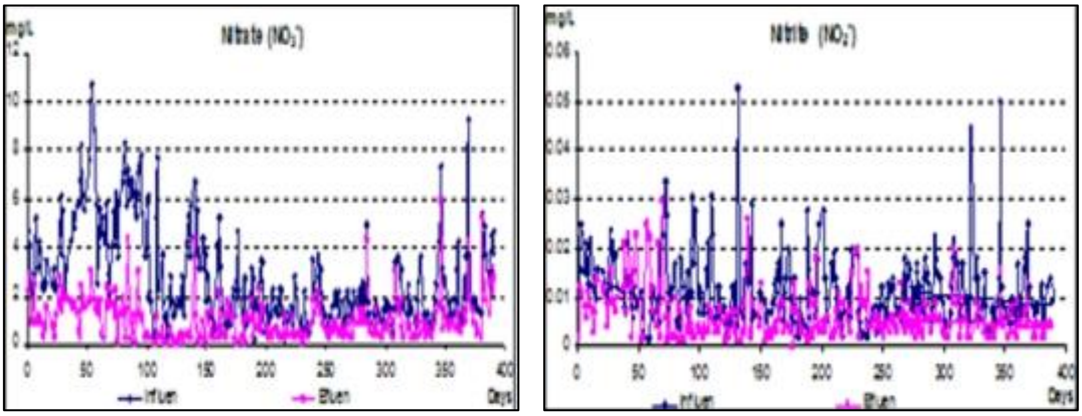

Figure 7: Nitrate and Nitrite concentrations at inlet and outlet of biofilm polishing column

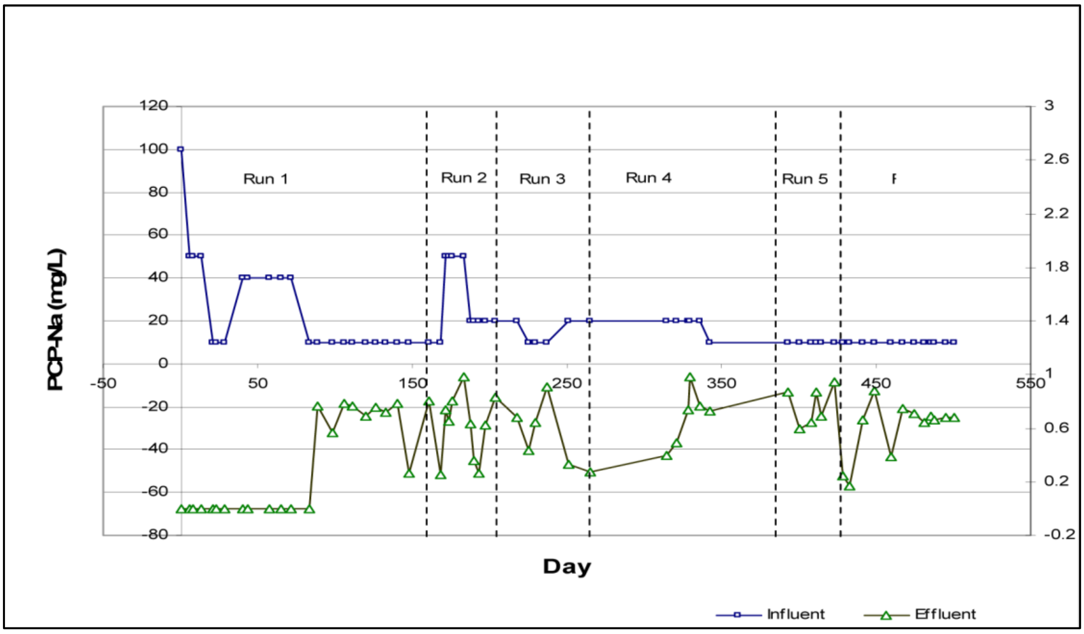

Figure 8: Performance of BACCOR at different residence times

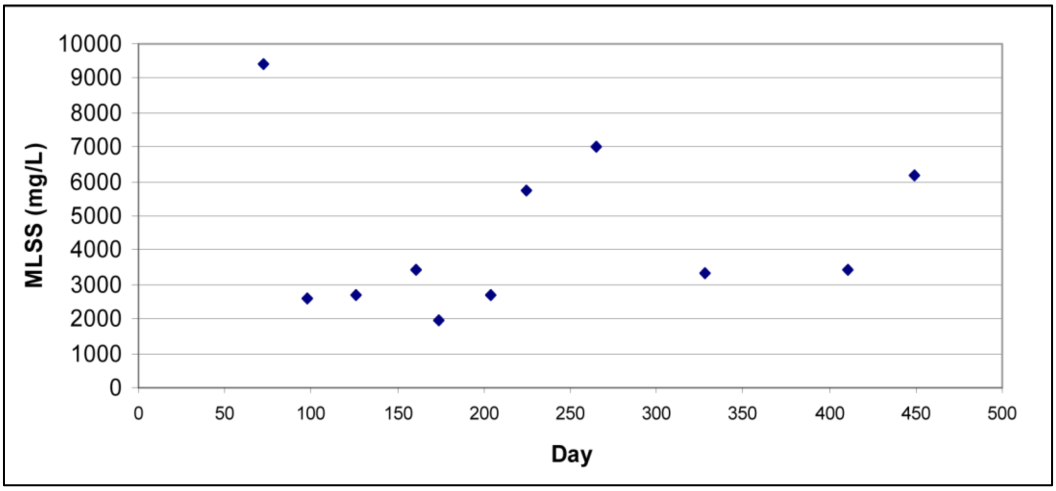

Figure 9: Biomass concentration in the biofilm reactor used for wastewater treatment

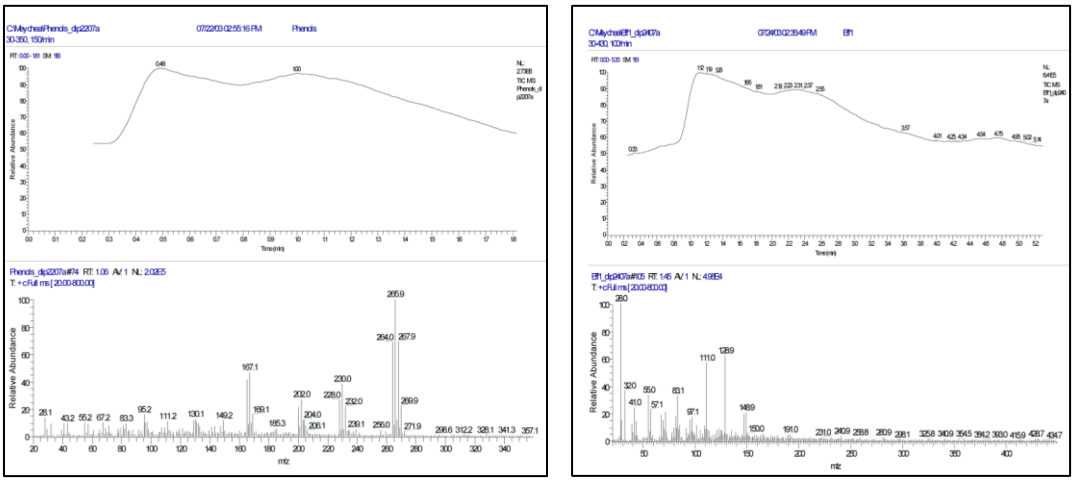

Figure 10: MS analysis chromatograms of extracts of GAC medium in the reactor, followed by extract of effluent from the reactor

Results on biofilm removal of Zinc in Figure 11 shows that removal ranges at about 60-95%. Besides that, this study also shows good COD removal, ranging at about 87-90% (Figure 12). Metal uptake by biofilm gradually increased with time and biomass growth (Figure 13). Figure 14 shows zinc loaded in biomass. Table 1 below compares biofilm zinc removal with those by other processes showing that even at high inlet concentration; removal by biofilm may reach up to 95%.

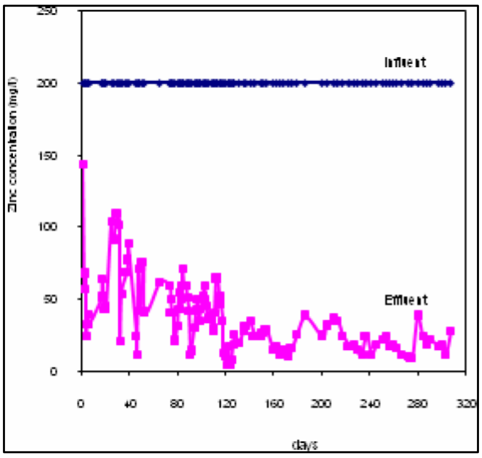

Figure 11: Zinc Concentration in Influent and Effluent

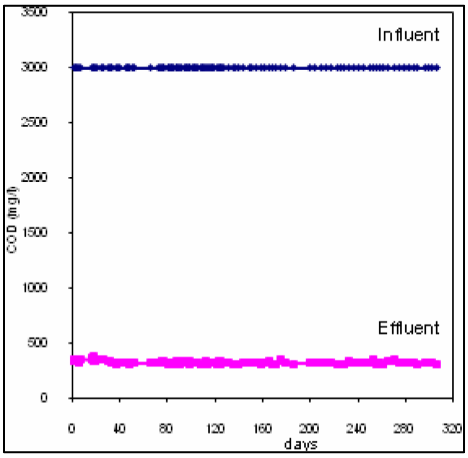

Figure 12: COD Concentration in Influent and Effluent

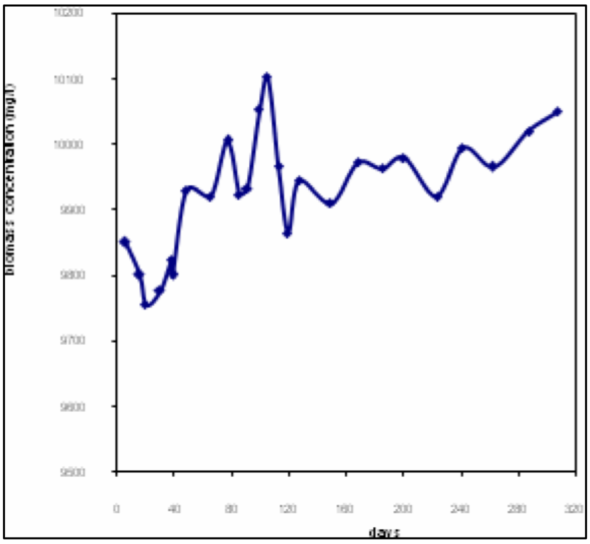

Figure 13: Biomass Concentration vs. Days

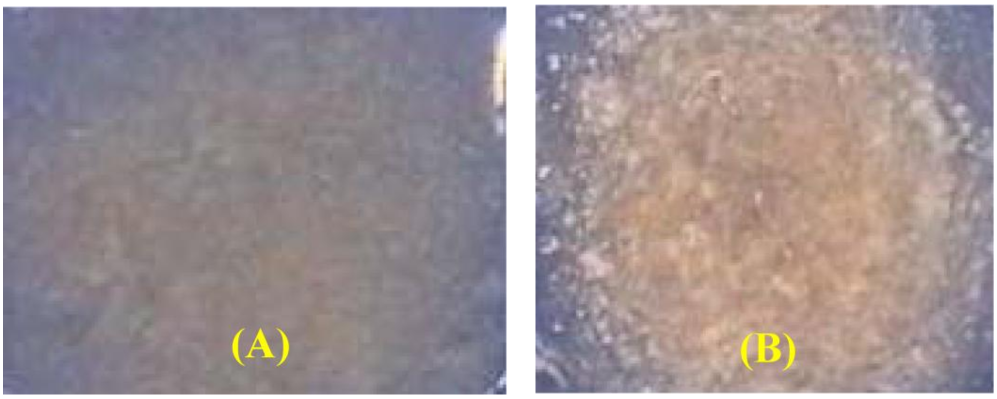

Figure 14: Biomass before metal absorption (A), and (B) Biomass after heavy metal absorption and precipitation

Table 1: Comparison of Zinc Removal by Biofilm and Other Processes

Study	Process	Zn in influent	Zn removal
This study	Expanded bed biofilm reactor	200 mg/l	60-95%
Bakkaloglu et al. 1998	Biosorption on biomass	41-45 mg/l	40-57%
Chu et al. 1998	Tide-tank system simulating mangrove wetland	1-25 mg/l	90-87%
Charerntanyarak 1999	Chemical lime coagulation and precipitation	450 mg/l	99%
Costley and Wallis 2001	Rotating biological Contactor (RBC)	n.a.	49-58%
Veeken & Hamelers 1999	Extraction with organic acids	n.a.	90-100%
Zhou et al. 1999	Fluidised bed	10-20 mg/l	92-95%

CONCLUSIONS

Studies using two biofilm pilot water treatment plants, each with a biofilter column as the main treatment unit, without addition of any chemicals, carried out using river water and rain water respectively have been found very effective for removal of suspended solids, dissolved organics, nutrients and heavy metals. The expanded bed process employed in both pilot plants could be operated over long periods without blockage, while giving high removal, steady performance. Such capabilities to remove trace pollutants of organics, nutrients and heavy metals, without chemical requirement, show good potential for use of the biofilm process to: (1) treat polluted river waters; (2) treat waters to meet the stricter drinking water standards, such as the new EU Drinking Water Directive, DWD, or the 98/93/EC; (3) provide affordable and sustainable drinking water treatment process. With these encouraging findings larger pilot units are now being run for treatment of river and ground waters. Studies using biofilm wastewater treatment processes to remove recalcitrant chlorinated organic (PCP) and a heavy metal have shown that biofilm processes can be used to substantially remove both recalcitrant chlorinated organics and heavy metals. Metabolite analysis via MS analysis of extracts of the GAC medium and effluent indicated biodegradation of PCP had occurred. Reductive dechlorination of PCP occurred in the reactor, showing that biofilms offered both oxidative and reductive conditions. Besides these special characteristics, no chemicals were employed in both water and wastewater biofilm treatments. Thus no chemical sludge was generated, besides lowering treatment costs due to chemicals. Biofilm processes as used here have potential to be further developed into cheaper, environmentally friendlier processes for treating water and wastewaters containing organics and heavy metals.

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