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Experimental Comparison of Two Modifications of Activated Sludge for Treatment of Furfural-Containing Wastewater

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Abstract

A case study is presented in which two modifications of activated sludge treatment of complex chemical wastewater are experimentally compared: a combination of common activated sludge with powdered activated carbon treatment (PACT), and bioaugmentation of activated sludge treatment (BAST). Industrial wastewater of Pars Oil Refinery that was passed through an oil recovery stage was used to investigate the effect of furfural on two treatment processes in the range between 100-2000 ppm. Furfural was added manually. For comparison, furfural, COD, MLSS (Mixed Liquor Suspended Solids) concentrations and SVI (Sludge Volume Index) were measured daily. The results show a little higher COD removal efficiency in PACT system and the same furfural removal in both methods. But, it should be mentioned that at low HRT (Hydraulic Retention Time), BAST system showed better results in both furfural and COD removal than PACT system. SVI measurement shows that settability of effluent sludge in BAST system was always better than in PACT system. Because of rapid growth of microbial biomass in BAST system, the MLSS concentration in this modification was higher than in PACT system and in this way, BAST system has a lower requirement to return sludge than PACT system. Finally, it could be concluded that BAST system may be an attractive alternative to existing PACT system and if the former is used, it will result in both high performance and optimum conditions with economical operation.

Keywords: *Activated Sludge, Powdered Activated Carbon (PAC), Bioaugmentation, Furfural*

Introduction

The presence of toxic organic compounds in receiving waters and water supplies has modified the emphasis of wastewater treatment during the past several decades. Historically, wastewater treatment systems have been designed to remove BOD, suspended solids, pathogenic organisms, and nitrogen and phosphorus, but the removal of these substances alone is no longer sufficient to protect the quality of the environment. Discharge regulations that impose limitations on specific substances, such as the 114 organic compounds designated as priority pollutants by the U.S Environmental Protection agency (USEPA) require evaluations of the capabilities of conventional wastewater treatment systems for removing such substances.

Some studies have indicated that conven-

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tional biological treatment such as activated sludge, will not be effective enough in removing all compounds to levels considered acceptable for discharge [1]. Removal of these substances will require modifications in or alternatives of the existing treatment systems. A variety of modifications and alternatives to conventional biological treatment processes have been suggested and evaluated in bench, pilot and full-scale treatment systems during the past 20-25 years. Of these, the addition of powdered activated carbon (PAC) to the aeration basins of activated sludge facilities has emerged as an attractive, integrated application of both biological degradation and adsorption technology for removal of organic compounds [2]. Activated carbons differ in their effectiveness in removing toxicity, and regeneration may affect adsorption efficiency. Since carbons vary in cost, tests of various carbons on specific wastewaters are required to select the most cost-effective one [3]. On the other hand, because of economic and solid-waste disposal considerations, it is generally necessary to regenerate spent carbon for reuse, via one of several techniques [4]. In this way, the use of activated carbons to remove organic compounds might not be an economical process in developing countries such as Iran.

In this report, a novel modification, bioaugmentation of activated sludge (BAST) system is introduced, which may be an attractive alternative to the conventional (PACT) system for removing toxic compounds in wastewater. Bacterial augmentation and bioaugmentation are terms that describe the direct addition of a selected microbial biomass in order to improve certain biological properties of a particular ecosystem [5]. This procedure has been used for decades in some ecosystems such as soil. In the field of wastewater treatment, the literature reports a few cases of successful bioaugmentation [6]. Because of widespread use of furfural (2-furancarboxaldehyde: C_4H_3OCHO) as the solvent in motor oil refineries in Iran, which increases the toxicity of wastewater and makes biological treatment very difficult, this chemical has been chosen as a toxic compound to be tested.

Materials and Methods

A Case Study with a Real Wastewater

Several studies have dealt with activated sludge biotreatment. However, most of them have been carried out using model compounds instead of real wastes. Although use of model compounds may help in gaining insight into suitability of the process under study, the efficiency of a specific treatment may significantly vary depending on the composition and nature of the wastewater to be processed. Therefore, in this work, experiments have been conducted using real wastewater generated in the Pars oil refinery located 20 km west of Tehran, Iran. In this refinery, oil material is extracted from lube cuts using solvents like furfural, methyl ethyl ketone and toluene. Presence of these solvents, especially furfural, increases the toxicity of wastewater and makes biological treatment very difficult. The effluent wastewater from the oil recovery plant in the main site of this refinery was taken to investigate the biotreatment of furfural-containing wastewater by modification of activated sludge. Table 1 shows characteristics of the real wastewater (upper and lower limits).

Table 1. Characteristics of the real wastewater

Temperature	pH	COD	Furfural
27 - 48 $^\circ C$	6.8-9	150-750 ppm	61-123 ppm

Experimental Set-up

The treatment process in this research was performed in two aerobic bioreactors of pilot scale. One of them was the bioaugmentation of activated sludge (BAS) and the other was the common activated sludge system with powdered activated carbon (PAC). Each of these bioreactors was a completely mixed activated sludge unit that consisted of a rectangular aeration basin and a settling unit with a working volume of 7 liters and 0.5 liters, respectively. Both units were made of transparent acrylic sheet. Air was introduced to the aerobic bioreactor through diffuser stones which provided additional mixing as well as oxygen at a rate ensuring sufficient oxygen concentration (4-5 mg/l). A continuous flow of feed was maintained using peristaltic pumps.

Determination of Optimum PAC Concentra-tion

Effectiveness of PAC in reducing furfural was evaluated by adsorption experiments in a batch mode. [7]

The experiments were conducted with a multiple shaking apparatus. Constant volumes (500 ml) of the wastewater were supplemented with three different furfural concentrations and with steady shaking for 24h at room temperature. After removal of the carbon by filtration through a membrane filter (0.45 μm pore size), the residual furfural was determined.

Source of Furfural-Degrading Micro-organism

It has been established that microbial metabolism of specific organic compounds is increased by prior exposure to the compound [8]. Thus, pollutant degradation is more rapid in contaminated environments than in pristine environments. This suggests that a greater number of microorganisms capable of utilizing furfural as a sole source of carbon and energy would be isolated from the site of highest furfural contamination in the polluted sludge. In this study, microbial isolates were obtained by sludge sampling from one of the wastewater channels of Pars oil refinery, which had been chronically exposed to furfural.

Isolation of Furfural-Degrading Bacteria

The enrichment culture technique was used for the isolation of desired organisms [9]. At first, one gram of contaminated sludge was suspended in 10 ml of distilled water and then allowed to sit for sufficient time for sedimentation of solid particles. The liquid phase was assayed for the presence of furfural-degrading bacteria. This mixed culture was further enriched in a mineral medium (g/l; K_2HPO_4, 5; $(NH_4)_2SO_4$, 3.5; $MgSO_4.7H_2O$, 0.06; mg/l: $CaCl_2.H_2O$, 0.6; $FeSO_4$. $7H_2O$, 2.4) by successive daily addition of furfural (as a sole source of carbon for microbial growth) and routinely transferred to a new medium every 3 weeks. The pH of the medium was maintained at 7. Individual strains from this consortium were isolated and subsequently maintained on nutrient agar plates and stored as slant cultures under oil at $4^{\circ}C$. Cultures were grown to a density of 10^9 cells/gr and then used for BAST system inocolum.

Analysis

Chemical oxygen demand, mixed liquor suspended solid (MLSS) and sludge volume index (SVI) were measured using standard methods [10]. Furfural concentration was measured using UV absorption-spectrum at 270 nm (Shimadzu).

Materials

Powdered activated carbon and furfural were obtained from Merck company. Other chemicals used in this study were of analytical or higher grades.

Results and Discussion

At first, adsorption experiments were conducted to determine the optimum PAC concentration, as described previously.

Tables 2 and 3 show the results of these experiments. The experiments showed that COD removal increased with increased PAC concentration up to 50 ppm, but at higher concentrations, COD removal percent did not change significantly and consequently, 50 ppm was chosen as the optimum concentration with economical consideration for PACT system.

Table 2. Determination of the optimum concentration of PAC (with 100 ppm furfural)

Concentration of PAC (ppm)	Residul Furfural (ppm)	Furfural Removal Percent
50	2.9	94
100	2.5	97.5
150	2	98

Table 3. Determination of the optimum concentration of PAC (with 500 ppm furfural)

Concentration of PAC (ppm)	Residul Furfural (ppm)	Furfural Removal Percent
50	124	75
100	70	86

To compare BAST and PACT systems, the two aeration tanks were initially seeded with activated sludge, obtained from one of the wastewater channels of Pars oil refinery and operated in a continuous flow mode with influent composed of real wastewater and additional furfural was added manually to control the content in the feed.
Powdered activated carbon was added with optimum concentration to aeration tank of the PACT system. On the other hand, the aeration tank of BAST system was inoculated with furfural-degrading bacteria. Then, in parallel, PACT and BAST systems were operated at the identical operating conditions, to provide for comparison of experimental results.
Figure 1 shows the COD removal percent versus HRT for both systems. As this figure shows, the COD removal percent in the PACT system was above 90%, except in HRT equal to 6 hours, in which case the efficiency of the system decreased because of washout problem for both sludge and activated carbon. The COD removal percent in BAST system was a little lower than PACT system in high HRT's (9, 8 and 12 h).

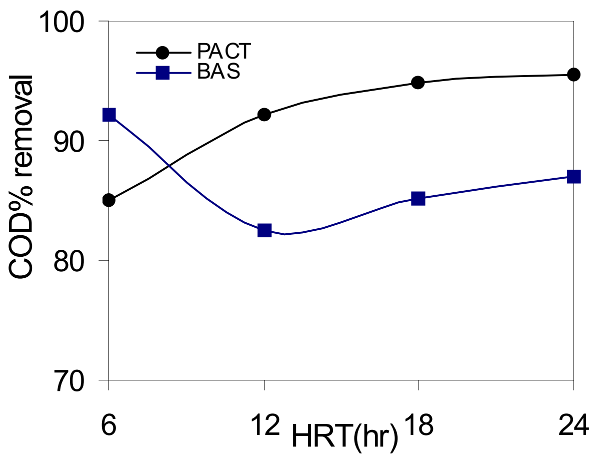

Figure 1. COD % removal vs. HRT (hydraulic retention time) in PACT & BAS systems

Because of high MLSS concentration (20000 mg/l) and poor mixing (oxygen deficiency), the removal percent decreased about 10% when HRT was increased to 12 h in BAST system.
Figure 2 shows the furfural removal percent versus HRT for both systems. Furfural removal percent was very high in both systems and did not come under 98%. In all HRT's, the furfural removal percent was higher than the COD removal percent for both systems. It is due to the fact that in the wastewater, there were other organic inhibitors like toluene, methyl ethyl ketone, etc., as well.
The results of experiments in PACT system shows a decrease in COD and furfural removal efficiency with decreasing the HRT, which also increased turbidity in effluent flow. It should be mentioned that in low HRT's (6 h), both COD and furfural removal percent in BAST were higher than in PACT. It could be concluded that BAST system showed high stability even in shorter hydraulic retention times and process efficiency was high even in low HRT's. Figure 3 shows that MLSS concentration in BAST was much higher than in PACT, so that it approached 20000 mg/l. The great difference between the MLSS concentration of two systems shows that the growth of furfural-degrading bacteria (isolated strain)

was more rapid than the growth of common mixed organisms in PACT system and this is one of the most important advantages of applying BAST system.

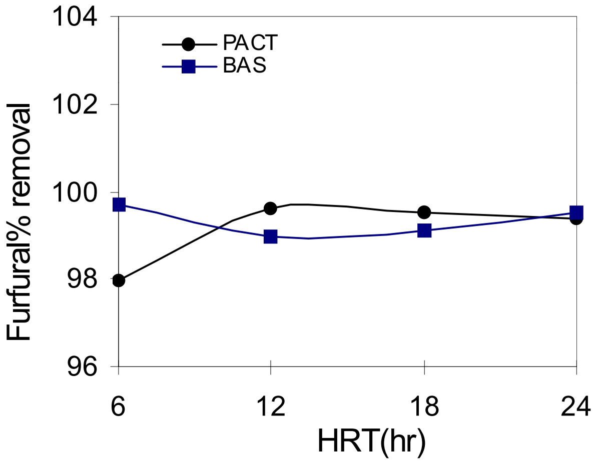

Figure 2. Furfural % removal vs.HRT (hydraulic retention time) in PACT & BAS systems

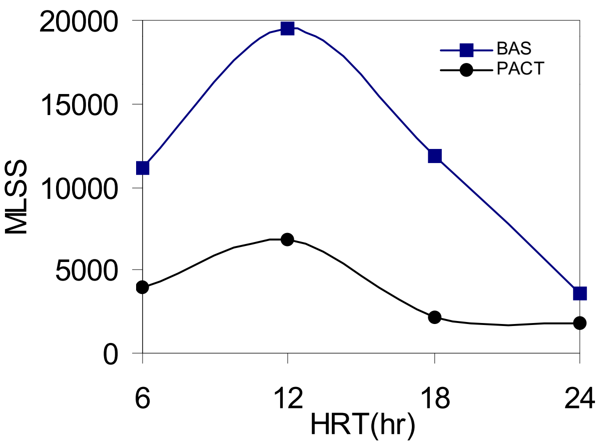

Figure 3. MLSS (mixed liquor suspended solid) vs. HRT (hydraulic retention time) in PACT & BAS systems

Sludge volume index (SVI) was also measured during the continuous operation to compare the settability of effluent sludge from each system.

Figure 4 shows that SVI varied between 31 to 84 ml/g for BAST and between 150 to 250 ml/g for PACT. Therefore, in the BAST system, the settability of effluent sludge was excellent even in an HRT of 6 h, and effluent flow from the settling section was completely without turbidity in all HRT's and sludge was so sticky and massive that it did not exit even with increasing the flow rate; consequently, under this condition, there is no requirement to recycle activated sludge. This is another important advantage of applying BAST system.

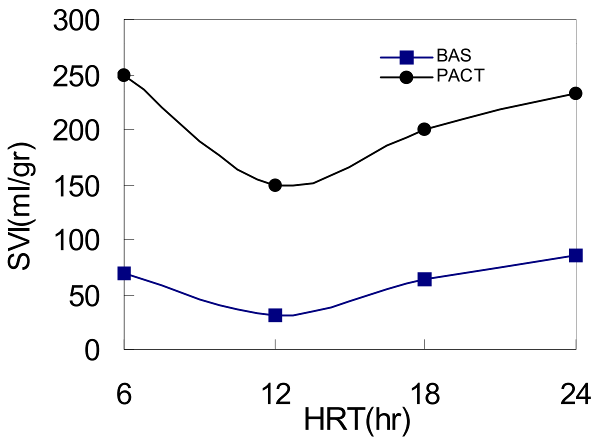

Figure 4. SVI (sludge volume index) vs. HRT (hydraulic retention time) in PACT & BAS systems

To study the influence of furfural and COD concentrations on removal efficiency, several experiments were carried out.

In each HRT, furfural concentration in the influent was increased up to 2000 ppm for the two systems. As it is shown in Figure 5, at an HRT of 12 h, changes in furfural concentration did not have a significant effect on the furfural removal performance and in all conditions, these efficiencies were high. It demonstrates that the systems are not sensitive to furfural concentration shocks. The same results were obtained for an HRT of 6 h (Figure 6). Furfural removal performance, especially for BAST system, was high (99%). The COD concentration in the influent was increased up to 3500 mg/l. In this case, again the change in COD percent removal was not sharp but sharper than furfural removal efficiency (Figures 7,8), especially at HRT = 6 h for PACT system, which as mentioned before, is due to the washout problem.

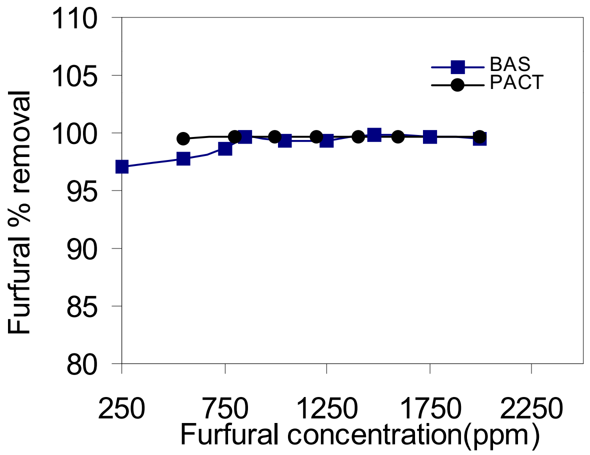

Figure 5. Furfural % removal vs. furfural input for HRT=12 hr in PACT & BAS systems

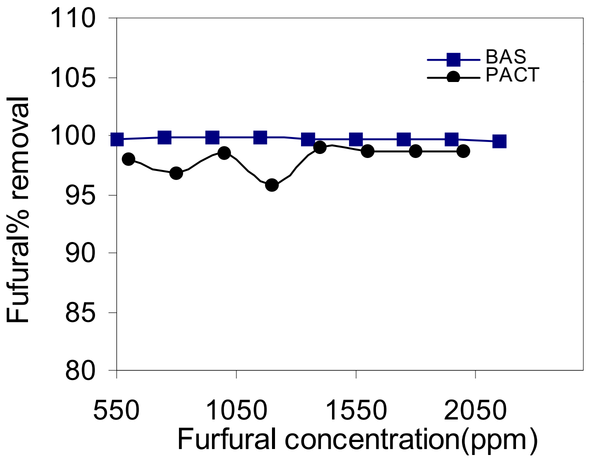

Figure 6. Furfural % removal vs. furfural input for HRT=6 hr in PACT & BAS systems

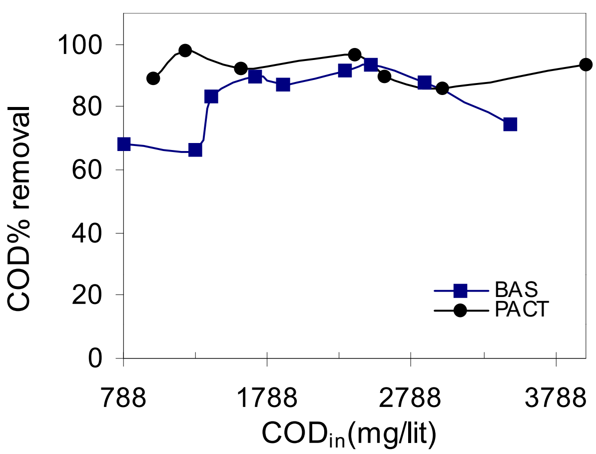

Figure 7. COD % removal vs. COD input for HRT=12 hr in PACT & BAS systems.

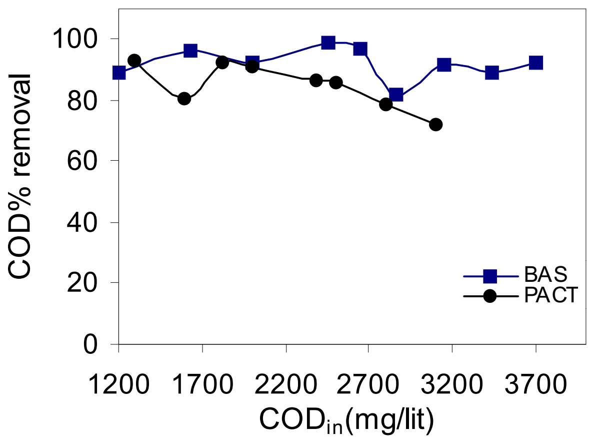

Figure 8. COD % removal vs. COD input for HRT=6 hr in PACT & BAS systems

Conclusions

Based on the results obtained from the experiments, it can be concluded that the main basis of preservative performance of PACT system for high furfural-containing wastewater treatment, is the adsorption ability of powdered activated carbon.

In other words, when furfural and other pollutants enter the system, activated carbon acts as pollution sinks, and after this rapid primary adsorption in the pores of carbon, biological treatment begins. But, when the influent flow rate increases, carbon and MLSS go out of the system and it results in poor treatment performance.

Vice versa, in BAST system, the sticky sludge produced in the system does not exit from the system easily, even in low hydraulic retention times.

The significant difference between the SVI's of the two systems shows high settability of BAST system effluent. Consequently, under these conditions, there is no requirement for final clarification and recirculation of the activated sludge. It is sufficient to design a conical reactor in bottom to discharge waste activated sludge by gravity.

As mentioned before, COD removal performance was a little higher in PACT system than in BAST system, but their furfural removal percent was the same. But, due to economical considerations, high price of activated carbon and capacity subsidence of carbon, it can be concluded that if BAST system is used, it will result in both high performance and optimum conditions with economical operation.

In conclusion, our studies have demonstrated that BAST system may be an attractive alternative to existing PACT system for furfural-containing wastewater treatment, especially in developing countries.

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