Treatment of municipal wastewater in Gaza strip in the presence of hydrogen peroxide

Samia M. Mokhtar[*], Khaled M. El-Sousy[**], Mahmoud M. Isa[***], and Monther F. Salem[****]

الملخص

ركزت هذه الدراسة على مرحلة الأكسدة الهوائية للمياه العادمة في وجود فوق أكسيد الهيدروجين، اعتمادا على مقالات سالفة شجعت على ذلك، حيث أخذت عينات حقيقية من محطة التجميع المركزية بمدينة غزة، استخدمت في هذه الدراسة، كما أنه قد تم بناء نظام محاكاه مصغر في المختبر مشابه لمحطة المعالجة التابعة للبلدية.

تم في هذا العمل الوصول الى الظروف المثلى لهذه المعالجة من كمية فوق أكسيد الهيدروجين و درجة الحرارة و امكانية استبدال التهوية الميكانيكية باضافة فوق أكسيد الهيدروجين. كما تم تتبع بعضا من الصفات الكيميائية و الفيزيائية و الميكروبيولوجية للماء المعالج و ذلك لالقاء المزيد من الضوء على التغيرات الحادثة أثناء عملية المعالجةو مقارنتها بالطريقة التقليدية باللاضافة الى الجانب الاقتصادي والذي لم يكن مشجعا.

Abstract

For real municipal wastewater samples, taken from the central collection station in Gaza city, aerobic oxidation of wastewater have been studied in the presence of hydrogen peroxide. A simulation for the real treatment station have constructed in the laboratory to study the effect of different parameters under the same real treatment conditions. Optimum conditions have been arrived for the ratio of H_2O_2:COD and temperature. Possibility of substitution of aeration with the addition of hydrogen peroxide have been tested. Physical, chemical, and microbiological properties of the treated wastewater have been followed through the course of treatment and compared with the classical treatment. The additional cost of treatment in the presence of H_2O_2 has been calculated and was not encouraging.

Key wards: Physical chemistry, kinetics, aerobic oxidation, wastewater treatment, hydrogen peroxide, COD, BOD, and TDS.

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1.Introduction

Numerous municipal facilities around the world are taking steps to reduce or eliminate the use of gaseous chlorine and to convert to the treatment by H_2O_2 as disinfectant. Environmental and safety concerns surrounding the use of hydrogen peroxide are some of the driving forces behind this movement[1]. It was reported also that the use of H_2O_2 as a bad smell inhibitor where it was supposed to oxidize directly the easily oxidized species such as sulfides and thioles[1].

The use of H_2O_2 as an oxygen supplier was also suggested in literature[1], it is thought that the presence of hydrogen peroxide up to some limit in the treated wastewater bulk especially through the aerobic oxidation stage may promote aerobic bacteria by increasing the concentration of dissolved oxygen beside the direct oxidation of the easily oxidized species[2].

In addition to the initial drop of COD the expected acceleration of the aerobic oxidation may lead to more economical process for the treatment of wastewater projects.

In the present research the influence of the addition of hydrogen peroxide is studied, optimum ratio of (H_2O_2 : COD) is to be estimated, optimum temperature also, the possibility of exchange aeration of the bulk by the presence of H_2O_2 is tested.

The influence of hydrogen peroxide on the physical, chemical and microbiological properties of the treated wastewater is followed and finally the economy of the use of H_2O_2 will be reported.

2.Experimental

2.1.Materials. H_2O_2 35 % w/w has been purchased from (Akross Belgium), Sulphuric acid 96 % was analytical grade (Merch), Potassium dichromate was analytical grade (B.D.H) products, KHP potassium hydrogen phthalate, MnO_2 powder were obtained from (B.D.H-U.K).Water used was distilled to the level of = 60 ppm (TDS).

2.2.Apparatus. Two identical treatment bathes, with identical aeration pumps, recycling pumps have been used as standard and measurement systems with the best possible simulation of the real treatment project.

COD (chemical oxygen demand), BOD (biochemical oxygen demand) and microbial contents (total coliform) determinations were conducted by using apparatus similar to the WHO standards[3,4,5,6,7,8]. Electrical conductivity (EC), conductivity total dissolved solids (TDS), dissolved oxygen (DO), pH, and Turbidity have been measured directly using Sens **ion**^{TM} **5** Conductivity Meter, Sens **ion**^{TM} **6** portable dissolved Oxygen Meter, Sens **ion**^{TM} **1** portable pH Meter, Turbidimeter Model 2100p respectively all from (Hach Company , U.S.A).

CECEIL /CE1020 Spectrophotometer (CECEIL Instrument, Cambridge –England) have been used at 600nm for spectrophotometric measurements using 1.0 cm quartz cells in COD measurements.

For (TDS oven method) BIFA – Laboratory Furnaces, temperature range 0.0 to 1050 °C have been used at 500^{0}C.

2.3. Methodology. The main aerobic oxidation process was always conducted for two identical municipal wastewater 19.0 L each, the standard sample and the experimental samples have been treated identically under the same conditions such as aeration power, recyclization power, working temperature etc. except the presence of H_2O_2, which was only in the experimental treated wastewater bulk, the proper amount of H_2O_2 solution was usually added at zero time. Samples have been taken identically for all the measurements conducted through the course of the process, which was always five days period.

COD, BOD and Total-coliform contents determinations were conducted according to the WHO standard procedures[3,4,5,6,7,8]. Except that for the samples containing residual H_2O_2, MnO_2 powder was used in relatively big amounts (1.0 g for each sample) to decompose H_2O_2 [9]which is supposed to interfere the COD standard procedure[10] then the samples were filtered to remove the MnO_2 catalyst. Electrical conductivity (EC), conductivity total dissolved solids (EC-TDS), dissolved oxygen (DO), pH, and Turbidity have been measured directly using portable instrument for each test. Inorganic total dissolved solids (IO-TDS) substrate method results have been obtained by subtracting the results of COD from the results of (Oven TDS) or/and (EC-TDS) obtained by the oven method for two identical sets of samples taken at for different time intervals from the treated wastewater bulks.

3.Results and Discussion

3.1. Optimum Conditions. For the aerobic oxidation of wastewater in the presence of H_2O_2, it follows from the results shown in (Table1) and (Fig.1a,1b) that the aerobic oxidation of wastewater in the presence of H_2O_2 had a first order kinetics with respect to COD (after the initial drop which was immediate). It follows from the results shown in (Table2) and (Fig.2) that the initial COD drop was increasing by increasing H_2O_2:COD ratio although the efficiency of causing higher initial drop seems to decrease by increasing the ratio (dCOD drop /dRatio), so lower ratios ware more efficient than higher ratios in this manner.

It follows from the results shown in (Table2) and (Fig.3) that the specific rate constant was increasing by increasing H_2O_2:COD ratio, the optimum ratio estimated from (Fig.3) was 1:1, H_2O_2:COD. From (Fig.2 and Fig.3) optimum ratio have been chosen to be(1:2 H_2O_2:COD) on the bases of maximum activity and more efficient COD initial drop.

Table (1): The relation between COD and time of treatment at ratio of $[H_2O_2]$: COD = (0.25:1.0). Recycling rate: 0.65 $m^3 .min^{-1}$, Bath capacity: 19.0 L, $[H_2O_2]_o$ = 642 ppm, Bulk Temp.: 31.0 ±0.5 °C.

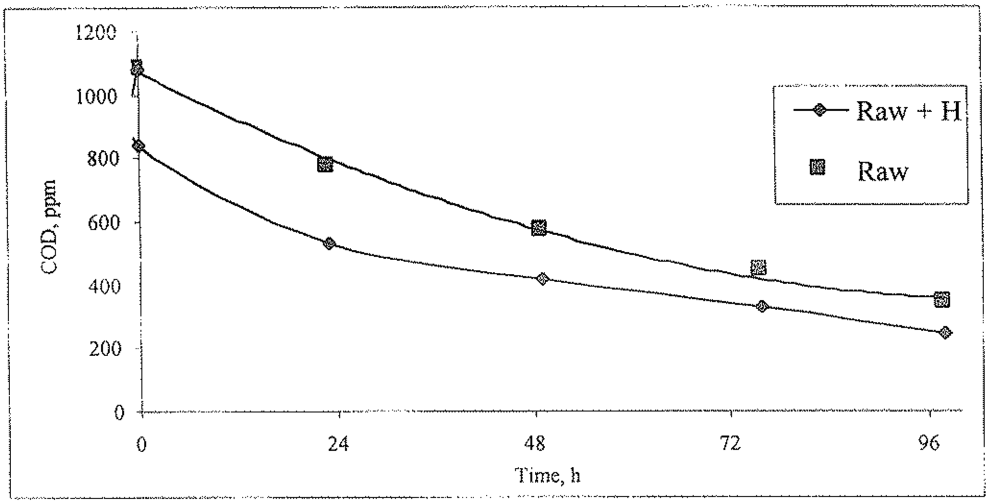
Time	Raw + H		Raw	
(h)	COD	ln COD	COD	ln COD
0	1080	7.0	1080	7.0
0	840	6.7	1080	7.0
23	530	6.3	770	6.7
49	420	6.1	570	6.3
76	330	5.8	445	6.1
98	245	5.5	340	5.8

Table(2): The relation between H_2O_2:COD weight ratio, COD drop, % of activation and the activation efficiency.

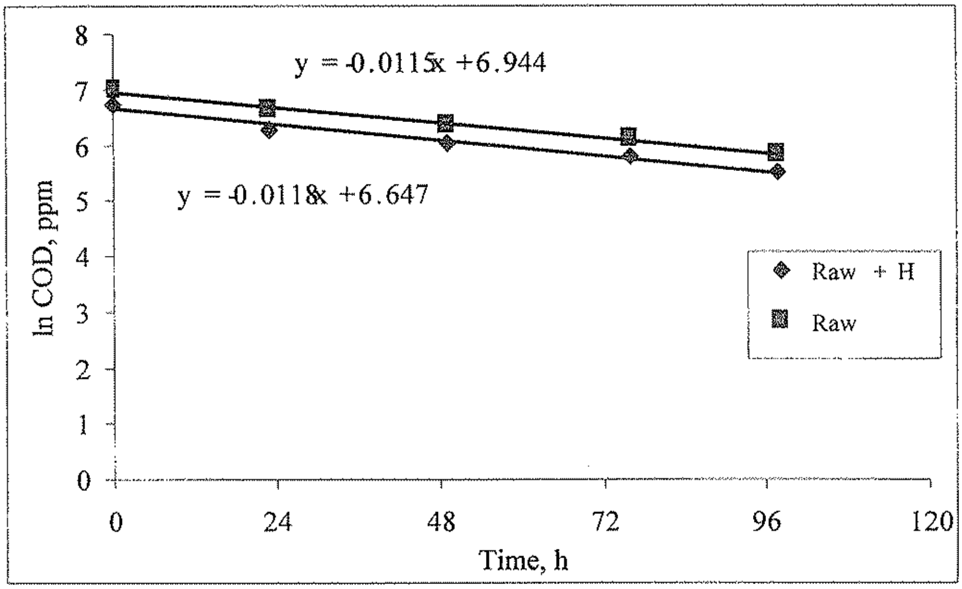
Volume of H_2O_2,mL	Ratio	COD drop	% of activation	* A/C
150	4:1	360	116	10.7
76	2:1	350	114	18.4
39	1:1	320	110	25.6
20	0.5:1	260	103	15
10	0.25:1	220	101	10

- A/C = Activation effeciency = Activation / Concentration.

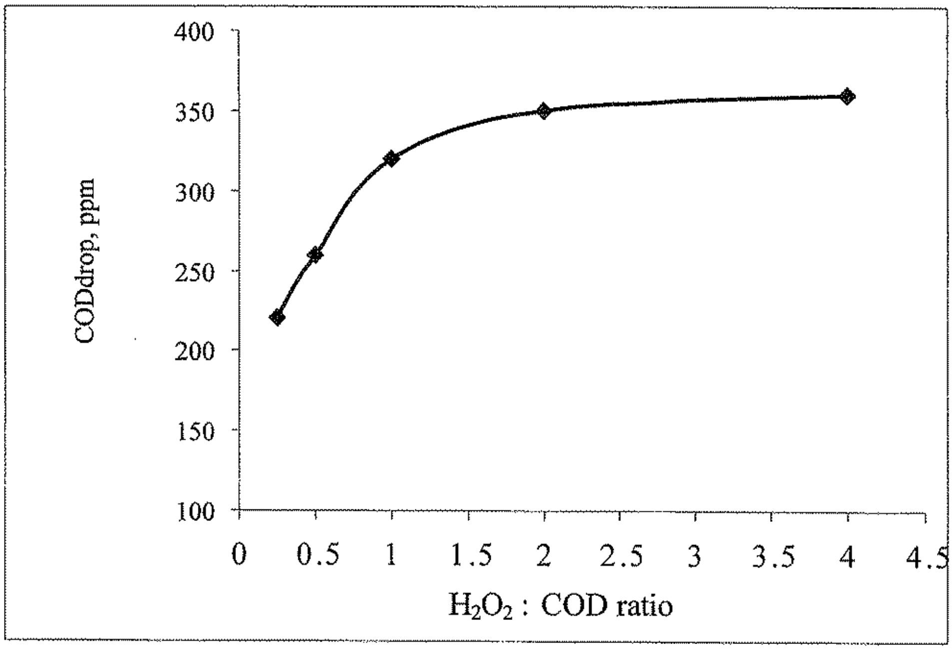
Influence of temperature have been studied, It follows from the results shown in (Fig.4) that the optimum temperature was the same in the presence and absence of H_2O_2, it was ≈20^0C, it follows also from (Fig.4) that the process have not an arrhenious-type behavior.



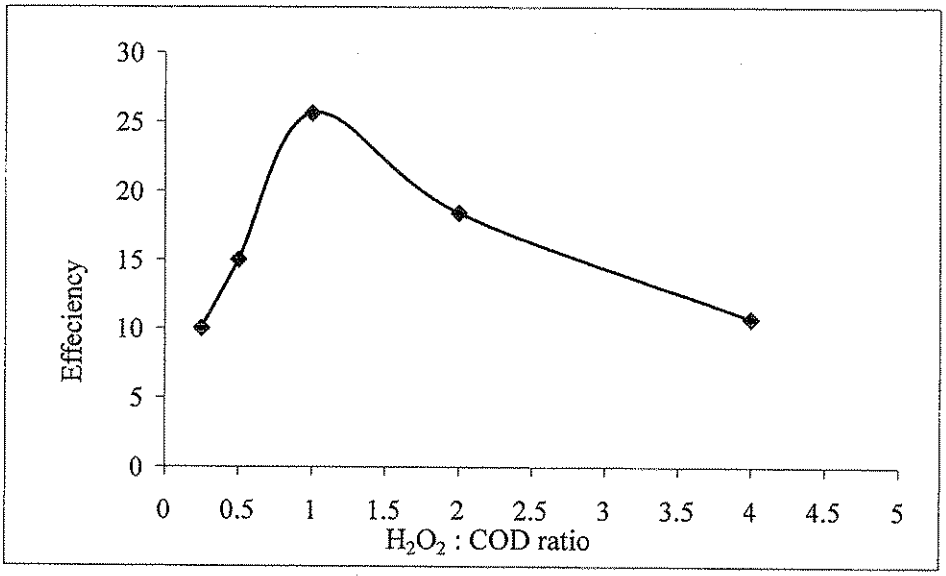
Figure(1.a): The relation between COD & Time in aerpbic oxidation of wastewater,
Recy-cling rate: 0.65 $m^3.min^{-1}$, Bath capacity: 19.0 L,
Bulk Temp.: 31.0 ±0.5 °C, $[H_2O_2]_o$ = 642 ppm.



Figure(1.b): The relation between ln COD & Time in aerpbic oxidation of wastewater,
Recycling rate: 0.65 $m^3.min^{-1}$, Bath capacity: 19.0 L,
Bulk Temp.: 31.0 ±0.5 °C, $[H_2O_2]_o$ = 642 ppm.



Figure(2): **The relation between H_2O_2 : COD weight ratio and the initial COD drop.**
Recycling rate: 0.65 $m^3.min^{-1}$, Bath capacity: 19.0 L, T=31.0 ±0.5 °C.



Figure(3): **The relation between the ratio of H_2O_2 : COD and actvation effeciency [(A-A0) x100/A0].**
Recycling rate: 0.65 $m^3.min^{-1}$, Bath capacity: 19.0 L, T= 31.0 ±0.5 °C.

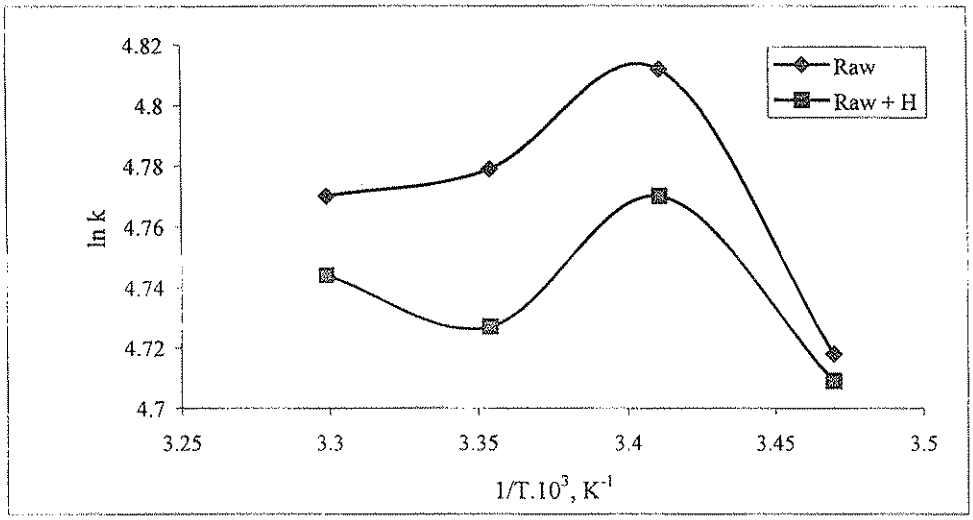
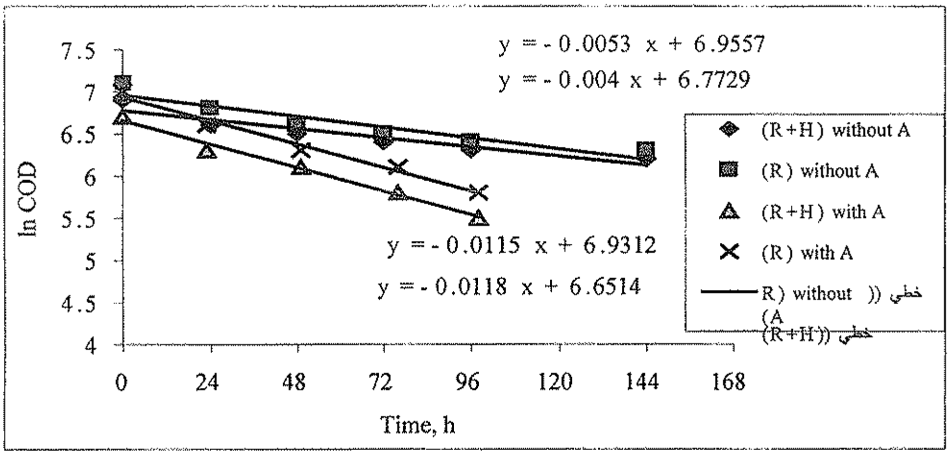


Figure.(4): **The relation between ln k and 1/T for the aerobic oxidation of wastewater,** Recycling rate: 0.65 m3 .min-1, $[H_2O_2]_o$ = 678 ppm, Bath capacity: 9.0 L.

Influence of aeration in the presence and the absence of H_2O_2 have been investigated, it follows from the results shown in (Fig. 5) that the order of reactivity under the same conditions was (H_2O_2 with aeration) > (aeration with no H_2O_2) > (H_2O_2 with no aeration) > (No aeration with no H_2O_2), possibility of using H_2O_2 as an alternative of aeration (to save energy) was ignored.



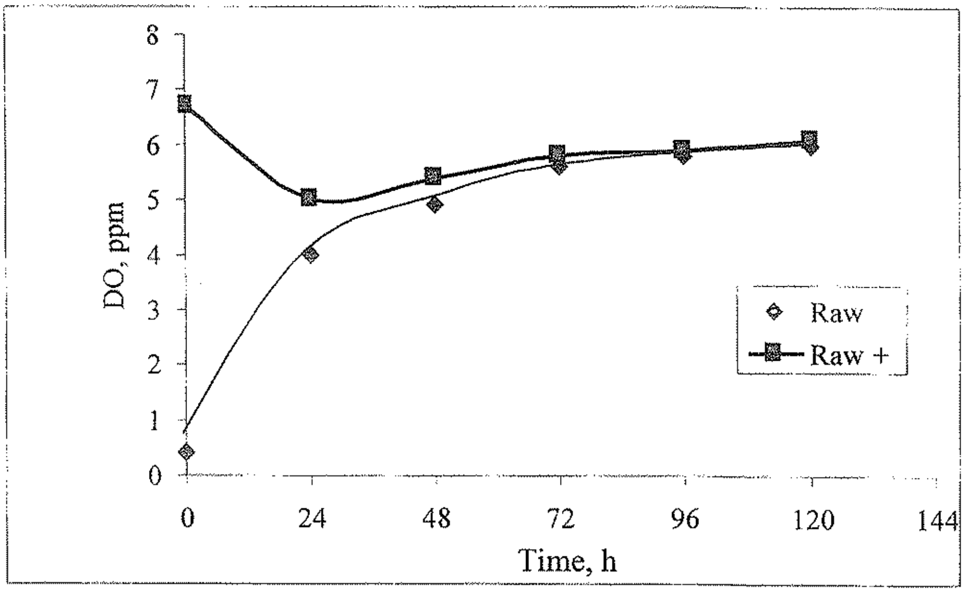
Figure(5): The relation between ln COD and Time for the aerobic oxidation of waste water for aerated, unaerated, treated by H_2O_2 and Untreated.
Bath capacity: 19.0.0 L.

3.2. Chemical, Physical and Microbial Properties. The effect of using H_2O_2 on the aerobic oxidation bulk have been investigated, it follows from the results shown in (Table3) that no real difference have been observed between the two wastewater bulks in the case of presence and absence of H_2O_2 for the values of pH, Turbidity, Conductivity, Oven TDS and EC TDS.

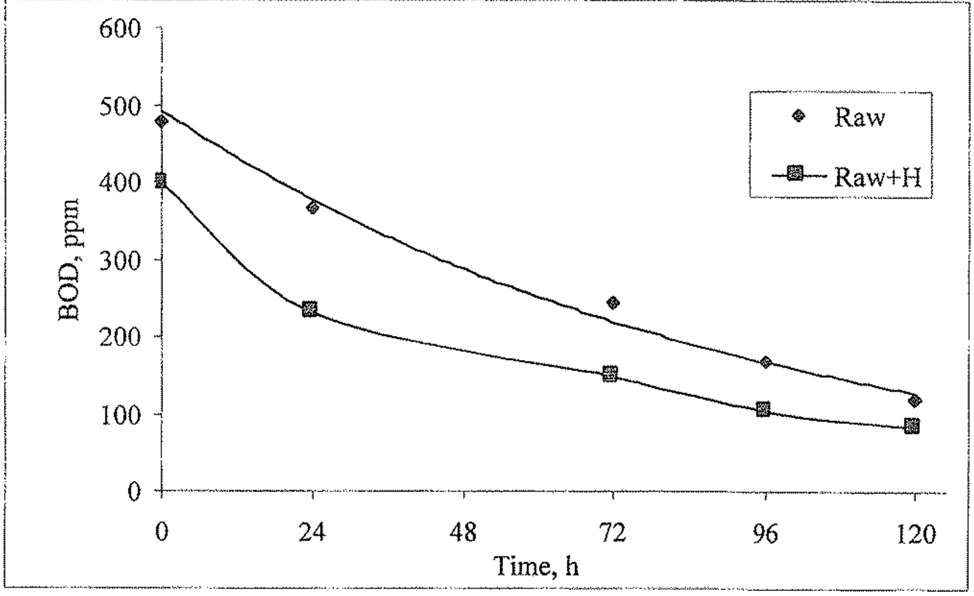
(Table3): Variation of pH, electrical conductivity, oven TDS EC-TDS and turbidity, along the period of aerobic oxidation of wastewater.
Recycling rate: 0.65 $m^3.min^{-1}$, Bath capacity: 19.0 L,
Bulk Temp.: 31.0 ±0.5 °C, $[H_2O_2]_o$ =642 ppm,.

Time, h	0	24	48	72	96	120
pH raw	7.69	8.1	8.29	8.4	8.52	8.44
pH raw + H	7.86	8.16	8.35	8.41	8.55	8.5
EC, mS/cm raw	2.98	2.86	2.77	2.71	2.62	2.56
EC, mS/cm raw + H	3.06	2.95	2.86	2.81	2.74	2.69
EC-TDS, (ppm) raw	1556	1542	1526	1511	1498	1492
EC-TDS, (ppm) raw + H	1570	1553	1539	1527	1515	1504
O-TDS (ppm) raw+H	1800	1750	1750	1700	1700	1750
O-TDS (ppm) raw	1750	1750	1700	1750	1700	1700
Turbidity, NTU raw	443	229	22.4	10.5	6.6	6.09
Turbidity, NTU raw+H	453	274	37	7.36	6.1	5.83

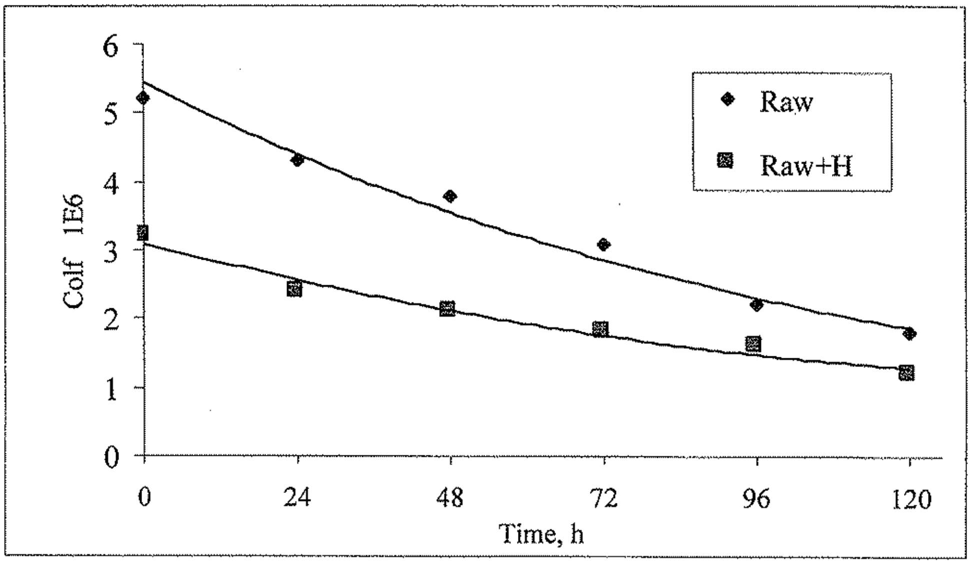
A remarkable difference have been observed when comparing DO in the presence and the absence of H_2O_2, as shown in (Fig. 6), DO was higher in the case of presence of H_2O_2, (specially in the beginning of the process) that is explained by the fact that H_2O_2 is an oxygen supplier for the wastewater bulk. When comparing BOD results in (Fig.7), along the period of treatment BOD was always higher in the case of treatment without H_2O_2 than the treatment with H_2O_2, that agrees with the results of COD. It was clear in (Fig.8) that the presence of H_2O_2 have lowered relatively the total coliform account, it is thought according to literature[2], beside the process activation



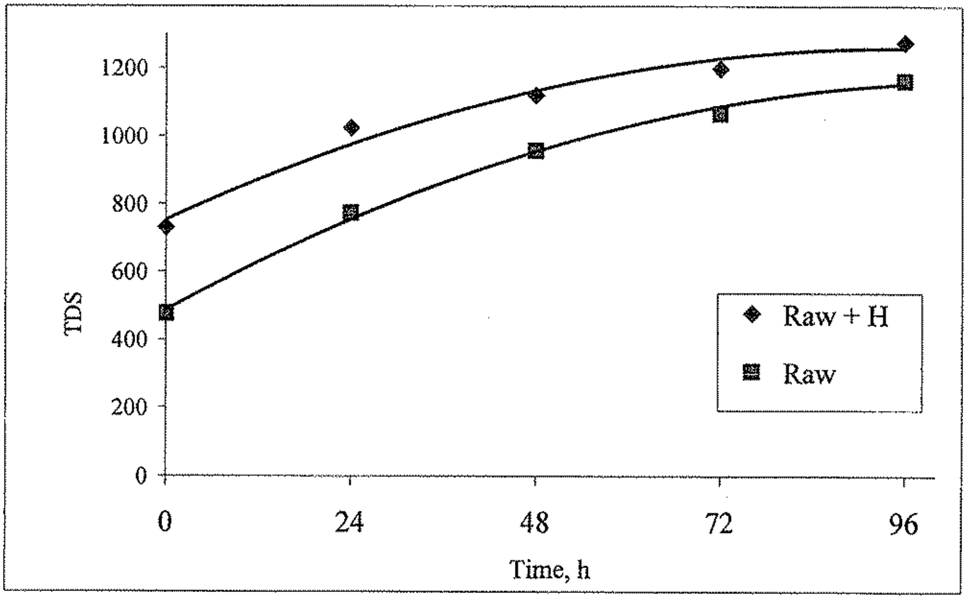
Figure(6): **Disolved oxygen concentration variation during the treatment Time.**
Recycling rate: 0.65 $m^3 .min^{-1}$, Bath capacity: 19.0 L,
Bulk Temp.: 31.0 ±0.5 °C, $[H_2O_2]_o$ = 642 ppm.



Figure(7): **Variation of biochemical oxygen demand with time of treatment.**
Recycling rate: 0.65 $m^3 .min^{-1}$, Bath capacity: 19.0 L,
Bulk Temp.: 31.0 ±0.5 °C, $[H_2O_2]_o$ = 642 ppm.



Figure(8): Total Cliform Cocentration during time of aerobic oxidation treatment.
Recycling rate: 0.65 $m^3 .min^{-1}$, Bath capacity: 19.0 L,
Bulk Temp.: 30.0 ±0.5 °C, $[H_2O_2]_o$ = 642 ppm.



Figure(9): The relation between TDS(EC)-COD) & Time. $[H_2O_2]_o$ = 642 ppm.
Recycling rate: 0.65 $m^3 .min^{-1}$, Bath capacity: 19.0 L,
Bulk Temp.: 31.0 ±0.5 °C, Oven Temp =500 ±0.5 °C,

estimated from the present kinetic study, that the presence of H_2O_2 activates aerobic bacteria in the same time it inhibits the anaerobic species.

It is clear in (Fig.9) that concentration of inorganic salts was increasing in each cases of treatment as a result of mineralization; it was higher in the case of using H_2O_2 than the treatment without using H_2O_2 along the period of treatment.

3.3. The Economical Side of the Use of H_2O_2 .

Regarding the international approximate price of commercial hydrogen peroxide solution which is nearly $ 1000 per Ton of 50% w/w[11], taking in consideration the most efficient weight ratio of H_2O_2:COD estimated from the present study; which was 1:2, the additional cost of treatment of one Ton of COD ≈ $500.

For the daily treatment of 100 000 cubic meter of wastewater in Gaza strip with average COD of 1000 ppm [12], it may need an additional cost for the municipal projects of treatment more than $ 100 000, It is thought the advantages of using H_2O_2 estimated in the present study does not deserve these extra expenses at the present time.

4.Conclusion

The aerobic treatment stage of wastewater in municipal projects can be accelerated by the addition of H_2O_2 at the beginning of this stage, in addition of the other advantages of the presence of hydrogen peroxide in the treated wastewater bulk like disinfections and bad smell inhibition. The main problem in using hydrogen peroxide is the relatively high expenses of this application.

5.Referances

1. Internet source: www.h2o2.com /applications /industrial wastewater/ bodcod .html.

2. Mohammed A. Keshta, Bait Lahia Wastewater Treatment Evaluation and Alternative Option of Treatment, International Institute for Infrastructural Hydraulic and Environmental Engineering, M.Sc. Thesis E.E.106 April(2000).

3. American Public Helth Association; American Water Works Association; Water Environment Federation, Standard Methods for Examination of Water and Wastew- ater, 19th Edition, (1995).

4. United State Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, (1979).

5. ARAB Republic of Egypt Ministry of State for Environmental Affairs, Methods for Sampling and Analysis of Water and Wastewater, Part 1: Method of Sampling p.207-217, October (1999).

6. Internet source: http:// soils1. cses.vt.edu/CH/biol-468/mfcoli. Html. Virginia Polytechnic Institute and State University.

7. Internet source: http:// science. Lander. Edu/rsfox/300 coli Lab. Html,Lander University, Copyright (2000).

8. United State Environmental Protection Agency,Microbio- logical Methods for Monitoring the Environment Water and Wastes, p. 108-112; 124, (1989).

9. El-sousy M. K., PhD theses, Pysicochemical invistigation of surfactants and the effect of some additives, 2001.

10. Talinli-I; Anderson-Gk, Interfernce of Hydrogen Peroxid on the Standard COD Test, Water-Research-Oxford. 26: 1, 107-110; 8 ref. (1992).

11. Internet source: peroxide online www.h202.com.intro.prev. (1999).

12. Palestinian National Authority, Educational Package of Environmental Subjects at GIE, By the support of United States Agency for International Development, p. 5-9, July (1999).