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Wastewater Treatment of Tanneries Industry through Bio-ozone-biotreatment

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Abstract**—***This paper reports the results obtained during an investigation aimed at evaluating the laboratory-scale performance of an innovative process integrated with ozonation for the efficient treatment of tannery wastewater. In this process, biological degradation which carried out in a sequencing batch biofilm reactor (SBBR), is combined with chemical oxidation by ozone. The tannery wastewater treatment was carried out on a real primary effluent coming from a centralized plant treating wastewater produced by a large tannery district in Iran. SBBR performance both without and with ozonation, was assessed with very satisfactory results. The results showed that the integrated process was able to achieve high removal efficiencies for COD, TSS, surfactants and color with residual concentrations much lower than the current discharge limits. In particular, in the latter instance of the recorded COD and TSS average removals were (93%) and (99%) in phase I and (97%) and (99%) in phase II respectively. During the investigation biofilm properties (biofilm concentration and biofilm density) and flow dynamics aspects (head loss, shear stress, bed porosity) were also studied. Furthermore, the process was characterized by a very low sludge production (i.e., 0.1 kg dry sludge/m3 of treated wastewater) and high biofilm density (i.e. 87-122 gVSS/Lsludge) both contributing to a rather high biofilm concentration (i.e. 31-44 gTSS/Lfilter) with interesting repercussions on treatment costs (about 1.5 € per m3 of wastewater).*

Keywords**—** *Ozonation, Tannery, Treatment, Wastewater*

I. INTRODUCTION

Production cycle of leather consists of a lot of chemical materials (such as acid, chromatic materials, natural and artificial sulphate oils, salt, and etc) which are used for changing animals` skins in order to be unchangeable. According to the much amount of such materials and having different kinds of chemical materials, treatment becomes more serious.

In fact after common treatment (adding chrome, primary sedimentation, biological oxidation, and secondary sedimentation) wastewater has not reached to the final amount of some parameters such as Chemical Oxygen Demand (COD), salt, or ammonia yet [1], [2].

According to the COD in this method the amount of organisms extinct usually decreases by adding activated carbon powder directly to the biological reactor or by the third valuable way that is Fenton process. The principle steps are as followings; adding Fe So_4 or Fe Cl_2, acidifying the sulfuric acid wastewater**,** oxidation ($H_2O_{2)}$, neutralizing [Ca (OH) $_2$] CPH, and using Fenton method for separating soda with the effect of 90% [3].

Productions arising by chemical sludge during PH neutralization(1 kg TSS/$m^{3)}$, and considerable use of chemical materials (such as Fe SO_4, Fe Cl_2, H_2SO_4, Ca (OH) $_2$) are the problems caused by the necessary acid condition of Fe`s concentration in treated wastewater in this method.

II. MATERIALS AND METHODS

The solution for conquering these problems is the method of combination of biological dissolution with ozone oxidation [4], [5]. The final step causes simplifying the chemical structure of biological dissoluble materials which is necessary for improving the biological dissolution. Although the effect of such a combination has become practical for treatment of wastewater and making it transparent, a serious attention has been paid to the possibility of alternative use of the system [6]. This system has been improved very well because of its considerable operation adaptability [7]. In fact it works under a searching condition which causes improvement of biological dissolution to a suitable condition like what happens in tannery`s wastewater because of bridles. Furthermore about the combined method, the alternative system causes the combination of the two methods in one unit [8], [9]. In this study the alternative system has been combined with ozonation and the effect of such multi part process is valuable for the wastewater treatment [10].

A cylinder reactor with a rising flow at the fixed temperature of 20^0C with an external ring for the wastewater flow with the help of a pump was used. The flow caused the micro-organisms and the under layer to be mixed in the reactor`s depth and increased the ability of the process for overcoming the over load in comparison with the continuous flow during bio-filteration [11]. During filling, the slope of concentration increased along the reactor that this slope became fixed when the flow continued again, and the contents were mixed. Because of the high flow (100 l/h), and the linear velocity, the increase of concentration`s slope was limited to the filling time and the beginning of the reactor`s phase. Plastic materials were located in SBBR in order to support the bio mass. Having a strainer-like substance at the top and bottom of the reactor prevented plastics` departure. Oxygen was provided by little bubble makers at the bottom of the reactor. At the beginning of each cycle the certain primary volume of wastewater was pumped in to the system, and then it flew along the whole reactor and finally left there. For removing the excess biological mass the bottom of the reactor had to be repeatedly cleaned by an air compressor and

cleaners. The cleaned materials such as VSS, TSS, were collected and measured. Parameters such as insoluble DO (dissolved Oxygen), temperature, and PH were successively regulated.

Ozonation was done in a reactor that ozonated air was regularly injected from wastewater in to it in order to perform the treatment. This reactor model was completely a combined model, therefore the reactor`s concentration was fixed in the liquid phase. For availability to a rate of impurity which is necessary for the ozone generator [12], [13], the air which was used as the source of oxygen was treated and processed before anything else in order to be cleaned out of any fat, moisture, hydro carbons, and dust, although ozone`s productions were changeable by the much electrical current and regulating the air. In this study these two parameters were arranged 0.8 A and 100 l/h respectively. Ozonated air was blown in to the reactor that here the magnetic mixer plate provided effective mixing conditions for the complete solubilization of gas in the liquid phase [14], [15]. At the end of ozonation phase the remaining ozone in the liquid phase was cleaned by about 5 hour air blowing.VSS, PO4-P, NO3-N, NH_4^+-N, and TSS are measured according to the standard methods.

With the acceptance of the SBBR operation`s conditions such as warranty of being metabolized completely from floating solid organics, it was possible to measure the bio productions according to the production of a specific sludge [16], [17]. It was measured by dividing bio production to the amount of COD [18].

The average experimental activities were specified by two periods A and B. A and B were off along the first period of ozonation unit, and the treatment plat`s laboratory was working. In this period each cycle was divided to four respective phases: filling, anoxic, aerobic, motive phase. At the beginning the nutrition was completely diluted with water and causes adaptability of micro-organisms with the bridles. This dilution was reduced to zero and at the end of the beginning step this adaptability occured. Period A included 3 parts that each one was identified by a especial operation`s condition. During the second period (B) biological vivification was accompanied with ozonation. In the first phase the wastewater was treated by the both aerobic and anoxic methods. Successfully a fixed amount of complete ozonated volume was returned to SBBR and treated again. Period B was in 2 steps which was possible to be identified by the different amounts of the ozonated volume (Table I).

TABLE I. Operation parameters during the runs of periods A and B.

Parameters	Period A			Period B	
	Run I	Run II	Run III	Run I	Run II
Organic Loading (kg COD /m^3d)	3	2.2	2.1	1.6	1.6
Kg BOD_5/ m^3d	1.9	1.4	1.3	1	1
Influent Flow Rate(L/cycle)	4	3	2	2	2
Ozonated Working Volume(L/cycle)	-	-	-	2	6
Cycle Time (h)	8	8	6	8	8
Cycle Time (min.)	480	480	360	480	480
Filling Phase (min.)	4	3	2	2	2
I Anoxic Phase (min.)	60	60	60	120	120
I Aerobic Phase (min.)	409	410	292	180	180
Drawing and Filling Intermediate Phase(min.)	-	-	-	10	20
II Anoxic Phase (min.)	-	-	-	60	50
II Aerobic Phase (min.)	-	-	-	103	103
Final Drawing Phase	7	7	6	5	5

TABLE III. Performances during the runs of Period B (Average Values).

Parameters	Phase	Run I	Run II
COD(mg/L)	Influent	3700	3700
	Influent [a]	3100	3100
	Intermediate Effluent [b]	285	185
	Ozonated Intermediate Effluent	262	155
	Final Effluent	255	125
TOC(mg/L)	Influent [a]	740	740
	Intermediate Effluent [b]	118	63
	Ozonated Intermediate Effluent	104	58
	Effluent	111	43
NH_4-N(mg/L)	Influent [a]	260	260
	Intermediate Effluent [a]	5.4	5
	Effluent	4	3
NO_X-N(mg/L)	Influent [a]	1	1
	Intermediate Effluent [b]	22.6	23
	Effluent	23	19
TSS(mg/L)	Influent	2200	2200
	Effluent	≈2	≈2
COD removal (%)		93	97
NH_4-N (%)		98	98.5
TSS removal (%)		99.9	99.9

III. Results and Discussion

A. Operation during period A (without ozonation)

Operation was done during 3 steps in period A that according to the experiment`s conditions in the first part of these 3 steps we reached the information which comes in table I.

We suppose that in step I over organic load had not been reached; the attempt in the second step was done in order to reach to COD limit to decrease the organic load. By the way as it is revealed in the table, this attempt does not have a positive result. So at last in steps I and II we can conclude that the amount of COD (280 mgO_2/L) in the treated wastewater provided the necessary COD limit for SBBR.

It is achieved that COD was cleaned in the best way during the first 2 hour and then the left amount was considered in the next 6 hours. Like step III in spite of being specified with the same organic load, the amount of excess COD was considerably more. With the consideration of this fact that in steps I and II nutrition was separated from the wastewater source which was replaced during step III, we can explain this conclusion that the other important point which should be taken in to consideration was the much difference between the COD measured at the end and the COD which was derived theoretically. The difference was because of storage process that occured because of the short period of filling. According to the removed ammonia, the available information revealed the high amount of removing which was done during nitrification, and showed this fact that ammonia nitrification was not related to the organic load. In alternative system the condition caused that these two processes of COD separation and nitrification happened after each other. In the experiment of Concentration-Time for COD and ammonia error was clear. In this test it was seen that nitrification began when COD was completely separated. According to NO_x-N as its final concentration in steps I and II was always more than the limits, in the third step the number of cycles was increased. These changes caused increase of nitrification simultaneously in SBBR, and nitrogen`s balance became more. In table II the value of all organic solid materials during a period and between two washer cycles is given. In this table the measured excretory materials might be less. This amount that showed the sustainable conditions is much less than what existed normally in the reactor.

B. Operation during period B (with ozonation)

In the whole duration of B when the vital acts became synchronized with ozone oxidation, wastewater became completely ozonated. The sample showed that the oxidation reaction completed after 60 minutes. When the value of ozone in the excess gas reached to the amount which existed in the effective gas, it was distinguished from the existing sample that it is possible to find the effective flow and the transferred ozone dose.

The same as Semibatch reactor, and based on the volume changes of reactor during the performance of the experiment the total amount of ozone which was out of the reactor at last became 217 mgO_3, and according to this method the value of TE and the transferred dose were respectively 58% and 30 mgO_3/L. The SBBR operation in two steps during period B is given in table II. The value of COD in the table shows that during step II, the treatment plant had a better operation (97%) than in step I (93%) with the COD concentration of 125mg/L which is less than the limit (170mg/L). The information that is given about COD and TOC proves that a very little volume of COD in the final wastewater during step II needs the two known processes to be performed during ozonation, so that they cause changing of some organic materials to mineral ones and also oxidation of some parts of organics. Now it is possible to measure the decreasing of COD arising by the little oxidation. The improvement of biological decreasing which was measured during ozonation (40-50 mgC_3/L COD_5) makes the occurrence of such oxidation. More over the recorded denitrification during the second phase of anoxic only happens when the organic biological vivificated combination occurs during ozonation phase. It is also proved that the concentration of NO_X-N at the end of step II in period B was less than that of step III in period A. No difference was recorded between the excretory production in period A and B, and the production of sludge was also less than before.

IV. Conclusion

After doing the experiments for treating tannery`s wastewater through a complete process based on the combined biological process in SBBR with chemical oxidation and especially by the use of ozone, the two main results that have been achieved in the treatment plant`s operation are suitable conclusions. First, more effect for removing COD (97%), Ammonia (98%), and Suspended Solids (99) was recorded. Second, the combined process is identified with very little solid productions, in fact the average production of sludge which was measured was 0.03 (kg VSS/kg COD), and it is very less than the sludge production through the common biological treatment method (0.3-0.5 kg TSS/kg COD). Treatment with ozone can play the role of a neutral against what activated carbon does in direct physical-chemical preparation of wastewater. Using ozone instead of activated carbon does not have a big effect on yearly costs, and provides a lot of inherent benefits.

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