

Remove Organic and Inorganic Contaminants in the Waste Oil Using MBBR, Nano Reactor and Physical Methods

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Abstract

The aim of this study was to evaluate the performance of pilots physical, biochemical and chemical, in series and together for waste water treatment plants, processing oil in the Persian Gulf's oil and gas. For this purpose a Skimmer tank, MBBR reactor, Nano reactor, UV tank was used. Incoming wastewater system effluent desalination unit. Hydraulic retention time for various different system is intended. If you reduce the retention time of 18 to 12 hours, removed COD from 91% to 76% reduced. It was also found that the total removal of carbon materials in part MBBR 78.2% and 21.8% of the biofilm floating microorganisms. The results indicate that the whole system, which consists of 4 pilot that each part of its eliminates COD in waste water, the ability to remove 91% of COD. Solution input load 1.766 Kg COD/m² was signed. Finally, after the passage of treated wastewater and filters in 4 stages, has a relatively uniform quality and desirable.

Keywords: MBBR; Skimmer tank; Organic; Nano reactor; COD; Wastewater

Introduction

Waste water is a problem in oil industry. Over the last decades there has been a growing interest in biofilm processes for waste water treatment. Moving bed biofilm reactor (MBBR) is an efficient alternative for organic carbon and nitrogen removal which combine the advantages of both the active sludge process and a biofilm reactor by incorporating free-floating carriers that provide a large surface area for colonization with no need for biomass recycling [1].

There are several reasons for the fact that biofilm processes often are being increasingly favored instead of activated sludge processes, such as the following:

- The treatment plant requires less space.
- The final treatment result is less dependent on biomass separation since the biomass concentration to be separated is at least 10 times lower.
- The attached biomass becomes more specialized (higher concentration of relevant organisms) at a given point in the processes train, because there is no sludge return.

There are already many different biofilm systems in use, such as trickling filters, rotating biological contactors (RBC), fixed media submerged biofilters, granular media biofilters, fluidized bed reactors etc.

They have all their advantages and disadvantages. The trickling filter is not volume-effective.

Mechanical failures are often experienced with the RBC'S. It is difficult to get distribution of the load on the whole carrier surface in fixed media submerged biofilters. The granular media biofilters have to be operated discontinuously because of the need for backwashing and the fluidized bed reactors show hydraulic instability [2].

Among various semiconductors, TiO₂ is one of the most efficient photocatalyst for the degradation of pollutants in aqueous suspension through the photogenerated strong oxidizing agents like hydroxyl radical and superoxide radical anions under UV light irradiation. It is pertinent to mention here that TiO₂ can only be excited by UV light

due to its large band gap energy (3.2 eV for anatase) which is not ideal to absorb visible light.

To overcome this problem research groups working in the area of photocatalysis are trying to extend the optical response of photocatalyst from UV to visible region by doping it with metal or non-metal into the TiO₂ lattice.

The various methods used for doping TiO₂ involve ion implantation, sol-gel reaction, hydrothermal reaction, solid-state reaction, etc.

Among these, one of the sol-gel processed is undoubtedly the simplest and the cheapest one which provides control on the size and shape of nano particles [3].

Few studies relating to the synthesis of molybdenum (Mo), Manganese (Mn) and Zinc (Zn) doped TiO₂ using different methods and its photocatalytic activity for the degradation of pollutants have been reported earlier. For example, in two separate studies Mo-doped TiO₂ has been synthesized using thermal hydrolysis and sol-gel method. In another study by Devi et al. Mn-doped TiO₂ was synthesized using sol-gel process and its photocatalytic activity was investigated by studying the degradation of a dye derivative amaranth. On the other hand, synthesis of Zn-doped TiO₂ using different methods and their activity for the degradation of dyes and organic pollutant has been reported in the literature [3].

Waste water with high levels of organic matter (COD) Phosphorous (P) and Nitrogen (N) cause several problems, such as eutrophication, oxygen consumption and toxicity, when discharged to the environment.

Biological processes are a cost-effective and environmentally sound alternative to the chemical treatment of waste water.

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Biological processes based upon suspended biomass (i.e., activated sludge processes) are effective for organic carbon and nutrient removal in municipal waste water plants. But there are some problems of sludge settleability and the need for large reactors and setting tanks and biomass recycling. Biofilm reactors are especially useful when slow growing organisms like nitrifiers have to be kept in a waste water treatment process.

During the past decade, it has been successfully used for the treatment of many industrial effluents including pulp and paper industry waste, poultry processing waste water, cheese waste, phenolic waste water, dairy waste water and municipal waste water [4].

This paper proposes a new methodology for treatment waste water. This study, there for, set out to assess the effect of Moving Bed Bio Reactor (MBBR), and the effect of Nano particle of TiO_2 doped Mn, Mo, Zn and UV lamp to removing oil in waste water. The present research explores, for the first time, the effect of Skimmer tank and MBBR and Nano particle in reactor and UV lamp (4 system) on waste water of oil industry. Due to practical constraints, this paper cannot provide a comprehensive review of removing oil from waste water with 4 systems. It is my experience of working with skimmer tank, MBBR, Nano particle, UV that has driven this research.

This paper begins by introducing Skimmer tank, it will then go on to MBBR system and Nano reactor, then UV, finally it will deal with removal of free oil and decreasing COD in waste water.

Material and Methods

A Schematic of pilot process concept is shown in Figure 1, where the treatment train consists of 2 tanks and 2 reactors.

The skimmer tank

In the Skimmer tank, remove oil free from the surface of waste water. The input current is entered at rate of 1 lit/hr.

The biofilm reactor (MBBR)

Carriers: In the MBBR, the biomass grows on carriers that move freely in the water volume by aeration [5]. The biofilm carriers are made of high-density polyethylene (density 0.95 g/cm^3). The size of the carrier varies from lengths of 7-15 mm and diameters of 10-15 mm. The carrier filling fraction (percentage of reactor volume occupied with carriers in empty tank) is normally 60-70% [5]. The Kaldnes carriers have a specific gravity of 0.96 with a specific biofilm protected surface area of $500 \text{ m}^2 \text{ per m}^3$ bulk volume of carriers. The Kaldnes biofilm carrier element is illustrated in Figure 2 [6].

Lab-scale reactor and waste water: A Laboratory scale Plexiglas with total liquid volume of 2 lit in the study (Figure 3). Diffusers were used for oxygen supply and mixing. The dissolved oxygen (Do) concentrations in the MBBR ranged from 0.2 to 5.00 mg o_2 /lit depending on the influent organic loading rates. The temperature and PH in the reactor varied from 28 to 31 c and 6.72 to 7.88, respectively [6] and the pressures varying between 0.1 and 0.5 bar [5].

Waste water: Effluent entering the fourth stage was the output unit 2 Ft in height desalter of Kharg Island in Iranian offshore Oil Company. In Figure 4 and Table 1, GC taken combined effluent shows. Synthetic oil was mixed with waste water in laboratory. The effluent from the first stage of the pilot project, from the skimmer tank to sign the final phase, removal and cleaning after several phases and the water from final phase was uniform and satisfactory quality and standard of environment. The calculated COD/N/P ratio of the syntheticwaste water was 100/5/1 [6]. The waste water was enriching with the macro-nutrients by adding

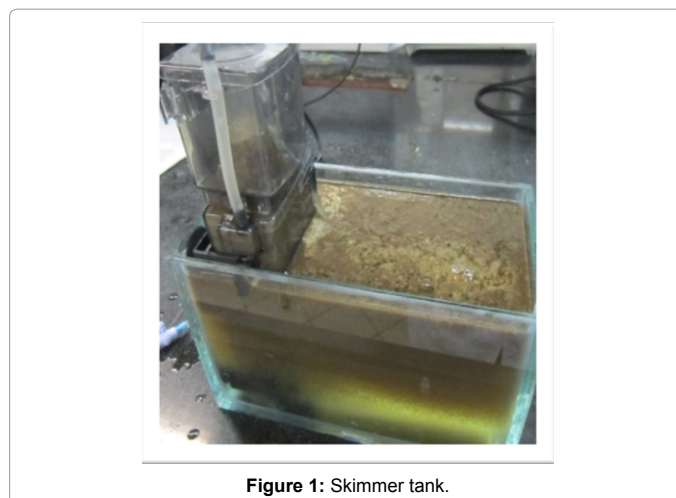


Figure 1: Skimmer tank.



Figure 2: Media K2.

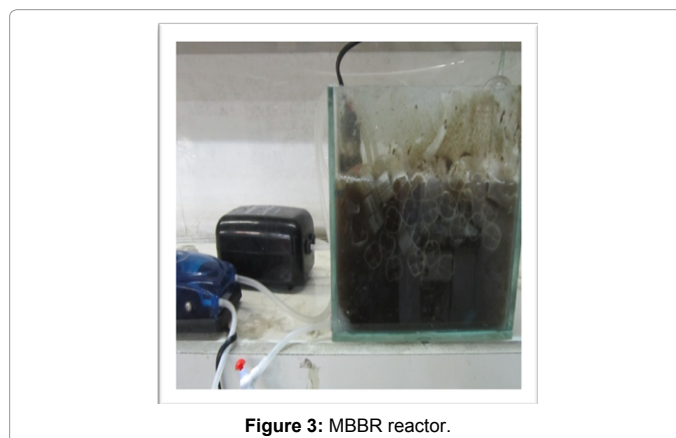


Figure 3: MBBR reactor.

urea as nitrogen source and K_2HPO_4 as phosphorus source [4]. $\text{NH}_4\text{-N}$ ranged from 25-125 mg/lit and $\text{po}_4\text{-p}$ ranged from 5-25 mg/lit were prepared and used as feed to the system. By the way, vermin-compost leachate was used for injection and enrichment of waste water.

Nano reactor

Synthesis TiO_2 doped Mn, Mo, Zn nano particle: TiO_2 nano particles were synthesized by sol-gel method using Titanium tetra

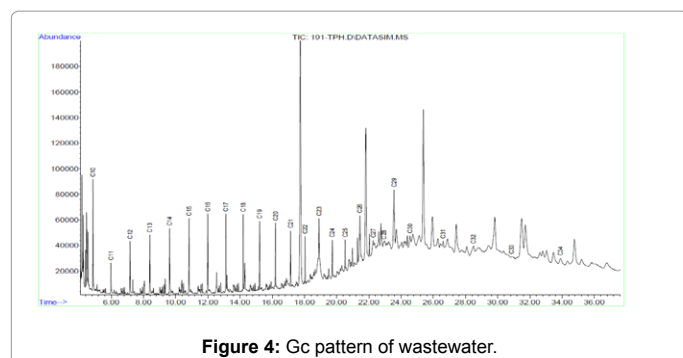


Figure 4: Gc pattern of wastewater.

No	Compound Name	RT (min)	Units	Amount
1	C10	4.863	ppm	1.304
2	C11	5.978	ppm	0.420
3	C12	7.167	ppm	0.617
4	C13	8.398	ppm	0.736
5	C14	9.622	ppm	0.732
6	C15	10.83	ppm	0.825
7	C16	11.996	ppm	0.884
8	C17	13.116	ppm	0.921
9	C18	14.19	ppm	0.883
10	C19	15.217	ppm	0.876
11	C20	16.198	ppm	0.798
12	C21	17.139	ppm	0.732
13	C22	18.032	ppm	0.603
14	C23	18.897	ppm	1.448
15	C24	19.727	ppm	0.459
16	C25	20.522	ppm	0.544
17	C26	21.439	ppm	1.759
18	C27	22.263	ppm	0.686
19	C28	22.931	ppm	0.122
20	C29	23.558	ppm	2.662
21	C30	24.556	ppm	0.623
22	C31	26.611	ppm	0.034
23	C32	28.485	ppm	0.049
24	C33	30.853	ppm	ND
25	C34	33.895	ppm	0.021
26	C35	0	ppm	ND

Table 1: The output unit 2 Ft in height desalter of Kharg Island in Iranian offshore Oil Company.

isopropoxid (TTIP) as titania precursor and doped with different concentrations of Molybdenum (Mo), Manganese (Mn) and Zinc (Zn) (0.5-1%) and characterized by standard analytical techniques such as x-ray diffraction (XRD) and scanning Electron Microscopy (SEM). The XRD analysis shows the partial crystalline nature and Rutile phase (Figure 5). The SEM images of doped TiO₂ at different magnifications also show the partial crystalline nature with rough surfaces (Figure 6).

Coating TiO₂ doped Mn, Mo, Zn in nano filter: TiO₂ doped nano particles were coated on filter plates Whatman N.34 and placed in an oven for 24 hours at a temperature of 34-42 c, pages was ready to install in reactor.

Nano reactor: A schematic of pilot process concept is shown in Figure 7. Doped nanoparticles on pages tray tower, when in fact these pages are filters that were built for the job, coats and waste water passes on these plates, such as fluid flow in the distillation tower. On

plates waste water dealing with these nano particles, mass transfer and removal of organic contaminants and treatment is better.

UV tank

A schematic of pilot process concept is shown in Figure 8. Treated wastewater from step 1 to 3, enter UV-Tank, and in the presence of UV light rays with a wavelength of 280 – 100 nm, refined and wastewater output has reached that limit environmental standards and can be used for watering plants and entering the environmental and sea. Data management and analysis were performed using SPSS, Xpert and Excle.

Results and Discussion

Experimental work in the laboratory was carried out in order to evaluate the efficiency of the system for the removal of organic matter and relationship between organic removal and abserved yield using a high loaded MBBR and Nano reactor.

Effluent total COD and COD removal rates versus time in Skimmer tank, MBBR, Nano reactor, UV-tank are show in Figure 9.

The XRD, SEM patterns of doped TiO₂ with Mo, Mn, Zn calcinated at 550 c for 4 h were analyzed [3].

All deped TiO₂ particles showed that particle crystalline nature and Rutile phase [3].

The average rutile crystallite size of doped and undoped TiO₂ nano particles was determined by Debye Scherer formula:

$$D = K \cdot \gamma / B \cdot \cos Q$$

Where D is the crystallite size, K the shape factore, γ the wavelength, Q the diffraction angle and B is the full width at half maximum [3].

The XRD, SEM is shown in Figures 5 and 6.

COD analysis

COD analysis in skimmer tank: An oil skimmer continues to remove oils as long as they are present. Depending on oil influx rate and the oil skimmer's removal rate, residual oil in the water maybe as low as a few parts per million. When residual oil reaches this level and further reduction is required, it may be more pratical to use a secondary removal method following skimming, such as MBBR.

COD analysis in MBBR: In order to observe the quality of the aqueous solution, chemical oxygen demand (COD) measurements were also carried out before and after the MBBR. As demonstrated in Figure 10 increasing inlet concentration up to 800 mg/l did not significantly affect the performance of the MBBR in COD removal and the efficiencies were over 91% for this parameter, although further increasing inlet concentration showed an adverse effect on the removal

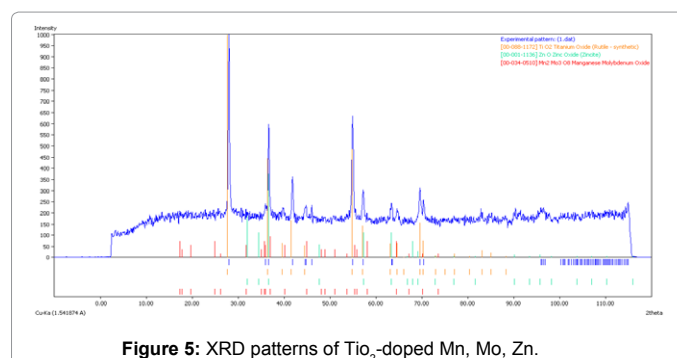


Figure 5: XRD patterns of TiO₂-doped Mn, Mo, Zn.

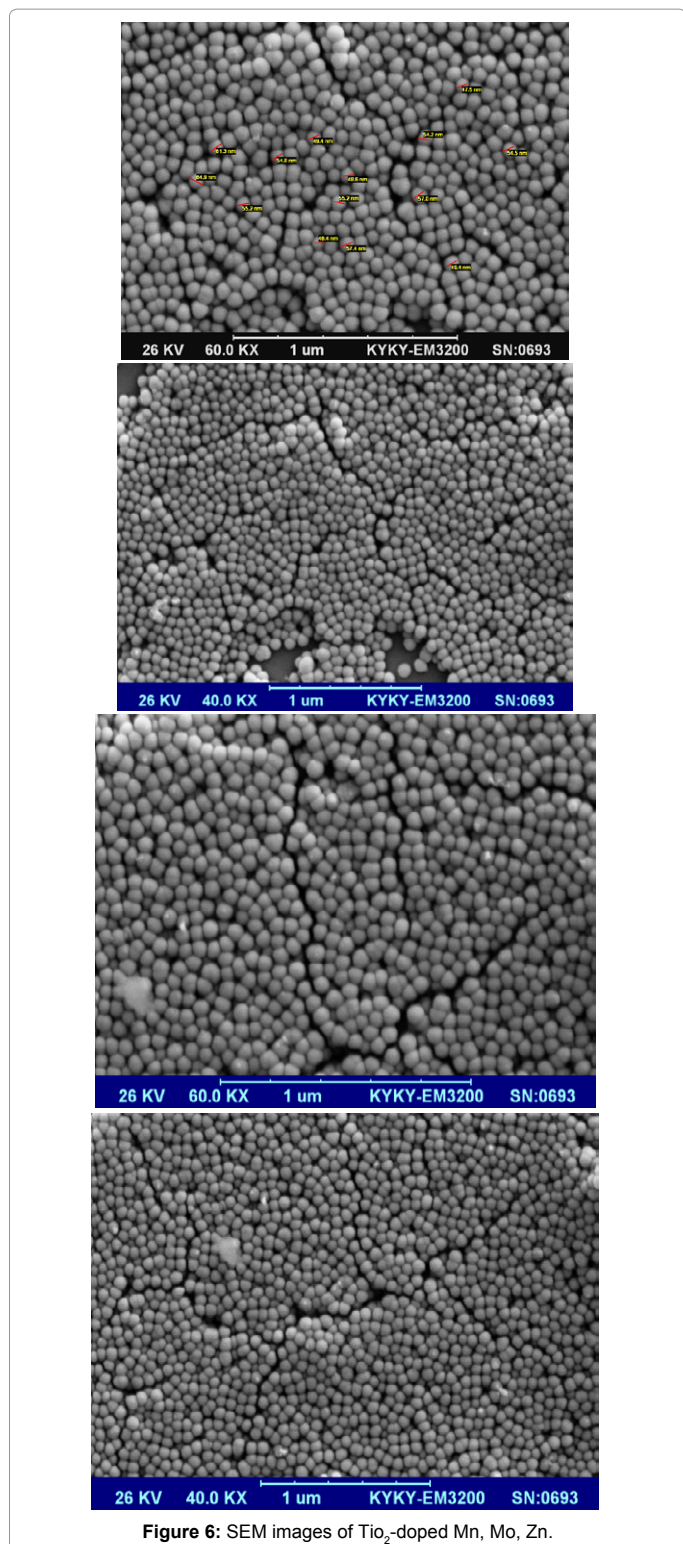


Figure 6: SEM images of Ti₂-doped Mn, Mo, Zn.

efficiency particularly, increasing inlet concentration to 1000 and 1400 mg/l resulted in decreasing COD removal 91% respectively.

Therefore the optimum surface loading rate based on inlet concentration (at HRT of 18 h) on the MBBR was found to be 6.62 g COD/m².day. Accordingly, the MBBR could effectively remove organic and inorganic contaminants in waste water, (Figures 10 and 11).

Figure 10 shows that organic and inorganic contaminants and COD removal efficiencies were not affected by reducing HRT down to 18 h and removal efficiencies of both parameters were greater than 91%.

The effect of salt content of wastewater ranging from 10 g/l to 70 g/l was assessed on the behavior of the MBBR under the previously optimized conditions given in Table 2.

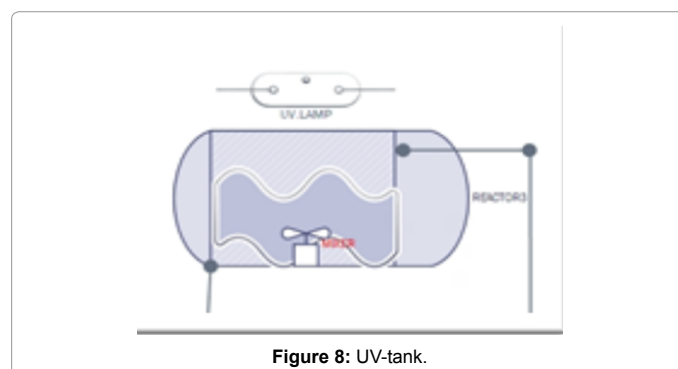
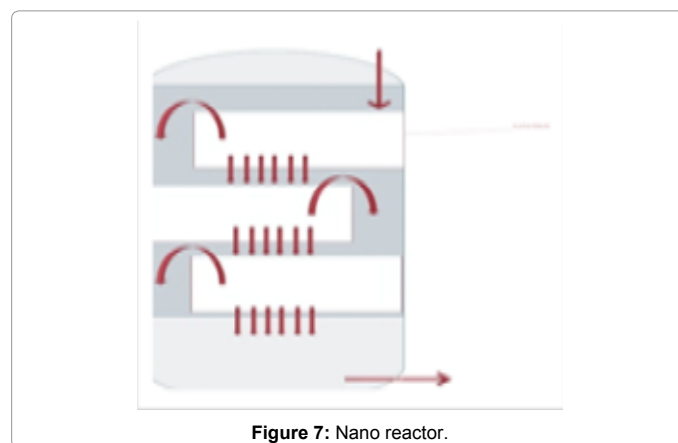
COD analysis in NANO reactor: A COD measurement by a photocatalytic oxidation sol-gel method using nano TiO₂ doped was investigated. In order to observe the quality of the aqueous solution, chemical oxygen demand (COD) measurements were also carried out before and after the treatment.

A significant decrease in the COD values was observed, which clearly indicates that the photocatalytic method offers good potential for the removal of organic and inorganic contaminants wastewater.

COD analysis in UV-tank: UV-VIS spectroscopy was suggested as fast and versatile monitoring tools for BOD and COD in water samples. This spectroscopy has also advantage of limiting measurements time for BOD from 5 days to few minutes and also limiting the usage of a large amount of expensive reagents. Absorbance of UV in wastewater to removal organic and inorganic contaminants shown in Figure 11.

Conclusion

4-steps process studied in this research, including pilot Skimmer tank, MBBR, Nano reactor and UV-tank that is, the ability to remove the COD has been quite successful. The amount MLSS rise, the resistance reactors against fluctuations will increase. The COD and organic and inorganic contaminants in wastewater much reduced in this 4 steps and process applicable on an industrial scale operation.



Experimental phases and MBBR operation timing schedule					
Phase	Day	Operation	C _{in} (mg/L) COD	Salt content (g/L)	HRT(b)
1	0-90	Biomass acclimation	107.5-1075	0-30	-
2	91-150	Effect of C _{in}	430-2580	30	24
3	151-190	Effect of HRT	1720	30	8-24
4	191-245	Effect of salt content	1720	10-70	18
5	246-247	Response to organic shock loading	-	30	18
6	248-249	Response to hydraulic shock loading	1720	30	-
7	250-251	Response to salt shock loading	1720	-	18

Table 2: COD analysis in MBBR.

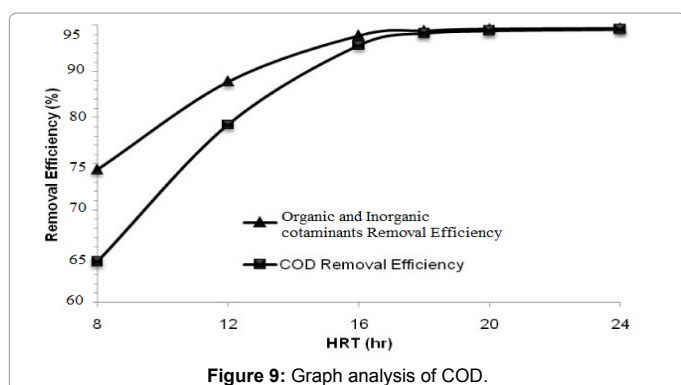
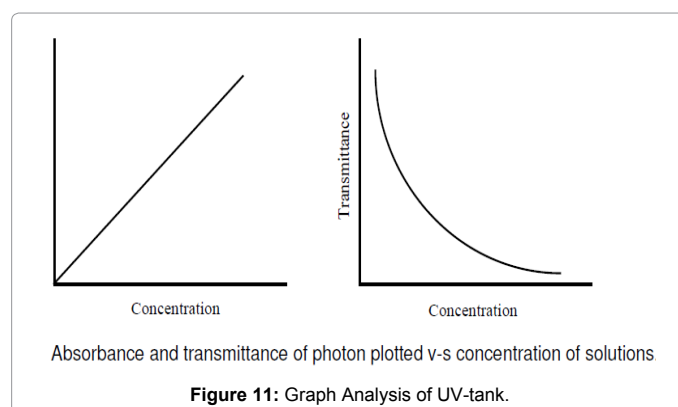


Figure 9: Graph analysis of COD.



Absorbance and transmittance of photon plotted v-s concentration of solutions

Figure 11: Graph Analysis of UV-tank.

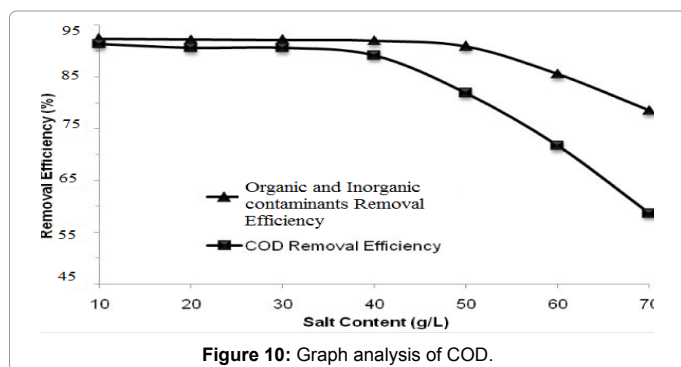


Figure 10: Graph analysis of COD.

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