

## Using Activated Sludge System To Reduce Furfural Concentration In A Refinery Wastewater

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### ABSTRACT

Furfural is used as a solvent in most refineries. The objective of this study is to make an activated sludge system to reduce furfural concentration in an industrial-oily wastewater. The used wastewater was from Behran oil refinery which passed from oil removing (CPI) stage. In the present study, microbial separation with exclusive cultivation was used for removal of Furfural By using activated sludge. The isolated microbes for decomposition of Furfural were gram-positive and catalase-negative and they were able to remove Furfural to 2000 ppm. The results of this study showed that the activated sludge system with microbes had a very good removal and deposition percentage. In the beginning, the microbes were raised in a pilot and during this period furfural concentration and sludge concentration (MLSS) were regularly measured. Besides, Sludge Volume Index (SVI) was measured to determine the amount of sludge deposition and at the end Kinetics constants of the sludge were determined. Then, sludge was transferred to the main reactor in the wastewater treatment of Behran oil Refinery and it was used in Industrial scale. Experimental results approved 95% Furfural removal.

**Key words:** Industrial wastewater, Furfural, activated sludge, microbial separation, exclusive Cultivation

### Introduction

Furfural is used as a solvent in industries (Zhang et al., 2011). Furfural solvent has high capability for separation a component of multi-components and especially in petroleum combinations to separate sulfur and carbonaceous compounds (Trickey, 1927). This substance is used to remove aromatics in refinery of industrial lubricant oils industry (Coto et al., 2006; Patel, 2007; Kemp et al., 1948). For the first time, this combination was made By German scientists in 1832 from evaporation of sugar in the presence of Sulfuric acid and Manganese dioxide (Monroe, 1921). However, its industrial application was done By Americans In 1920. Furfural is a toxic aldehyde and it is pale yellow or colorless oily liquid and it turns into brown or red in the presence of air or light (Kim et al., 2011). Its smell is similar to bitter almond oil or Benz aldehyde. Furfural can be prepared in synthetic or natural way (Li Shen and Martin K. Patel, 2010). Direct contact with this substance should be avoided since this substance causes sensitivity of in the skin, eye, mucous membranes, even the destruction of the liver, kidney and osteoporosis (Osha 1996).

According to Industrial Application of Furfural especially in refineries, it is an inevitable substance in the wastewater units. Therefore, it is essential to provide a good method for the treatment of this wastewater. The carried out studies in filterability of the waste contained furfural shows that furfural can be decomposed in the small amounts by aerobic and anaerobic bacteria and nitrate-reducing and methane-producing bacteria can use this substance as carbon source. Methane-making bacteria are quickly destroyed in the concentrations over 1000 mg / lit furfural. Acid-producing bacteria and Yeast are the Best furfural decomposers and they convert furfural to fatty acids, alcohol, acetic acid and Hydroxymethyl Furat. One of the appropriate and economic methods for industrial wastewater treatment including refinery waste water is usually biological treatment system. If the activated sludge for removal of specific contaminants is prepared by microbial separation, it will have high efficiency. In this method, furfural decomposer microbes were transferred to the constructed pilot unit in Behran oil refinery which they were previously sampled from one of the waterways in Pars Oil Refinery and were raised in an experimental bio-reactor in Sharif Industrial University. Then, the

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necessary processes for raising the microbes were done.

### Material and Methods

In the primary sector, a bio-reactor with the volume of 7 liters was used in the laboratory. The input sewage for output system was from the fat removing unit of Pars Oil Refinery. This section was carried out in three stages. In the first stage, inactivated sludge from one of the waterways of Pars Oil Refinery were spilled into the bio-reactor and aerated. Within 4 months, continuous aeration and COD measurement showed that the percentage of COD removal will not be more than 40%. The second stage of microbial separation from sludge was carried out in 5 phases as following:

- 1 – Enrichment
- 2 – Separating decomposer microbes and microbes compatible with furfural
- 3 - Transmission of microbes from liquid environment to solid environment
- 4 – Filtering
- 5-Selecting the best isolated microbes

Ten different microbes were isolated by doing these stages and two microbes were determined with the highest percentage of Furfural disposal by putting them in appropriate cultivation environments. The activated sludge reactor was started to work by inoculating these two microbes. In the third stage, furfural concentration was raised to about 2000 mg/lit with various interval times (6, 12 and 24 hours). In each stage, the values of COD, SVI and

$$(1) \text{Munud Equation} = \frac{dx}{dt} = ux = Y \frac{ds}{dt}$$

$\frac{ds}{dt}$

=Cell growth rate [Mass/ (Volume x Time)]

U= Growth rate (time)

$$U = U_{max} \left( \frac{S}{K_s + S} \right) \quad \text{The growth time is expressed as follows:} \quad (2)$$

Maximum growth rate (1/time)

$$U_{max} = U_m =$$

$$K_s = \left( U = 1/2 U_m \right)$$

Constant concentration of saturated Substrate self-corrosion speed Is expressed by following equation:

$$\frac{dx}{dt} = K_e x$$

K= self-corrosion constant (1/time)

X= Cell concentration (Mass/Volume)

Mass balance equation for a reactor in steady-state and without return flow is as follows:

Aggregation = [increasing due to growth]-[reduction due to output self-corrosion.

$$dx.V = V.U.xdt - V.K_e.x.dt - Qxdt$$

Furfural were measured. Moreover, sludge kinetics constants were obtained Using Munud equation and Cellular mass balance. In the second part, this microbe was transferred to Behran oil refinery. In this section, firstly 10 strains were prepared using main microbes. These microbes were cultivated in Nutrient Agar and in 80 centigrade oven. After raising and preparing, microbes were transferred to the pilot unit with approximate volume of 500 liters and the continuous aeration was started. The furfural increasing into this section was started from about 50 ppm. In 4 months; furfural concentration was gradually increased to 2000 mg / lit. Figure 1 shows furfural concentration process and the obtained concentration with retention time of 24 hours in 5 months using the pilot.

In each time that Furfural was added, P and N Nutrients were also added. At all stages of adding furfural, the ratio of P: N: COD was tried to be equal to 1: 5: 100. Hence, after this section, appropriate sludge with high deposition capability was obtained.

Figure 1 - the process of increasing output furfural concentration with retention time of 24 hours in 5 months using the pilot

Besides, Kinetics constants of the activated sludge with those specific microbes and the results from the pilot unit were calculated by using the following equations (Munud and cell mass balance) in steady state and without return flow.

Figure 1 Shows Furfural physical characteristics.

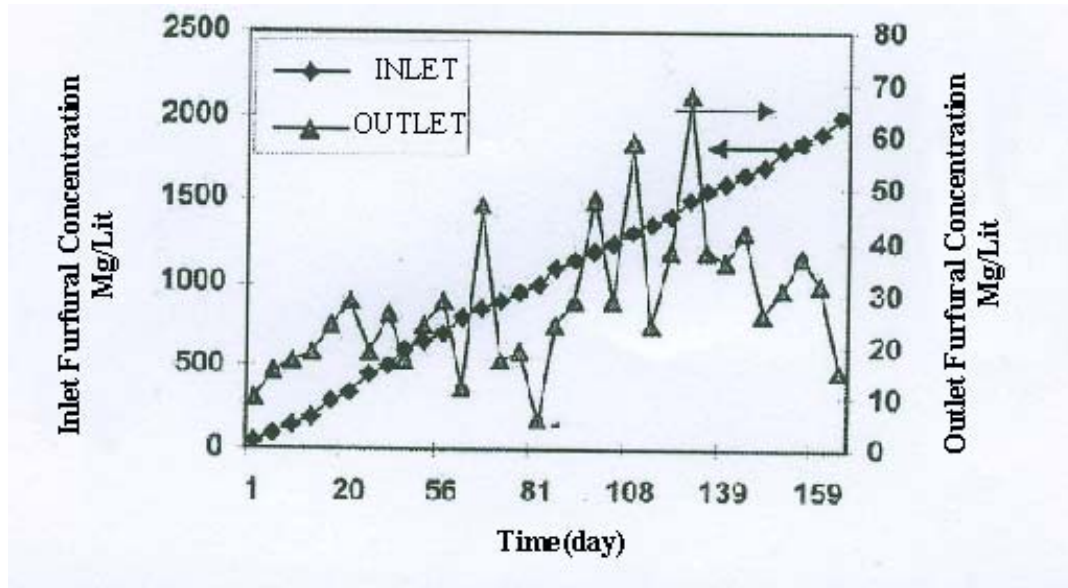


Fig. 1: Furfural physical characteristics.

The increase rate of effluent furfural concentration on retention time of 24 hours in 5 months of operation. Inlet and outlet of furfural concentration has shown by different symbols in the graph.

*Industrial applications of raised Sludge:*

Some investigations were performed during several months by technical staff of Ab Pardazane Bahar Company in Behran oil refinery which the results revealed that furfural wastewater flows were not mixed with the rest of the sewage and they were separately sent to refinery. Subsequently, according to the biological nature of refinery, its designing was in a way that its operations on furfural wastewater was firstly done in pretreatment. After obtaining sufficient furfural concentration for biological treatment (common activated sludge method), the flow was added to the rest of the sewage. Furfural wastewater is about 100 m<sup>3</sup>/day and different furfural concentrations from 500 mg /lit sometimes to 10000 mg / lit is entered to pretreatment unit. Furfural is formed 10% of the total wastewater. The furfural output concentration of 100 mg/lit for pretreatment makes no problem in activated sludge systems because of fining after joining the rest of the sewage. In the pretreatment, designing was done in a way that furfural wastewater flow after a few stripping steps in consecutive tanks with concentration of 2000 mg / lit or less, is inserted into the terminal section of pretreatment which is biological reactor (treated with special sludge). The reactor is made based on the results from laboratory

and pilot and with a retention time of 24 hours. After the completion of constructional and electromechanical operations of wastewater treatment of Behran oil refinery, contents of sludge in the pilot was transferred to main reactor in the pretreatment unit. In 2 months by increasing the volume and the gradual increase of furfural, the reactor with approximate volume of 100 m<sup>3</sup> and containing sludge were ready to be utilized. Furfural wastewater flow towards pretreatment was actually set up with the arrival of sewage to refineries. However, the furfural concentration was sometimes much more than the stated design principles of in the contract (2000 mg / lit). in the output of pretreatment, furfural concentration was approximately 100 mg / lit and even less in most cases.

*Results of pilot studies:*

In experimental reactor and the pilot with the retention time of 24 hours and with furfural concentration up to 2000 mg / lit, the furfural removal was up to 98 per cent. During the experiments, the amount of MLSS was regularly measured and it reached to 2500 mg / lit and Also SVI value was between 50 and 150 mg / lit which represented good deposition capabilities of the sludge.

By using equations (1) and (2) and (3) and (4), two following equations are obtained. These two equations are a form of  $Y = ax + b$  equation that the intended Kinetics constants can be acquired by drawing the lines and obtaining slope and intercept.

## Result and Discussion

In this system, with specific activated sludge (which was prepared from bacterial isolation) efficiency of furfural removal was up to 52-99 percent in experimental reactor with the retention time of 24 hours and concentrations up to 2000 mg / lit furfural. In the pilot unit, the removal efficiency was 98%. The main reactor was designed in

industrial scale based on the results from the reactor and pilot unit. Raised sludge was successfully transferred to the reactor. The results indicate that the sludge is capable of industrial wastewater treatment (includes other pollutants except furfural) with concentrations up to 2000 mg / lit and even higher. The following figures show the experimental results of pretreatment in Behran Oil Refinery.

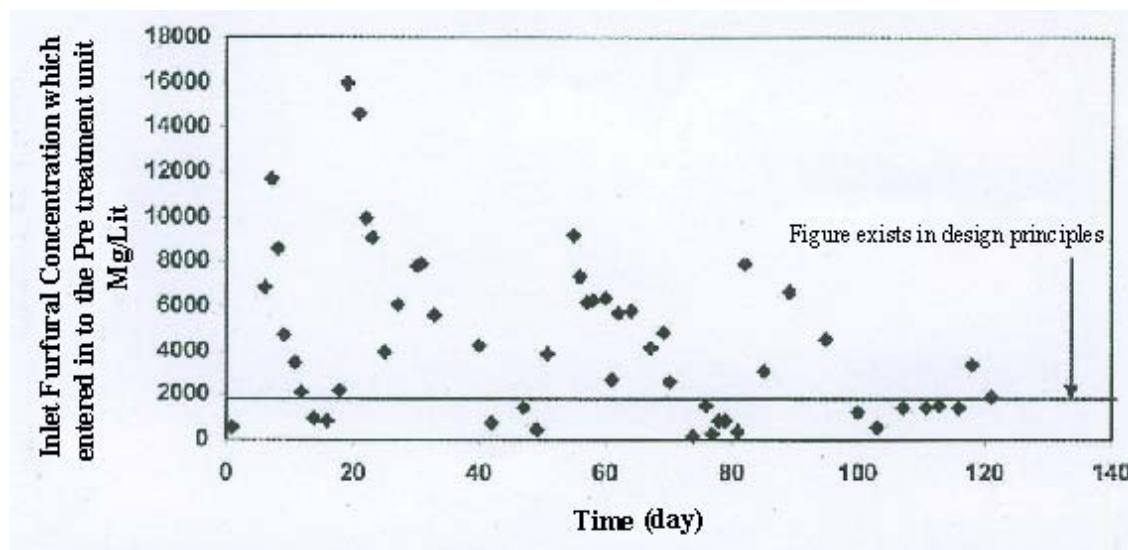


Fig. 2: The input furfural concentration to the pre-treatment unit in the last five months of the year 2011.

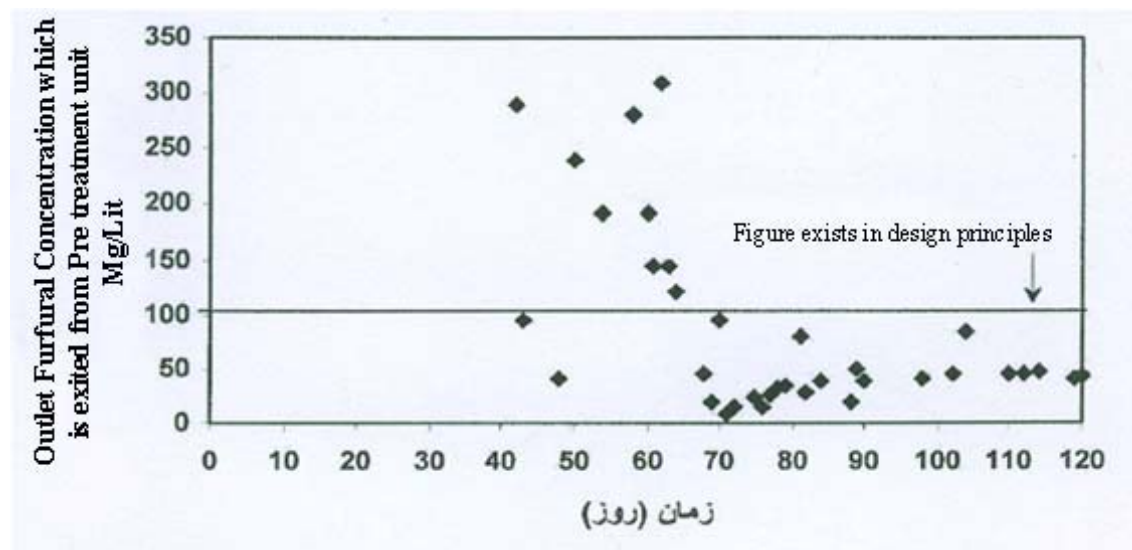


Fig. 3: The output Furfural concentration from pre-treatment in four months in the last five months of the year 2011.

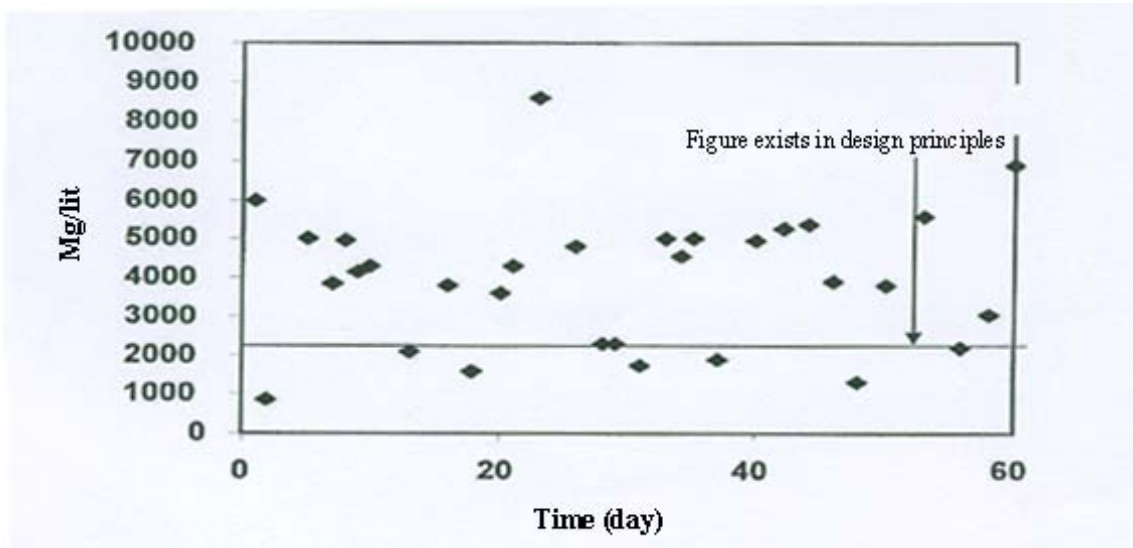


Fig. 4: Concentration of input Furfural to the pre-treatment unit In the first two months of the year 2012.

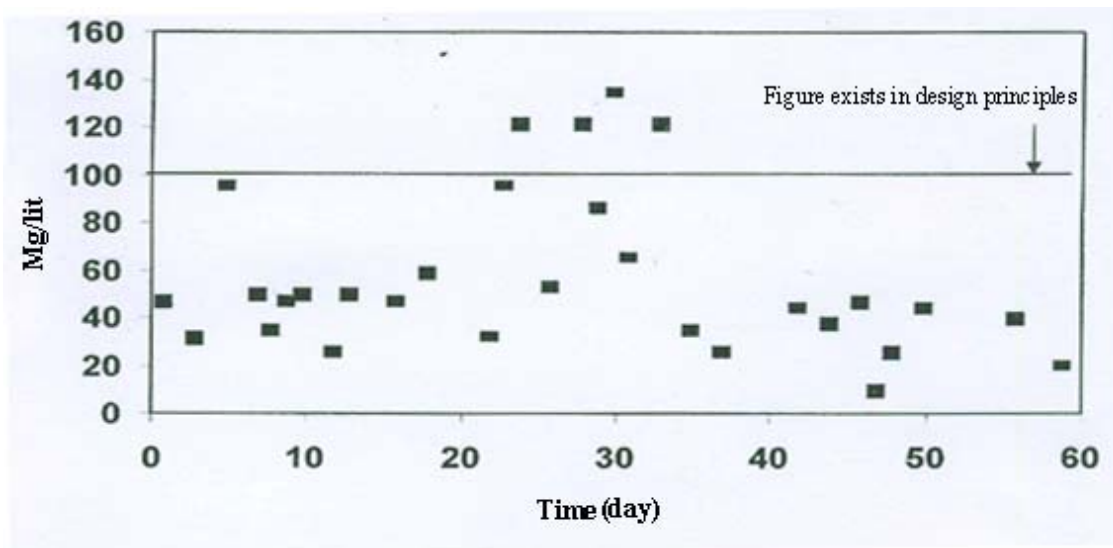


Fig. 5: Concentration of output Furfural from The pretreatment unit In the first two months of the year 2012

**Conclusion:**

According to this research using a system of activated sludge is a reasonable process to reduce Furfural concentration in a refinery wastewater. Since Furfural is toxic aldehyde and it is so harmful for skin and health, therefore this process can be used as a suitable procedure to eliminate or reduce the amount of furfural in the refinery wastewater. WHO has established very strict rules and recommended the producers and plants owner to obey these rules and don't damage the environment and human's health So activated sludge process can be nominated as one of the efficient way to diminish the disadvantages of Furfural in the refinery wastewater.

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