



TRIALS TOWARDS APPROACHING EFFECTIVE REMEDIATION OF INDUSTRIAL WASTE-WATER

Saad, S.M.M.; Foda, F.A.; El-Deeb, A.E. and M.A.El-Shaarawy

J. Egypt. Soc. Toxicol.
(Vol. 29:35-42 July 2003)
WWW.estoxicology.org

Dept. of Agric. Chemistry, Fac. of Agric. Moshtohor, Zagazig Univ.

ABSTRACT

The chemical analyses of waste-water disposed from Oil and Soap Company in Kafr El-Zayat, El-Gharbia, Egypt showed high contents of oil and grease, total dissolved solids, total suspended solids and some other parameters *i.e.*, biological oxygen demand (B.O.D.), chemical oxygen demand (C.O.D.) beside of some heavy metals. In this research different treatments have been applied to get rid of (or at least eliminate) these wastes.

Firstly, the waste water was diluted with artesian water at the ratios of 3 : 1 and 2 : 1. The dilution of waste-water gave significant differentiations under the different ratios with all parameters of diluted waste-water. Chemical remediation by using different reagents significantly decreased the main pollutants but to extents still higher than those of the National Regularity Standards.

Secondary, biological remediation was carried out by using microorganisms, which gave significant improvement for reduction of pollutants. On the other hand, the interaction effect of dilution, chemical and bioremediation have been proved to be very efficient in reducing contents of the organic, inorganic contaminants and other pollutants, where average removal values of B.O.D., C.O.D. and both oil and grease were 98.14%, 98.10% and 99.8%, respectively. Consequently, the quality of treated waste-water disposed from Oil and Soap Company became compatible with National Regularity Standards, Egyptian Law No. 48 (1982).

Key words: Waste-water, dilution, chemical remediation, bioremediation.

INTRODUCTION

The oil and soap industry is one of the major industries in Egypt which contributes greatly to the pollution of the River Nile. The major hazards created by waste-water from this industry are usually due to the presence of oil and grease in the effluent or disposed water. Such liquors often contain emulsion substances which aggravate the problem and cause immense difficulties for water treating (Abou El-Ela *et al.*, 1990). The waste-water of these factories is highly contaminated with both organic and inorganic pollutants which are discharged into the River Nile. The discharged waste amounted 650 m³ per hour. In terms of biological oxygen demand (BOD), the organic load carried by this volume of water was estimated to be 44702 kg BOD/day (Mahrous, 1992).

Generally, the application of physical, chemical and biological treatments aimed at providing the most appropriate solution for handling domestic and most industrial waste-water. The chemical treatment process may consist of rapid mixing of chemicals such as charcoal, potassium dihydrogen phosphate (KH₂PO₄) and calcium carbonate (CaCO₃) with the waste-water, followed by heating, setting, and biological treatment. Such technique proved to be the most effective process in the treatment of many industrial wastes, especially the oil water-wastes (Eckenfelder, 1989).

The oily wastes can be treated by several delete methods. Emulsions may be broken by physical, chemical and biological processes (Barker *et al.*, 1970). El-Gouhari *et al.* (1987) studied the feasibility of treating waste-water from an industrial complex (Oil & Soap and Canned Food) using air floatation and chemical coagulation followed by sedimentation. Chemical Oxygen Demand (C.O.D.) removal was only 52%. Residual values were still high and did not agree with the regulatory discharge standards. When activated sludge treatment was used as a post treatment, average residual B.O.D., C.O.D., oil and grease values were 30, 92 and 8.3 mg/L, respectively.

Abdel-Shafi (1992) studied the precipitation of nickel, copper and manganese salts by using different chemical coagulants from industrial waste-water. The obtained results indicated that the chemical treatment of industrial waste-water by using of 220 mg/L lime removed more than 89% of copper salt. But, when the pH was raised up to 8.5, the removal rates of copper, nickel and manganese salts were more than 94%. The use of 3 g/L limestone precipitated about 96% of all salts. Addition of 70 mg/L of aluminum sulfate [Al₂(SO₄)₃] in combination with sodium hydroxide (NaOH) increased the precipitation of the above salts mentioned up to 98%.

Mahrous (1992) treated waste-water discharged from oil and soap industry by using physio-chemical separation

followed by biological treatment. Sodium chloride was used as a chemical agent at optimal pH value and dosage, Nalco "400" was also added as a coagulant at the final stage of treatment. He showed that this technique has been proved to be very efficient in removing the organic contaminants. The oil removal value achieved 99.8% and the B.O.D. and C.O.D. reached 98.8% and 98.2%, respectively.

Abou-El-Aula *et al.* (1994) treated the final effluent of an oil and soap Company by dissolved air floatation followed by biological treatment via completely mixed activated sludge process. Characterization of the end-of-pipe effluent indicated that the waste-water was highly contaminated with organic as well as inorganic pollutants. Plain dissolved air floatation removed up to 60% of oil and grease. However, dissolved air floatation followed by completely mixed activated sludge process produced a good quality effluent amenable for waste-water disposal into surface water or other uses. Average residual values of B.O.D., C.O.D. and oil and grease were 34 mg O₂/L, 69 mg O₂/L and 15 mg/L, respectively.

Doma (1996) reported that the anaerobic treatment of oil and soap waste-water showed significant improvement. Removal values of C.O.D., B.O.D. and suspended solids reached 74%, 73% and 89% at a retention time of 10 days. Activated sludge post-treatment attained extra removal values. After sequenced anaerobic-aerobic treatment, the C.O.D. and B.O.D. removal reached 99% and 98%, respectively. The discharge of such wastes without adequate treatment into water bodies can cause destruction to the aquatic life and impair the beneficial use of water for different purposes.

Egypt is currently facing serious water quality problems. The Nile water quality has been deteriorated at an accelerated rate during the last decade. Industrial effluents are discharged into the River Nile with no/or inadequate treatment. Different treatments such as physical, chemical and biological techniques are tried in the current work on discharged water from Oil and Soap Company at Kafer El-Zayat aiming at reducing its contents of both organic and inorganic, pollutants before being discharged into the River Nile in an attempt to put them within the permissible values reported by the National Regularity Standards of Egypt (Low No. 48, 1982 and its modifications).

MATERIALS AND METHODS

Source of industrial waste-water:

The waste-water samples under this investigation were obtained from Oil and Soap Factory at Kafer-El-Zyat, El-Gharbia, Egypt.

Physico-chemical characteristics of the waste-water:

The physico-chemical analyses of the waste water were carried out according to the methods outlined by the

standard American Public Health Association (1992). The value of pH was determined electrometrically using pH-meter.

To determine the different chemical oxygen demand (C.O.D.) values contributed by the different fractions of the waste-water, namely, total (tot), suspended (S.S.) colloidal (col) and soluble (sol), the samples were filtered using a band black ribbon filter paper No 589 with a pore size of 7.4 µm. The differences between the COD_{total} and COD_{filtered} equal the COD_{suspended} i.e. > 7.4 µm. The filtrate of the waste-water consisted of both colloidal and soluble fractions (it is referred to as initial filtrate) by filtration through 0.45 µm filter paper, the two fractions were separated. The final filtrate gives the COD_{soluble} fraction, and the differences between the initial filtrate and the final one i.e. (the soluble fraction) equal the COD of the colloidal fraction.

$$\text{C.O.D. total} - \text{C.O.D. filterate} = \text{C.O.D. suspended}$$

$$\text{Filtrate} - \text{soluble} = \text{C.O.D. colloidal}$$

Biological oxygen demand (B.O.D.); total dissolved solids (T.S.S.); suspended and dissolved solids; sulfides; total hardness (T.H.); calcium; magnesium and oil and grease were determined according to the methods described by the American Public Health Association (1992). Heavy metals (Fe, Mn, Zn, Ni, Pb and Cu) were determined by Atomic Absorption Spectrophotometer PERKIN-EL MER 2380. Sodium (Na) was determined by Flame Photometer.

Dissolved oxygen, inorganic phosphate and florides were determined according to the methods described by the American Public Health Association (1955).

Total bacterial count i.e. coliform bacteria as an indicator for contamination was carried out according to the method described by Frank *et al.* (1943) at the Laboratories of Ministry of Health, Tanta, El-Gharbia Governorate, Egypt.

Treatments of the industrial waste-water:

Dilution of waste-water with artesian water:

The waste water was diluted with artesian water at the ratios of 3 : 1 and 2 : 1 waste-water to fresh water.

Chemical remediation:

Different reagents i.e. activated charcoal, potassium dihydrogen phosphate (KH₂PO₄) and calcium carbonate (CaCO₃) were used. All chemical reagents were obtained from El-Nasr Pharmaceutical Chemicals Co. These materials were respectively mixed together by weight at different ratios as follows: 1:1:1; 2:1:1; 1:2:1 and 1:1:2 g/L waste-water.

Biological remediation:

This process was carried out before and after treatment of the waste-water under investigation using a mixture of microorganisms i.e. Sarcodina alga, Rotifers and Ciliated protozoa.

Statistical analysis:

Least significant difference (L.S.D.) was calculated at 0.05 level of significance according to Snedecor and Cochran (1980).

RESULTS AND DISCUSSION

Physical and chemical characteristics beside of heavy metal concentrations of raw waste-water:

The chemical analysis and metal concentrations of the raw waste-water disposed from Oil and Soap Company at Kafr El-Zayat are shown in Tables (1 and 2).

The obtained results showed that the pH value was 11.37, the turbidity value of waste-water was found to be 1388 NTU. Also, the raw waste-water contained a considerable concentration of total solids. The values of total dissolved solids and total suspended solids were 3136 mg/L and 23355 mg/L, respectively.

On the other hand, oil and grease concentration reached 8735 mg/L. Moreover, the biological oxygen demand (B.O.D.) and chemical oxygen demand (C.O.D.) were 2867 and 4642 mg O₂/L, respectively. From the above mentioned results, it can be seen that the (C.O.D.) was much higher than the (B.O.D.). These results are in agreement with those obtained by Abou-El-Ela *et al.* (1990).

Table (1): Physical and chemical characteristics of the raw waste-water disposed from the Oil and Soap Company.

Parameters	Before treatment	Standard*
pH	11.37	6-9
Temperature (°C)	52.0	-
Turbidity (NTU)	1388	50 NTU
Electrical conductivity (E.C., µmol/cm)	4481	-
Biological Oxygen Demand (mg O ₂ /L)	2867	60
Chemical Oxygen Demand (mg O ₂ /L)	4642	100
Permanganate value (mg/L)	1164	25
Dissolved oxygen (mg O ₂ /L)	Nil	Up to 4 mg/L
Total dissolved solids (mg/L)	3136	2000
Total suspended solids (mg/L)	23355	60
Oil and grease (mg/L)	8735	15
Total hardness	1388	-
Calcium hardness (mg/L)	912	-
Magnesium hardness (mg/L)	470	-
Sodium (mg/L)	844	-
Sulphides (mg/L)	7.88	1.0
Inorganic phosphates (mg PO ₄ ³⁻ /L)	40.76	5.0
Fluorides (mg/L)	6.20	1.0
Colon bacterial count/100 cm ³	15208	5000

* National Regularity Standards, Egyptian Law No. 48 (1982).

However, the permanganate value, calcium, magnesium, sodium, sulphides, inorganic phosphate and fluorides concentrations were 1164, 912, 470, 844, 7.88, 40.76 and 6.20 mg/L, respectively.

Also, the raw waste-water under investigation contained high amounts of heavy metals i.e. iron, manganese, zinc, nickel, lead and copper whose concentrations were 3.11, 3.13, 7.90, 2.28, 2.25 and 3.20 mg/L, respectively (Table 2). The above results indicated that the heavy metal concentrations were slightly higher than those obtained by Abdel-Shafi (1992), but obviously exceeding the corresponding values reported by the National Regularity Standards, Egyptian Law No. 48 (1982).

Table (2): Heavy metal concentrations of the raw waste-water disposed from the Oil and Soap Company.

Elements (mg/L)	Before treatment	Standard*
Iron	3.11	1.5
Manganese	3.13	1.0
Zinc	7.90	5.0
Nickel	2.28	0.1
Lead	2.25	0.5
Copper	3.20	1.5

* See footnote of Table (1).

Effect of dilution on physical and chemical characteristics beside of heavy metal concentrations of the waste-water:

Physical and chemical characteristics of waste-water before and after dilution with fresh artesian water are presented in Table (3). There were significant reductions in all physical and chemical parameters due to dilution with the artesian water. Values of oil and grease were reduced by 22.69 and 26.39% after dilution at the ratios of 3 : 1 and 2 : 1, respectively. Total dissolved and suspended solids were reduced by 3.79 and 5.23%, respectively when the waste-water was diluted at a ratio of 3 : 1. The corresponding reduction values achieved when the waste-water was diluted at a ratio of 2 : 1 were 10.52 and 9.83%, respectively. Also, the dilution ratio 3 : 1 caused the efficiency percentages of reducing turbidity, biological oxygen demand (B.O.D.), chemical oxygen demand (C.O.D.), permanganate

value and total hardness to be 23.05, 17.26, 12.15, 14.60 and 13.90%, respectively. The corresponding efficiency percentages achieved due to dilution of the waste-water at a ratio of 2 : 1 were 29.25, 25.74, 16.74, 18.56 and 21.04%, respectively. However, Table (4) shows that the reductions occurred in heavy metal concentrations due to dilution of the waste-water at the ratio of 3 : 1 were 13.83, 11.82, 13.42, 31.14, 20.44 and 31.88% for iron, manganese, zinc, nickel, lead and copper, respectively. The corresponding reduction values achieved at the dilution ratio of 2 : 1 were 29.58, 23.32, 15.57, 37.28, 33.78 and 38.13%, respectively. From the above mentioned results, it could be observed that dilution of waste-water by using fresh artesian water at a ratio of 2 : 1 gave more reduction efficiency percentages in the different studied parameters higher than the corresponding ones achieved due to dilution at a ratio of 3 : 1. These results are in agreement with those obtained by Somaya *et al.* (1992) and Zaid (1996).

Table (3): Effect of dilution by artesian water on physical and chemical characteristics of the used waste-water.

Parameters	Before treatment	Waste-water : Artesian water 3 : 1	Efficiency %	Waste-water : Artesian water 2 : 1	Efficiency %	L.S.D. at 0.05
pH	11.37	10.46	8.00	9.83	13.54	0.15
Temperature (°C)	52.0	39	25.00	36	30.77	1.15
Turbidity (NTU)	1388	1068	23.05	982	29.25	20.85
Electrical conductivity (E.C., $\mu\text{mol}/\text{cm}$)	4481	4310	3.82	4009	10.53	17.50
Biological oxygen demand ($\text{mg O}_2/\text{L}$)	2867	2372	17.26	2129	25.74	59.09
Chemical oxygen demand ($\text{mg O}_2/\text{L}$)	4642	4078	12.15	3865	16.74	79.57
Permanganate value (mg/L)	1164	994	14.60	948	18.56	54.25
Dissolved oxygen ($\text{mg O}_2/\text{L}$)	Nil	0.29	Nil	0.43	Nil	0.03
Total dissolved solids (mg/L)	3136	3017	3.79	2806	10.52	11.92
Total suspended solids (mg/L)	23355	22134	5.23	21060	9.83	82.61
Oil and grease (mg/L)	8735	6753	22.69	6430	26.39	818.42
Total hardness	1388	1195	13.90	1096	21.04	23.88
Calcium hardness (mg/L)	912	789	13.49	723	20.72	15.76
Magnesium hardness (mg/L)	470	406	13.62	373	20.64	8.12
Sodium (mg/L)	844	787	6.75	701	16.94	4.28
Sulphides (mg/L)	7.88	6.34	19.54	5.93	24.75	0.03
Inorganic phosphates ($\text{mg PO}_4^{3-}/\text{L}$)	40.76	36.63	10.13	32.41	20.49	1.11
Fluorides (mg/L)	6.20	5.74	7.42	4.99	19.52	0.22
Colon bacterial count/ 100 cm^3	15208	13883	8.71	13038	14.27	622.59

Table (4): Effect of dilution by artesian water on heavy metal concentrations of the used waste-water.

Elements (mg/L)	Before treatment	Waste-water : Artesian water 3 : 1	Efficiency %	Waste-water : Artesian water 2 : 1	Efficiency %	L.S.D. at 0.05
Iron	3.11	2.68	13.83	2.19	29.58	0.19
Manganese	3.13	2.76	11.82	2.40	23.32	0.18
Zinc	7.90	6.84	13.42	6.67	15.57	0.10
Nickel	2.28	1.57	31.14	1.43	37.28	0.32
Lead	2.25	1.79	20.44	1.49	33.78	0.40
Copper	3.20	2.18	31.88	1.98	38.13	0.36

Table (5): Effect of chemical remediation on the physical and chemical characteristics of the used waste-water.

Parameters	Before treatment	After chemical treatment						L.S.D. at 0.05		
		1:1:1* g.L ⁻¹	Efficiency %	2:1:1* g.L ⁻¹	Efficiency %	1:2:1* g.L ⁻¹	Efficiency %		1:1:2* g.L ⁻¹	Efficiency %
pH	11.37	8.80	22.60	8.60	24.36	8.87	21.99	10.85	4.57	0.06
Temperature (°C)	52.0	37.0	28.85	36.0	30.76	36.0	30.76	37.0	28.84	0.73
Turbidity (NTU)	1388	424	69.45	393	71.69	315	77.30	422	69.66	17.85
Electrical conductivity (E.C., µmol/cm)	4481	3436	23.32	3347	25.31	3205	28.48	3352	25.20	6.58
Biological oxygen demand (mg O ₂ /L)	2867	965	66.34	888	69.03	806	71.19	896	68.75	10.11
Chemical oxygen demand (mg O ₂ /L)	4642	1863	59.87	1788	61.48	1680	63.81	1801	61.20	10.01
Permanganate value (mg/L)	1164	587	59.57	562	51.72	498	57.22	579	50.26	7.31
Dissolved oxygen (mg O ₂ /L)	Nil	1.15	-	1.93	-	2.20	-	1.73	-	0.12
Total dissolved solids (mg/L)	3136	2405	23.31	2342	25.32	2243	28.48	2346	25.19	4.57
Total suspended solids (mg/L)	23355	1978	91.15	1758	92.47	1664	92.88	1812	92.24	25.67
Oil and grease (mg/L)	8735	987	88.70	784	91.02	752	91.39	825	90.56	18.98
Total hardness	1388	986	28.96	817	41.14	766	44.81	844	39.19	18.29
Calcium hardness (mg/L)	912	650.67	28.65	539.22	40.88	505.56	44.57	557.04	38.92	12.07
Magnesium hardness (mg/L)	470	335.24	28.67	277.78	40.90	260.44	44.59	286.96	38.94	6.22
Sodium (mg/L)	844	521	38.27	486	42.42	414	50.95	471	44.19	10.99
Sulphides (mg/L)	7.88	4.55	42.26	4.07	48.35	3.58	54.57	3.89	50.63	0.08
Inorganic phosphates (mg PO ₄ ³⁻ /L)	40.76	30.17	25.98	28.41	30.30	24.15	40.75	29.60	27.38	0.43
Fluorides (mg/L)	6.20	4.20	32.26	2.88	53.55	2.12	65.81	2.87	53.71	0.16
Colon bacterial count/100 cm ³	15208	9935	34.67	9806	35.52	9631	36.67	9807	35.51	73.12

* Activated charcoal : KH₂PO₄ : CaCO₃

Table (6): Effect of chemical remediation on heavy metal concentrations of the used waste-water.

Elements (mg/L)	Before treatment	After chemical treatment						L.S.D. at 0.05		
		1:1:1* g.L ⁻¹	Efficiency %	2:1:1* g.L ⁻¹	Efficiency %	1:2:1* g.L ⁻¹	Efficiency %		1:1:2* g.L ⁻¹	Efficiency %
Iron	3.11	2.24	27.97	2.07	33.44	1.93	37.94	2.15	30.87	0.09
Manganese	3.13	1.98	36.74	1.88	39.94	1.70	45.69	1.88	39.94	0.05
Zinc	7.90	6.26	20.75	5.91	25.18	5.77	26.96	5.93	24.93	0.06
Nickel	2.28	1.75	23.25	1.67	26.75	1.59	30.26	1.71	25.00	0.04
Lead	2.25	1.74	23.56	1.67	25.78	1.60	28.89	1.66	26.87	0.04
Copper	3.20	2.83	11.56	2.55	20.31	1.95	39.06	2.49	22.19	0.09

* Activated charcoal : KH₂PO₄ : CaCO₃

Effect of chemical remediation on physical and chemical characteristics of the waste-water:

Data presented in Table (5) reveal that all the used chemical reagents could significantly reduce all the studied parameters of the waste-water. This occurred regardless of the ratio of mixing these reagents together. However, it is worthy to indicate that mixing the chemical reagents at the ratio of 1 : 2 : 1 g L⁻¹ waste-water was generally of the best reducing effect on all the measured parameters except for the pH value where the mixing ratio 2 : 1 : 1 g L⁻¹ showed the highest reduction percentage.

The effect of the mixed chemical reagents on reducing the different heavy metal contents (Table, 6) of the waste-water seemed closely related to that aforementioned i.e. mixing these reagents at a ratio of 1 : 2 : 1 g L⁻¹ was of the highest reducing effect on the waste-water content of the heavy metals under investigation. It is of importance also to indicate that the other mixing ratios although were of less pronounced effect on reducing the considered heavy metal content of the waste-water yet the reduction percentages were also significant. Chemical reagents probably adsorbed a significant part of the inorganic pollutants and hence decreased their values in the waste-water. This conclusion stands in well agreement with those of Huang and Blanenship (1984), Etzer and Hughes (1984) and Peters *et al.* (1985) who found that charcoal was the best adsorbent for inorganic pollutants as well as C.O.D. On the other hand, soluble phosphate might undergo chemical precipitation through reaction with some heavy metals present in the waste-water forming insoluble metal phosphates e.g. Fe₂(PO₄)₃, FePO₄ and Pb₃(PO₄)₂ and so on (Balba, 1990). Calcium carbonate (CaCO₃) is known to adsorb metals on its surfaces. The phenomenon of adsorption

is inversely related to the size of the CaCO₃ particles, i.e. the smaller the size of the CaCO₃ particle, the higher its surface area and consequently the higher its adsorptivity. Moreover, CaCO₃ may react with heavy metals leading to precipitating them in the form of CO₃²⁻ (Balba, 1990).

Effect of bioremediation on physical and chemical characteristics of the waste-water:

This process was carried out before and after dilution of waste-water at the ratio 2 : 1 which already gave the most promising reduction effect on the most pollutants. Table (7) reveals that the bioremediation process could result in significant reduction in values of all pollutants whether the waste-water was diluted or not. The turbidity, B.O.D. and C.O.D. reduction values reached were 78.82, 73.14 and 68.10%, respectively when the bioremediation was accompanied with waste-water dilution at ratio 2 : 1 as compared with the corresponding values attained due to bioremediation but without dilution. The biological remediation together with the dilution process showed the best reduction of total suspended solids (T.S.S.) and oil and grease whose reduction percentages achieved 93.19 and 91.75%, respectively.

Table (7) indicates also that the dissolved oxygen increased to 2.08 mg O₂/L due to bioremediation with dilution. Also, reduction of total hardness, sodium, sulphidies, inorganic phosphate, florides and colon bacterial count reached 50.43, 56.99, 51.14, 37.07, 38.71 and 48.58%, respectively. Moreover, heavy metal reductions (Table, 8) of Fe, Mn, Zn, Ni, Pb and Cu reached 33.44, 30.67, 16.46, 16.67, 20.00 and 30.94%, respectively. These results agree with those obtained by Abou-El-Aula *et al.* (1994), El-Gouhari *et al.* (1987) and El-Sarwi *et al.* (1997)

Table (7): Effect of bioremediation on physical and chemical characteristics of the used waste-water.

Parameters	Without diluted			With diluted 2 : 1		L.S.D. at 0.05
	Before treatment	After treatment	Efficiency %	After treatment	Efficiency %	
pH	11.37	8.62	24.19	8.11	28.67	0.12
Temperature (°C)	52.0	36.0	30.77	37	28.85	1.44
Turbidity (NTU)	1388	390	71.90	294	78.82	6.13
Electrical conductivity (E.C., µmol/cm)	4481	3450	23.01	3185	28.92	48.92
Biological oxygen demand (mg O ₂ /L)	2867	900	68.60	770	73.14	11.40
Chemical oxygen demand (mg O ₂ /L)	4642	1832	60.53	1481	68.10	29.45
Permanganate value (mg/L)	1164	585	49.79	472	59.45	5.91
Dissolved oxygen (mg O ₂ /L)	Nil	0.92	-	2.08	-	0.21
Total dissolved solids (mg/L)	3136	2415	22.99	2230	28.89	35.37
Total suspended solids (mg/L)	23355	1981	91.52	1590	93.19	54.03
Oil and grease (mg/L)	8735	982	88.76	721	91.75	37.89
Total hardness	1388	991	28.60	688	50.43	14.64
Calcium hardness (mg/L)	912	654.06	28.28	454	50.22	9.66
Magnesium hardness (mg/L)	470	336.94	28.31	234	50.22	5.46
Sodium (mg/L)	844	517	38.74	363	56.99	18.17
Sulphidies (mg/L)	7.88	4.05	48.60	3.85	51.14	0.11
Inorganic phosphates (mg PC ₄ ³ /L)	40.76	30.89	24.21	25.65	37.07	1.35
Florides (mg/L)	6.20	4.21	32.10	3.80	38.71	0.18
Colon bacterial count/100 cm ³	15208	9492	37.59	7820	48.58	106.93

Table (8): Heavy metal concentrations after bioremediation of the used waste-water.

Elements (mg/L)	Without diluted			With diluted 2 : 1		L.S.D. at 0.05
	Before treatment	After treatment	Efficiency %	After treatment	Efficiency %	
Iron	3.11	2.41	22.51	2.07	33.44	0.11
Manganese	3.13	2.06	34.19	2.17	30.67	0.08
Zinc	7.90	6.75	14.56	6.60	16.46	0.07
Nickel	2.28	1.92	15.79	1.90	16.67	0.05
Lead	2.25	1.88	16.44	1.80	20.00	0.10
Copper	3.20	2.89	9.69	2.21	30.94	0.10

Interaction effect among dilution, chemical and bioremediation on physical and chemical characteristics of waste-water:

Data presented in Tables (9 and 10) reveal that, dilution, chemical or bioremediation solely though could reduce significantly all measured parameters of the waste-water yet these parameters remained higher than the corresponding ones reported by National Regularity Standards of Egypt low No. 48 (1982).

Sequential treatments of the waste-water by dilution, chemical reagents and finally bioremediation, on the other hand, could succeed in reducing values of the different physical and chemical parameters of this waste-water to values lower, generally, than those reported by the National Regularity Standards of Egypt (low No. 48, 1982 and its modifications). Thus, such a sequential remediation is highly recommended as an efficient technique for active remediation of all waste-waters such as that disposed from the Oil and Soap Company at Kafer-El-Zyat, El-Gharbia, Egypt.

Table (9): Interaction effect among dilution, chemical and bioremediation on physical and chemical characteristics of the used waste-water.

Parameters	Before treatment	Diluted 2 : 1 waste-water : artesian water	Chemical remediation 1 : 2 : 1* g.L ⁻¹	Bioremd- iation	Mixed treatment	Efficiency by mixed treatment %	L.S.D. at 0.05
pH	11.37	9.83	8.87	8.11	7.60	33.16	0.17
Temperature (°C)	52.0	36.00	36.0	37.0	33.8	35.00	1.44
Turbidity (NTU)	1388	982	315	294	46	96.69	10.85
Electrical conductivity (E.C., $\mu\text{mol}/\text{cm}$)	4481	4009	3205	3185	2824	36.98	42.73
Biological oxygen demand (mg O ₂ /L)	2867	2129	806	770	54	98.12	42.34
Chemical oxygen demand (mg O ₂ /L)	4642	3865	1680	1481	89	98.08	59.25
Permanganate value (mg/L)	1164	948	498	472	23	98.02	7.28
Dissolved oxygen (mg O ₂ /L)	Nil	0.43	2.20	2.08	4.24	-	0.35
Total dissolved solids (mg/L)	3136	2806	2243	2230	1977	36.96	30.38
Total suspended solids (mg/L)	23355	21060	1664	1590	56	99.76	34.55
Oil and grease (mg/L)	8735	6430	752	721	14	99.84	349.73
Total hardness	1388	1096	766	688	186	86.60	29.61
Calcium hardness (mg/L)	912	723	506	454	123	86.51	20.68
Magnesium hardness (mg/L)	470	373	260	234	63	86.60	10.07
Sodium (mg/L)	844	701	414	363	154	81.75	15.66
Sulphides (mg/L)	7.88	5.93	3.58	3.85	0.84	89.34	0.08
Inorganic phosphates (mg PO ₄ ³ /L)	40.76	32.41	24.15	25.65	4.51	88.93	0.82
Fluorides (mg/L)	6.20	4.99	2.12	3.80	0.84	86.45	0.16
Colon bacterial count/100 cm ³	15208	13038	9631	7820	4729	68.90	262.19

* Activated charcoal : KH₂PO₄ : CaCO₃

Table (10): Interaction effect among dilution, chemical and bioremediation on heavy metal concentrations of the used waste-water.

Elements (mg/L)	Before treatment	Diluted 2 : 1 waste-water : artesian water	Chemical remediation 1 : 2 : 1* g.L ⁻¹	Bioremed- iation	Mixed treatment	Efficiency by mixed treatment %	L.S.D. at 0.05
Iron	3.11	2.19	1.93	2.07	0.99	68.17	0.20
Manganese	3.13	2.40	1.70	2.17	0.82	73.80	0.10
Zinc	7.90	6.67	5.77	6.60	4.08	48.35	0.15
Nickel	2.28	1.43	1.59	1.90	0.08	96.49	0.12
Lead	2.25	1.49	1.60	1.80	0.39	82.67	0.07
Copper	3.20	1.98	1.95	2.21	1.02	68.13	0.12

* Activated charcoal : KH₂PO₄ : CaCO₃

REFERENCES

- Abdel-Shafi, H.I. (1992): Precipitation of Ni, Cu and Mn from industrial waste-water by chemical coagulation. *Bulletin of the National Research Center*, 17(3): 153-160.
- Abou-El-Aula, S.; A.M.A. Ashmawi and H. Salah-El-Din (1994): Combined treatment of waste-water from Oil and Soap industry. *Scientific Bulletin of the Faculty of Engineering*, 29(4): 18-31.
- Abou-El-Ela, T.A.; S.E. Fayed and M.M. Neazy (1990): Zooplankton as a parameter of pollution of the Nile water in Egypt. *Proceedings of the Zoological Society, A.R. Egypt*, 21: 203-217.
- American Public Health Association (1955): *Standard Methods for the analysis of water and sewage* 10th. N.Y.
- American Public Health Association (1992): *Standard Methods for the analysis of water and sewage* 18th. N.Y.
- Balba, A.M. (1990): Calcareous soil properties and management. *Alex. Sci. Exch.*, 11: 2-38.
- Barker, J.E.; V.W. Floiz and R.J. Thompson (1970): "Treatment of oil waste-water mixtures", Presented at Annual Conf. AICHE, Chicago, (1970).
- Doma, H.S.A. (1996): Application of biological treatment technology for waste-water purification. Note summary in Arabic and English bibliography leaves, 256-311.
- Eckenfelder, W.W.J. (1989): *Industrial water pollution control*. 2nd Ed. McGraw-Hill International Ed. Civil Engineering Series.
- El-Gouhari, F.A.; S. Abou El-Ella and H.I. Ali (1987): Management of waste-water from soap and food industries: A case study. *The Science of the Total Environment*, 66: 203-212.
- El-Sarwi, A.A.; H.F. El-Gammal and I.G.A. Rashed (1997): Biological treatment of a hazardous chemical industrial waste-water. *J. of Environmental Sciences*, 13: 67-93.
- Etzer, A. and D.E. Hughes (1984): Adsorption of copper, lead and cobalt by activated carbon. *Wat. Res.*, 18: 927-933.
- Frank, R.; M.C.E. Theroux; F.El. Edward and M.S. Criedriege (1943): *Laboratory Manual or Chemical and Bacterial Analysis of Water and Sewage*. W. Leroy Mall Mann, Ph.D. 3rd Ed. London.
- Huang, C.P. and D.W. Blanenship, (1984): The removal mercury (II) from dilute aqueous solution by activated carbon. *Wat. Res.*, 18: 37-46.
- Mahrous, Y.M. (1992): The use of NaCl and Nalco "400" for treating waste-water from oil and soap factories. *Scientific Bulltin of Ain-Shams Univ., Fac. of Engineering*, 27(2): 525-532.
- Peters, R.W.; T.J. Walker; E. Eriksen; J.E. Peterson; T.K.Y. Chanc and W. Lee (1985): Waste-water treatment-physical and chemical methods. *J. Wat. Pollut. Control Fed.*, 57: 503-517.
- Snedecor, G.W. and W.G. Cochran (1980): "Statistical methods" 17th Ed. Iowa State Univ. Press Ames., Iowa, USA.
- Somaya, A.H.; Kandil, N.F.; Abu Sinna, M.A. and Selem, M.I. (1992): Effects of irrigation with Bahr El-Bakr drain water on: 1- Some soil chemical properties and yield. *Com. In. Sci. and Dev. Res.*, No. 670.
- Zaid, M.S. (1996): A study on the effect of treated irrigation waters varied in their quality on some soil properties and plant growth. PH.D These, Fac. of Agric., Al-Azhar Univ., Cairo, Egypt.

محاولات للتوصل إلى معالجة لمياه الصرف الصناعي الملوثة
صلاح مصطفى محمود سعد
عبد النبي السيد الديب
فرحات فودة على فودة
محمد عبدالجواد الشعراوى

قسم الكيمياء الزراعية - كلية الزراعة بمشتهر - جامعة الزقازيق/ فرع بنها

يعتبر نهر النيل المصدر الرئيسى للمياه فى مصر للاستخدام فى الأغراض المختلفة مثل الزراعة والصناعة لذا فإن الحفاظ عليه من أى تلوث يعتبر مسئولية قومية ملحة. وتهدف هذه الدراسة إلى معالجة مياه الصرف الناتجة من مصانع الزيوت والصابون (شركة اسكندرية للزيوت والصابون) بمدينة كفر الزيات حيث تنتج هذه المصانع الزيوت والصابون بمختلف أنواعه، ولذلك فإن مياه الصرف الناتجة من هذه المصانع تحتوى على مواد عضوية وغير عضوية بتركيزات عالية علاوة على نسبة الزيوت والشحوم التى قد تصل إلى ٧٠% من نسبة هذه الملوثات وقد اشتملت هذه الدراسة على دراسة الخواص الطبيعية والكيميائية. وكذلك طرق المعالجة لمياه الصرف الناتجة من هذه المصانع. وقد أوضحت النتائج أن الخواص الطبيعية والكيميائية لمياه الصرف الناتجة من هذه المصانع وكذلك تركيز العناصر الثقيلة قبل المعالجة كما يلي: رقم الحموضة (pH) ١١,٣٧، درجة الحرارة ٥٢°م، التوصيل الكهربى ٤٤٨١ ميكرومول/سم، الأوكسجين الحيوى الممتص ٢٨٦٧مجم/لتر، الأوكسجين الكيماوى الممتص ٤٦٤٢ مجم/لتر، وقيمة البرمنجنات (P.V.) ١١٦٤ مجم/لتر ولا يوجد بها أوكسجين ذائب ومجموع الأملاح الذائبة الكلية ٣١٣٦مجم/لتر والمواد العالقة الكلية ٢٣٣٥٥ مجم/لتر والزيوت والشحوم ٨٧٣٥ مجم/لتر والكبريتيدات ٧,٨٨ جزء/مليون، الفوسفات غير العضوى ٤٠,٧٦ مجم "فوق"أه"/لتر، والفلوريدات ٦,٢٠ مجم/لتر بينما نسب كل من الحديد، المنجنيز، والزنك، والنيكل، الرصاص والنحاس فكانت ٣,١١، ٣,١٣، ٧,٩٠، ٢,٢٨، ٢,٢٥، ٣,٢٠ مجم/لتر على الترتيب، والعد الاحتمالى لمجموع البكتريا القولونية ١٥٢٠٨/١٠٠سم^٣.

وقد تم استخدام ثلاث طرق للمعالجة هي:

١. طريقة التخفيف: وتشمل التخفيف بنسبة ٢ : ١، ٣ : ١ (ماء صرف : ماء إرتوازى) وذلك على أساس الحجم وكان أنسب تخفيف من النتائج المتحصل عليها هي نسبة خلط ٢ : ١.
٢. الطريقة الكيميائية: وقد استخدمت بهذه الطريقة ثلاث مواد كيماوية بنسب خلط مختلفة وهي (الفحم النباتى النشط وأحادى فوسفات البوتاسيوم وكربونات الكالسيوم) وكانت نسب الخلط كالتالى: ١ : ١ : ١، ٢ : ١ : ١، ١ : ٢ : ١، ١ : ١ : ٢ جم/لتر بالوزن بترتيب المواد المخلوطة وكانت أنسب طريقة خلط من واقع النتائج المتحصل عليها هي ١ : ٢ : ١ جم/لتر.
٣. الطريقة البيولوجية: وهذه الطريقة تستغل بعض التفاعلات البيولوجية للكائنات الحية الدقيقة حيث يتم تحويل المواد العضوية إلى مواد ثابتة غير ضارة وتم استخدام الحماة المنشطة "activated sludge" وذلك عن طريق أحواض لتجميع مياه الصرف وإعطاء فرصة للميكروبات للتغذية على هذه الملوثات. ولما كانت كل طريقة من الطرق السابقة للمعالجة لم تتوصل إلى الحدود والمعايير المنصوص عليها بالقانون فقد تم استخدام الثلاث طرق معا بطريقة متدرجة وذلك باستخدام أنسب المعاملات بكل طريقة فقد تم استخدام التخفيف بنسبة ٢ : ١ ثم الطريقة الكيماوية بنسبة خلط ١ : ٢ : ١ ثم دخولهما على المعالجة البيولوجية أى استخدام الثلاث طرق معا وكانت كفاءة التخلص من الزيوت والشحوم ٩٩,٨٤% الأملاح الذائبة الكلية ٣٦,٩٦%، الأوكسجين الحيوى الممتص ٩٨,١٢% والأوكسجين الكيماوى الممتص ٩٨,٠٢%. المواد العالقة ٩٩,٧٦%، الفوسفات غير العضوى ٨٨,٩٣% والفلوريدات ٨٦,٤٥%. أما العناصر الثقيلة فكانت كفاءة الطريقة فى انخفاض نسب كل من الحديد ٦٨,٤٧%، والمنجنيز ٧٧,٨٠%، الزنك ٤٨,٠٢٨%، والنيكل ٩٦,٤٩%، الرصاص ٨٢,٦٧%، والنحاس ٦٨,١٣%، أما العد الاحتمالى للبكتريا القولونية/١٠٠سم^٣ فكانت كفاءة هذه الطريقة ٦٨,٩٠%. وقد توصلت طريقة خلط الثلاث طرق السابقة لمعالجة مياه الصرف الناتجة من هذه المصانع إلى حدود المعايير المنصوص عليها بالقانون ٤٨ لسنة ١٩٨٢م.