Treatment of Automobile Service Station Wastewater by Coagulation and Activated Sludge Process

Debabrata Mazumder and Somnath Mukherjee

Abstract — **The present study is aimed to explore the pollution potential of automobile service station wastewater and to treat the same. The wastewater samples were collected from different servicing points of a typical automobile garage and then characterized for parameters like pH, Total solids, Total Suspended Solids, Chemical Oxygen Demand (COD) as well as Oil and Grease. A composite sample was also prepared on the basis of wastewater generation pattern. The characterization results revealed that oil and grease and COD were two major pollution parameters of concern. The composite oily wastewater was firstly treated using coagulants like alum, $FeSO_4$ and $CaCl_2$. The results showed that removal is feasible for initial oil concentration in the range of 300 – 600 mg/L for the alum dose of 100 - 400 mg/L, alum + bentonite dose of 20 - 250 mg/L and $FeSO_4$ dose of 50 - 200 mg/L. Subsequently, treatment of the composite wastewater with acclimated suspended biomass (activated sludge) resulted about 18 – 68% removal efficiency for initial oil and grease concentration of 300 – 600 mg/L under the batch period of 18 – 30 hours.**

Index Terms— **oily wastewater, automobile service station, treatment, coagulation, activated sludge process.**

I. Introduction

On-site wastewater treatment is a prospective direction towards the reduction of pollution load to the municipal or combined urban wastewater. One of such areas is automobile service station and car-washing. Some of the existing petrol pumps, fuel service stations are facilitated with car-washing. The large Car washing pools of garage and service stations are insisted upon by the respective pollution control boards to provide necessary treatment for the effluents. Professional car wash systems create wastewater that can have a great impact on the environment, if not properly managed and discharged. Contaminants in wash wastewater include oil and grease, detergents, phosphates, hydrofluoric acid, ammonium bifluoride products (ABF) etc. Oil and grease and detergents, including biodegradable detergents can be poisonous to fish. On the other hand, Phosphates, which are plant nutrients can cause excessive growth of nuisance plants in water bodies. Hydrofluoric acid, ammonium bifluoride products are harmful to living organisms [14].

Analysis of effluent wastewater from a large number of automatic vehicle washing facilities in Göteborg, Sweden exhibited a relatively high content of organic pollutants [8]. Soluble oil wastes are emulsion of oil in water and it just contains three components – the dispersed phase (oil), some emulsifying agents and the external phase. Emulsion may be broken by chemical, electrical or physical methods. Chemical methods are in widest use for treatment of oily wastewaters [5]. Kurian and Natarajan (1997) studied 40 samples from 10 automobile service stations and found total suspended solids, BOD_5, COD and oil and grease concentration in the range of 610 – 4950 mg/L, 75 – 570 mg/L, 270 – 1640 mg/L and 14 – 420 mg/L respectively [4]. Chemical treatment of the representative sample of such wastewater with alum and chitosan resulted in the effluent quality, satisfactory for disposal into the municipal sewer.

Reed *et. al.* (1998) performed pilot plant studies for a West Virgina, USA based company that produced high amount of oil containing wastewater [9]. Various treatment technologies such as dissolved air floatation (DAF), ultrafiltration (UF), biological filter even constructed wetlands were considered for treatment of such wastewater. Out of all the technologies, ultrafiltraion methodology was found to be most efficient. Pak and Chang (2000) reported that the wastewater generated from car-washing facility was characterized by relatively low organic and high phosphorus content [7]. The treatment of a simulated oil-in-water emulsion containing *n*-octane was investigated by means of dissolved-air flotation and jar-test [12]. The use of polyelectrolytes was not suitable to effectively treat the studied emulsions, whereas the addition of ferric chloride and the subsequent application of dissolved-air flotation were observed to be very efficient.

A highly saline offshore oilfield wastewater was microfiltrated through mixed cellulose ester (MCE) membranes, resulting in average oil and grease removal of 92% [2]. Then the permeate effluent was fed into a 1-L air-lift bioreactor containing polystyrene particles of 2 mm diameter, used as support material. After 210 days operation at a minimum hydraulic retention time (HRT) of 12 h, significant improvement in the effluent quality was achieved.

Mueller et al. (2003) reported a study on removal of oil and grease along with COD from de-emulsified oily automotive wastewater by adsorption technology using five adsorbents namely PAC, anthracite and three other modified clay

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adsorbents [6]. Out of five adsorbents, activated carbon and anthracite found to show highest and lowest adsorption capacity respectively towards removal of oil and grease concentration up to 30 mg/L. Ahmed et al. (2005) carried out a study with Palm oil mill effluent (POME) containing about 4000 mg/l of residual oil using three types of adsorbents – Chitosan, Activated carbon and Bentonite [1]. Chitosan showed the best removal compared to the other adsorbents. Chitosan, activated carbon and bentonite at the dosages of 0.5 g, 8.0 g and 10 g/L respectively had successfully removed 99% of residual oil from POME.

Zhao et al. (2006) investigated the performance of immobilized microorganisms namely B350M and B350 to pre-treat oil-field wastewater before desalination as an alternative to the conventional activated sludge (CAS) process [13]. During 142 days operation with hydraulic retention time (HRT) of 4 hours and volumetric load 1.07 kg COD (m3 d)−1 at last, the reactor immobilized with B350M and B350 showed average oil removal efficiency of 94% and 86% respectively. In a study the biological aerated filter (BAF) was used to treat the oil-field produced water [11]. The oil removal efficiency was observed to be 76.3% – 80.3%, when the hydraulic loading rates varied from 0.6m·h−1 to 1.4m·h−1.

Cañizares *et al.* (2008) compared the efficiencies of the chemical and the electrochemical break-up of oil-in-water (O/W) emulsions with hydrolyzing aluminium salts [3]. They obtained that the efficiency of the treatment depended on the total concentration of aluminium in the salts [$AlCl_3$ or $Al_2(SO_4)_3$]. The break-up of the emulsions was only observed in the range of pHs between 5 and 9. Aluminium hydroxide precipitates were found to be the primary species present in solution that favored the breaking process. In the light of above past experiences, a laboratory scale research investigation was undertaken to explore the feasibility of treatment of wastewater emanated from the car washing and automobile service station of a garage, owned by Kolkata Municipal Corporation in West Bengal, India.

II. Experimental

A. Description of Site

The present study was conducted in a garage at Kolkata in West Bengal, India. The garage is owned by Kolkata Municipal Corporation and usually handles the operation of heavy vehicles like Tripper truck, Dumper placer etc. These are used for carrying solid wastes either from container location or from transfer station. There are altogether 40 nos. of vehicles including recovery unit, storage van, trekker, jeep etc. in the garage. The activities of the Garage yard include the following:
(1) Tyre repairing section, (2) Body building section, (3) Engine overhauling section, (4) Vehicle running maintenance section, (5) Break down maintenance section, (6) Vehicle washing and servicing section, (7) Ancillary section, (8) Machine shop and (9) Procurement cell for collecting spare parts of vehicles.

B. Wastewater Survey

The wastewater is predominantly generated from washing of different types of vehicle. In the existing facility 2 to 3 vehicles are serviced on rotation basis. The washing is done by spraying high pressure water jets through nozzle guided by compressor motor assembly. Usually 2 - 3 kilo litres of water is used per day for washing of 2 to 3 nos. of vehicle. Grease gun is used to trigger lubricants to different parts of the vehicles as a routine procedure. Each garage unit is facilitated with one washing bay. For washing purpose, vehicles are aligned on the bay and high pressure water jet is sprayed on the vehicles. The washed wastewater is then drained to municipal sewerage system through the washing bay. The washing bay is made of cement concrete platform. The spent water containing dirts, oils and other solids is drained through gutters and then collected in a pit. The whole content of the raw effluent is led to the municipal drainage system through overflow system.

C. Collection and Preparation of Wastewater Sample

The investigation was carried out by grab sampling from the vehicle wastewater collection pit of washing area of the garage. The Supernatant wash was collected in a 2 litres capacity plastic container after settling for 1 hr. Another 2 litres sample was collected in the other container during the next vehicle washing operation. The process was continued for five successive vehicle washing operations in the same day and samples were collected @ 2 litres for 5 different heavy vehicles for one run of investigation. The samples collected from five consecutive operations were thoroughly mixed in a separate bucket of 20 litres capacity and then allowed to settle for 24 hrs. Supernatant of that composite sample of 10 litres volume was collected for further analysis and investigation. Such sampling process was adopted for 12 times at various dates.

D. Characterization of Wastewater

Different parameters like pH, Total solid, Total suspended solid, COD and Oil and Grease of the sample were measured in the Environmental Engineering Laboratory, Bengal Engineering and Science University, Shibpur. The results of characterization of different samples including the composite samples are presented in Table 1.

TABLE 1 : RESULT OF CHARACTERIZATION OF WASTEWATER SAMPLES FROM VARIOUS SOURCES

Sample Source	pH	Chemical Oxygen Demand (mg/L)	Total Solids (mg/L)	Total Suspended Solids (mg/L)	Oil and Grease (mg/L)
Heavy Vehicles	6.4 - 7.0	255 - 445	1200 - 6000	400 – 2000	400 - 800
Light Vehicles	7.1 - 7.6	227 - 378	800 - 1500	600 – 750	150 - 700
Composite Samples	6.2 - 6.6	280 - 360	1800 - 2500	1500 - 2000	300 – 700

E. Experimental Procedure

The removal of oil from garage wastewater was investigated by the chemical treatment method adopting coagulation and flocculation with different chemicals and the biological method using suspended active biomass. The method of coagulation and flocculation was carried out by standard "Jar Test" apparatus. In this set-up, five samples with different doses of coagulant added could be treated simultaneously or separately as required in the beaker of 1000ml capacity. 500 ml of the composite sample in each beaker was flocculated by individual stirrer rotated by a common driving shaft connected to a variable speed electric motor. The speed and time of mixing were adjusted to find out the optimum result for a specified coagulant dose. The activated sludge process (ASP) was employed to treat the oily wastewater by means of well-acclimated biomass culture under suspended growth condition. A biological reactor of about 2.5 litres active volume was operated under batch mode with adequate aeration and varying residence periods and biomass concentrations. All the parameters in characterization and treatability study were measured as per Standard Methods [10].

The chemicals used to perform coagulation and flocculation study are (a) Alum [$Al_2(SO_4)_3.14H_2O$], (b) Alum with Bentonite powder (a soil material with high plasticity), (c) Ferrous Sulphate ($FeSO_4$, $7H_2O$) and (d) Calcium Chloride ($CaCl_2$) with Bentonite. Optimum pH required for effectiveness of coagulation was achieved by addition of required amount of lime water. Experimental samples prepared with initial oil and grease concentration of 300 mg/L and 600 mg/L were stored in two separate storage tanks of 20 litres capacity. Afterwards, the samples were allowed for a detention period of about 24 hours with a view to separate "free oil" if any. Sample was withdrawn by dipping pipette at different levels inside the container. Optimum chemical dose corresponding to maximum removal of oil was determined by conducting "Jar Test". Temperature of wastewater sample in the storage tank and during coagulation-flocculation was recorded by a thermometer.

In case of biological method, domestic wastewater was collected from a near-by drain and then its constituent microorganisms were fed with a gradually increasing dosage of oily wastewater. During acclimation, pH, MLSS (mixed liquor suspended solid) and oil and grease concentration were regularly measured to check the degree of acclimation. The acclimation phase was considered to be over after about 40 days, when steady biomass growth was observed for a specific quantum of oil and grease removal. After the acclimation of suspended biomass, the biological reactor was subjected to a varying biomass and oil and grease concentration in the range of 2000 – 3000 mg/L and 300 – 600 mg/L respectively under varying batch periods of 18 – 30 hrs. All the parameters as in acclimation were measured for both the initial and final condition. The performance of the biological reactor was expressed in terms of percentage removal of oil and grease over a certain time period.

III. Results and Discussion

A. Performance of Coagulation and Flocculation

The performance of coagulation and flocculation of wastewater samples with initial oil and grease concentration of 300 and 600 mg/L under Jar Test are shown in Table 2 and Table 3 respectively. The results as obtained in coagulation-flocculation experiment using different coagulants for destabilization of emulsified oil and grease are also plotted in Figure 1 to Figure 4. It is evident from all the figures that percentage removal of oil and grease increased when the chemicals were added in higher concentrations.

TABLE 2 : Performance of Coagulation and Flocculation of Wastewater with Initial Oil and Grease concentration of 300 mg/L

Coagulant used	pH	Coagulant Dose (mg/L)	Initial conc. of Oil and Grease (mg/L)	Residual conc. of Oil and Grease (mg/L)	Removal (%)	Temp. (^{0}C)
Alum	7.8	100	300	200	33	33
		125	300	150	50	
		150	300	100	66	
		175	300	50	83	
		200	300	Nil	100	
Alum + Bentonite	7.6	20	300	195	35	29
		30	300	146	51	
		40	300	98	67	
		50	300	48	84	
		60	300	Nil	100	
$FeSO_4$	10.5	50	300	190	37	32
		75	300	140	53	
		100	300	95	68	
		125	300	45	85	
		150	300	Nil	100	
$CaCl_2$ +Bentonite	7.5	100	300	205	32	33
		150	300	155	48	
		200	300	105	65	
		250	300	52	83	
		300	300	Nil	100	

Note : *Lime water was used for adjusting pH*

The results of coagulation-flocculation showed that the requirement of alum was higher than $FeSO_4$, but almost equivalent to $CaCl_2$, while acting together with Bentonite powder. It has been observed that chemical process can remove oil and grease with high efficiency and even 100% removal is also possible. Bentonite powder performed very well as a coagulant aid particularly with alum and it lowered necessary alum dose. The pH required to carry out coagulation with alum is close to neutral value and there is no change of pH in presence of Bentonite powder also. It is to note that pH required for alum coagulation is matching with that of the real garage wastewater necessitating no adjustment. Although $FeSO_4$ is required in lesser amount with respect to alum, raising the pH to alkaline stage (about 10.5) is essential. The removal of oil and grease by $CaCl_2$ in presence of Bentonite powder is not promising even with high dosage of $CaCl_2$. It was observed that $CaCl_2$ along with Bentonite produced signficant volume of sludge in comparison to other coagulants.

TABLE 3 : Performance of Coagulation and Flocculation of Wastewater with Initial Oil and Grease concentration of 600 mg/L

Coagulant used	pH	Coagulant Dose (mg/L)	Initial conc. of Oil and Grease (mg/L)	Residual conc. of Oil and Grease (mg/L)	Removal (%)	Temp. (^{0}C)
Alum	7.7	100	600	450	25	30
		200	600	300	50	
		300	600	200	66	
		350	600	100	83	

		400	600	nil	100	
Alum + Bentonite	7.6	50	600	400	33	28
		100	600	300	50	
		150	600	200	66	
		200	600	100	83	
		250	600	nil	100	
$FeSO_4$	10.2	100	600	250	58	32
		125	600	200	67	
		150	600	150	75	
		175	600	100	83	
		200	600	Nil	100	
$CaCl_2$ +Bentonite	7.6	100	600	500	22	33
		200	600	350	42	
		300	600	200	66	
		400	600	50	91	
		500	600	Nil	100	

Note : *Lime water was used for adjusting pH*

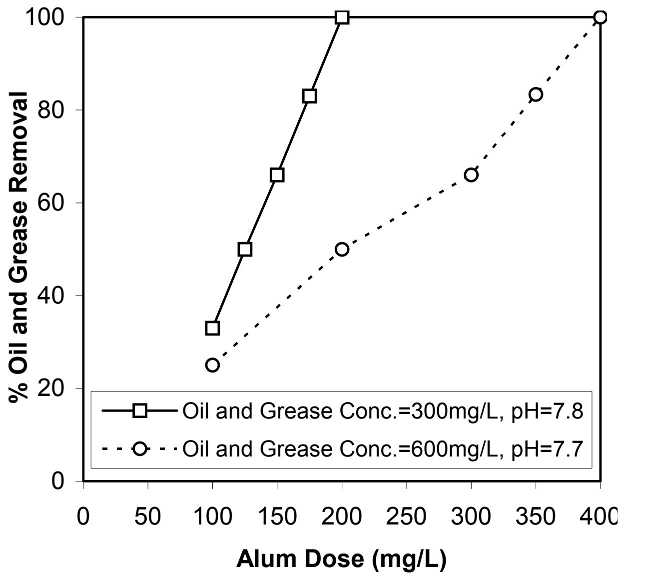

Figure 1: Performance of Oil and Grease removal under varying Alum doses

Figure 1 reveals that removal of oil and grease takes place with a fast rate and linearly in case of initial concentration of 300 mg/L. The rate of removal decreases considerably for initial oil and grease concentration of 600 mg/L particularly for the low range of alum doses. Addition of Bentonite powder to alum drastically improved the rate of oil and grease removal and performance curves are observed linear in both cases (Figure 2). Figure 3 showed that $FeSO_4$ dose as low as 100 mg/L was required to cause a removal in the tune of 50% and more for oil and grease concentration of 300 and 600 mg/L. Similar to the earlier cases the rate of removal is low in case of higher initial concentration and it is not linear at all. It is evident from Figure 4 that $CaCl_2$ doses of at least 150 and 250 mg/L are required to achieve 50% or more removal in case of 300 and 600 mg/L of oil and grease concentration respectively. Comparatively higher dosage of $CaCl_2$ is required even in presence of 1 gm of Bentonite to ensure better removal efficiency indicating low potential of $CaCl_2$ in this regard.

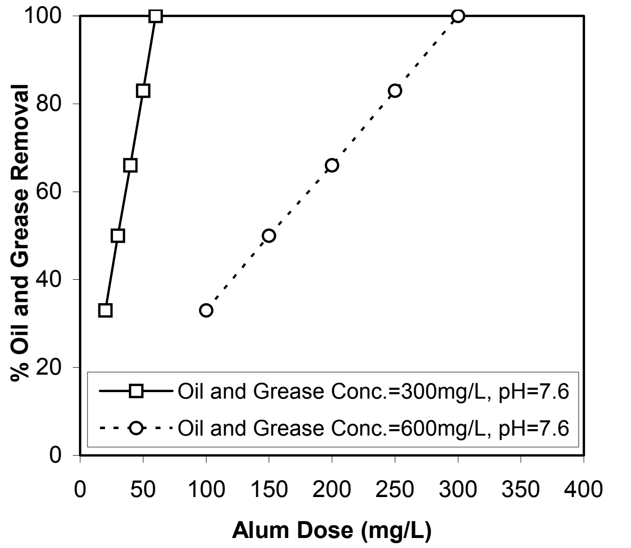

Figure 2: Performance of Oil and Grease removal under 1 gm Bentonite and varying Alum Doses

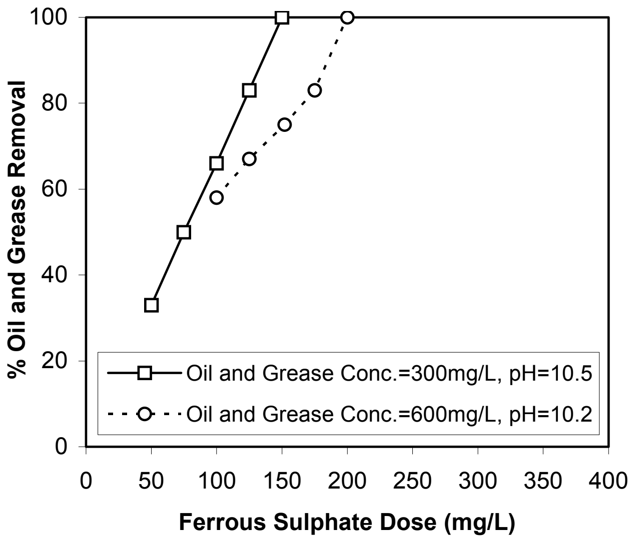

Figure 3: Performance of Oil and Grease removal under varying $FeSO_4$ Doses

B. Performance of Biological Reactor

The performance of the biological reactor using suspended growth microorganism for oil and grease removal is presented in Table 4. The results of this batch study showed the percent removal of oil and grease subjected to varying biomass concentration over different batch periods. As an operating parameter, Food to Microorganism ratio (F/M ratio) is introduced, which represents "available oil and grease per unit amount of biomass in the reactor" i.e. the ratio of concentration of "oil and grease and suspended biomass". In order to calculate the (F/M) ratio, the reactor volume, the suspended biomass and the initial oil and grease concentration are designated as V, X and S_0 respectively. The values of percent removal of oil and grease are plotted with respect to (F/M) ratio for different batch periods as shown in Figure 5.

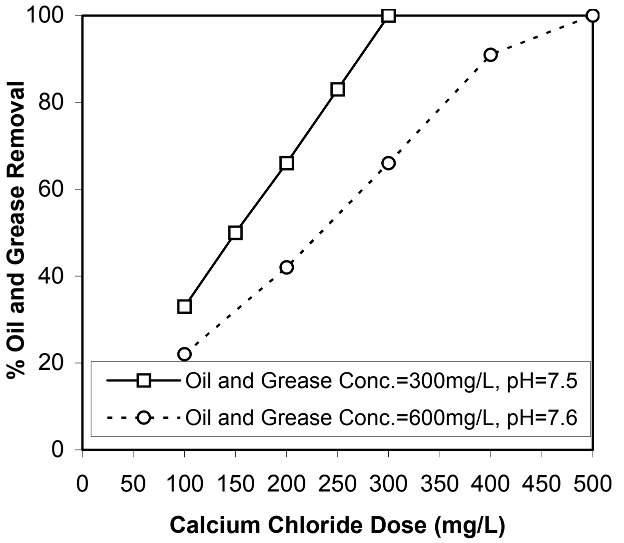

Figure 4: Performance of Oil and Grease removal under 1 gm Bentonite and varying $CaCl_2$ Doses

TABLE 4 : PERFORMANCE OF BIOLOGICAL REACTOR FOR OIL AND GREASE REMOVAL UNDER BATCH STUDY COD REMOVAL PERFORMANCE

Run No.	pH	Batch Period (hr)	Suspended Biomass Conc., X (mg/L)	Oil and Grease Conc., S_0 (mg/L)		F/M Ratio $= \frac{V.S_0}{V.X} = \frac{S_0}{X}$	% Removal
				Initial	Final		
1.	7.4	18	2000	300	245	0.150	18.3
2.	7.6	18	2250	300	228	0.133	24.0
3.	7.3	18	2500	300	212	0.120	29.3
4.	7.6	18	2750	300	206	0.109	31.3
5.	7.5	18	3000	300	195	0.100	35.0
6.	7.4	24	2000	300	205	0.150	31.7
7.	7.6	24	2250	300	186	0.133	38.0
8.	7.5	24	2500	300	174	0.120	42.0
9.	7.7	24	2750	300	145	0.109	51.7
10.	7.5	24	3000	300	120	0.100	60.0
11.	7.4	30	2750	300	126	0.109	58.0
12.	7.6	30	3000	300	95	0.100	68.3
13.	7.4	24	2500	600	458	0.240	23.6
14.	7.6	24	2750	600	416	0.218	30.7
15.	7.5	24	3000	600	362	0.200	39.7
16.	7.6	30	2250	600	324	0.266	46.0
17.	7.5	30	2500	600	305	0.240	49.2
18.	7.6	30	2750	600	262	0.218	56.3
19.	7.5	30	3000	600	248	0.200	58.6

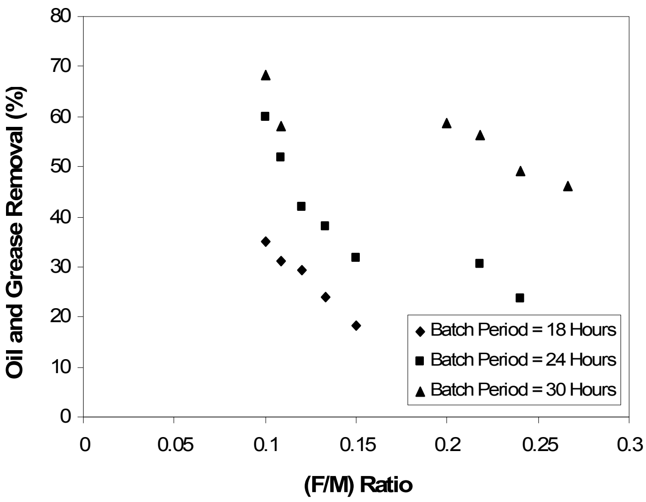

Figure 5 : Percent Removal of Oil and Grease Vs. (F/M) ratio

The performance of biological treatment of automobile service station wastewater reveals that the removal efficiency decreases with the increase in (F/M) ratio (Figure 5). In case of a batch period of 18 hours, only 35% removal was attained for a biomass concentration of 3000 mg/L at (F/M) ratio of 0.1. A long batch period of 24 hours or more is required to achieve a removal efficiency of about 60% at the same (F/M) ratio. Since, MLSS concentration is an important parameter related to (F/M) ratio, it is possible to increase the applied oil and grease concentration for higher biomass quantity. But, there was some difficulty in sludge separation for biomass concentration greater than 3000 mg/L because of too tight sludge matrix. Therefore, the batch period was enhanced to 30 hours, which showed about 70% removal efficiency for a biomass concentration of 3000 mg/L at a (F/M) ratio of 0.1. It is obvious that the oil and grease removal efficiency has been reduced on account of higher (F/M) ratio, in turn lower biomass concentration. Considering all the facts, a biomass concentration of about 3000 mg/L and (F/M) ratio of 0.1 can be recommended for appreciable removal of oil and grease under varying batch periods as necessary.

IV. CONCLUSIONS

The following conclusions can be drawn from the present study:

- The wastewater contained high amount of suspended solids and oil and grease as maximum as 2000 mg/L and 800 mg/L respectively. The large quantity of oil was present both in emulsified and non-emulsified form.
- Chemical coagulation by Alum, Alum along with Bentonite powder, Ferrous sulphate and Calcium Chloride in presence of Bentonite powder may be practiced for complete removal of oil and grease.
- Alum performed well for low concentration of oil and grease (up to 300 mg/L) and addition of Bentonite powder ensured appreciable removal efficiency for high concentration in the tune of 600 mg/L.
- Ferrous sulphate is an effective coagulant for the removal of oil and grease in the range of (300 – 600) mg/L, which is required in comparatively low amount. However, in

such a case raising the pH is essential to achieve alkaline condition.

- Calcium chloride also performed well in presence of Bentonite powder, but with a comparatively high amount. It also produced a significant quantity of calcium containing sludge, which may be cumbersome to get dewatered.
- Biological treatment of automobile service station wastewater is feasible under batch mode, but it would take at least 30 hours to attain the removal efficiency of 70% or more for a biomass concentration of 3000 mg/L and at a (F/M) ratio of 0.1.

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