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Treatability of Metal Finishing Wasterwater in Alexandria

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Abstract: Metal finishing wastes discharged to sewers may be harmful to sewer structure and toxic to treatment plant organisms. This study aims to study the charactristics and treatability of wastes representing the different types of metal finishing in Alexandria. Ten samples from each of the studied three metal finishing types have been collected over one year. The samples were subjected to complete physical and chemical analysis. Two treatment approaches were applied: precipitation and adsorption. The results of analysis indicated that the wastewater effluent violate the decree 44/2000. pH, conductivity, dissolved solids, total phosphate, and some heavy metals are examples of the parameters violated the decree limits. The results of the precipitation treatment using different doses of lime indicated that with increasing in pH, the reduction of all the measured paramerers increased. pH of 9.5 [8.5 in case of anodizing waste] have given the best reduction of all the measured parameters and became complied with the decree limits. The results of activated carbon adsorption treatment in pH range from 4.5 to 7.5 indicated that adsorption efficiency increased with pH increasing. pH of 7.5 has been shown the best reduction of all the measured parameters and were complied with the decree limits. The study ended by some recommendations which can be followed to protect both the public health and the sewerage system from the effects of this kind of waste.

INTRODUCTION

Wastewater, solid waste and air emissions are generated by the metal finishing processes. Kinds of wastewater include industrial wastewater, spent plating baths, spent process baths, strip and pickle baths, and exhaust scrubber solutions.[1] Releases of pollutants from metal finishing to water include acids, phosphate-containing detergents, electroplating solutions, organic finishing.[2] Metal finishing wastes discharged to sewers may be harmful to sewer structure and toxic to treatment plant organisms.

Review the litrature has shown that removal of heavy metals have been achieved through different ways such as coagulation and precipitation,[3] bipolar electrochemical precipitation, chemical reduction, adsorption by activated carbon,[4] adsorption by adsorptive particulate flotation, chemical oxidation and biological treatment, and some physical technologies.[5,6] Other miscellaneous methods include electrochemical methods, hydrometallurgical processes which included

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thermal degradation, filtration, and solvent extraction, liquid-liquid extraction methods, automated solvent extraction technique.[7] USEPA's waste management hierarchy recommended waste management via source reduction, recycling and reuse, and as a last resort, environmentally sound treatment and disposal.[5]

In Alexandria, industrial and domestic wastes are discharged into a combined sawerage system. The available treatment processes are not designed to handle industrial wastewater. This study aims to study the characreistics and treatability of wastes representing the different types of metal finishing in Alexandria.

MATERIAL AND METHODS

One company from each type of metal finishing [electroplating, galvanizing, and anodizing] has been selected to be studied in details. The electroplating type has been represented by a small enterprise [employees less than 5], and both of galvanizing and anodizing has been represented by a medium enterprise [employees ranged 5-50]. The sampling has been carried out once a month from each company and the program extended over one year. The samples have been collected from the end-of-pipe of each company. The samples collection, preservation, and analysis were performed according to Standard Methods for the Examination of Water and Wastewater.[8]

Pilot treatment methods have been performed on the end-of-pipe industrial wastewater of the three metal finishing industries selected. They have been included chemical treatment using precipitation by lime and adsorption by powdered activated carbon [Barney Chency NL type] [10g/l] at different pH's. Following filtration, all residual metal concentrations in the treated effluent were determined using Atomic Absorption Spectrometry.

RESULTS AND DISCUSSION

1. Evaluation of end-of-pipe wastewater

The results of the annual mean values of the physico-chemical analysis of samples collected from the end-of-pipe wastewater of the different metal finishing factories are presented in table [1].

PH values ranged between 5.9 and 7.6 for electroplating waste, and 5.4 and 9.3 for galvanizing waste. The low values were not agreed with decree 44/2000[9] pH limits [6-9.5]. All the other recorded pH values in electroplating waste were in agreement both Sapari et al.[6] [6.25-8.40] and decree 44/2000[9] limits. On the other hand, with galvanizing waste all the other recorded pH values were agreed with decree 44/2000[9] limits. However, some of these results were not in compliance with Rodenkirchen[10] [6.7-7.6]. For anodizing waste, pH values ranged between 1.8 and 2.5. All the recorded pH values were not in compliance with decree 44/2000[9] limits.

The results of conductivity and total dissolved solids for electroplating, galvanizing, and anodizing wastes [annual mean values of 724, 2046, 2390μs/cm for conductivity and 448, 1755, and 1881mg/l for TDS] were high. This was due to the used strong acids, residual-plating salts, and other conducting impurities. The values of conductivity in the electropolating waste were higher than that found by Sapari et al.[6] [286-523 μs/cm]. The TDS values in the

Table [1]: Results of mean, range, and standard deviation of annual mean values of physico-chemical analysis of the final effluent of metal finishing factories, Alexandria, 2002

Factory	Electroplating			Galvanizing			Anodizing		
	Mean	Range	S.D	Mean	Range	S.D	Mean	Range	S.D
pH		5.9-7.6			5.4-9.3			1.8-2.5	
Conductivity [uS/cm]	724	360-1021	192	2046	1375-2825	519	2390	1304-3490	746
TDS [mg/l]	448	296-641	134	1755	1144-3042	614	1881	1254-2767	532
S.S [mg/l]	148	61-290	76	287	205-379	69	276	200-382	70
Cl- [mg/l]	176	150-190	15	707	450-950	163	425	150-650	191
SO_4^{--}[mg/l]	116	50-210	48	401	270-620	139	460	300-650	141
Total PO_4^{---} [mg/l]	0.5	0.01-1.5	0.406	0.71	0-2.4	0.79	521	180-930	228
COD [mg/l]	54	43-73	10	72	46-95	19	86	43-108	18
CN [mg/l]	0.0012	0-0.002	0.0005	0.0033	0.003-0.004	0.0005	0	0	0

electroplating waste were in agreement with Sapari et al.[6] [224-432mg/l]. However, they were not in compliance with UNEP et al.[11] [2400mg/l]. The total phosphate results in anodizing waste showed high results [annual mean value of 521mg/l] and violated the decree 44/2000[9] limit [25 mg/l].

In electroplating, galvanizing, and anodizing wastes COD has been recorded low concentrations with annual mean values of 54, 72, and 86mg/l, respectively. These values complied with Steward[12] [BOD was below 25-30mg/l and COD can be higher, depending on the amount of oil and grease removed from the processed metal surfaces]. They also agreed with decree 44/2000[9] limits [600 and 1100 mg/l, respectively].

The results of cyanide in electroplating and galvanizing wastes [annual mean values of 0.0012 and 0.0033mg/l, respectively] showed very low concentrations. These values agreed with decree 44/2000[9] limit [0.2mg/l]. The cyanide content in electroplating waste agreed with UNEP et al.[11] [0.08 mg/l] and below the concentrations found by Sapari et al.[6] [4.07-26mg/l]. On the other hand, the cyanide content in galvanizing waste was not in compliance with Hall et al.[13] [0.8 mg/l].

The results of the annual mean values of heavy metals concentrations analysis of samples collected from the end-of-pipe wastewater of the different metal finishing factories are presented in table [2].

In electroplating waste, the results of Cr, Ni, Pb, and Cu [annual mean values of 40.42, 5.376, 1.120, and 2.233mg/l, respectively] showed high concentrations. They were violating decree 44/2000[9] limits [0.5, 1,1, and 1.5mg/l, respectively]. The results of Ni, Pb, and Cu were higher compared with the results of Hannah et al.[14] [0.9, 0.6, and 0.7mg/l, respectively]. The results of Cr, Ni, and Cu were higher compared with Yost et al.[15] [9.8, 1.56 and 0.4mg/l, respectively]. The value of Cr was very high compared with results of Sapari et al.,[6] Cochran et al.[16] and UNEP et al.[11] [12.43, 0.5, and 0.6 mg/l, respectively]. However, Ni and Cu were lower than UNEP et al.[11] [18 and 10mg/l, respectively], and Srinivasan[17] [58.69 and 63.57mg/l, respectively]. On the other hand, Ni results were almost within the range found by Cochran et al.[16] [6.7 mg/l]. Lead results

Table [2]: Results of mean, range, and standard deviation of annual mean values of heavy metals analysis of the final effluent of metal finishing factories, Alexandria, 2002

Factory	Electroplating			Galvanizing			Anodizing		
	Mean	Range	S.D	Mean	Range	S.D	Mean	Range	S.D
Zn [mg/l]	1.786	0.672-3.295	0.825	32.959	14.324-45	8.166	4.871	2.452-8.619	1.818
Cr [mg/l]	40.422	1.484-92.841	33.259	3.978	1.049-8.049	2.006	0.323	0.034-0.846	0.335
Ni [mg/l]	5.376	2.141-9.401	2.352	2.253	0.005-7.482	2.704	0.154	0.013-0.394	0.121
Cd [mg/l]	0.163	0.001-0.409	0.151	0.161	0.001-0.819	0.269	0.025	0.003-0.095	0.026
Pb [mg/l]	1.12	0.003-2.392	0.872	0.162	0.013-0.534	0.168	0.282	0.075-1.191	0.331
Cu [mg/l]	2.233	0.041-3.853	1.383	1.409	0.135-4.384	1.481	1.707	0.134-3.081	1.103
Fe [mg/l]	9	3.414-14.314	3.559	55.464	16-97.414	30.741	4.024	1.464-7.358	1.922
Al [mg/l]							16.715	5-75.314	21.66

Table [3]: Results of physico-chemical analysis of the final effluent of metal finishing factories treated by lime dose of 25mg/l, Alexandria, 2000

Factory	Electroplating		Galvanizing		Anodizing	
Parameter	Before Treatment	After Treatment	Before Treatment	After Treatment	Before Treatment	After Treatment
pH	7.3	9.5	7.1	9.5	2.3	8.5
Conductivity [uS/cm]	584	361	2116	1235	3183	1360
TDS [mg/l]	433	164	1516	759	2312	841
S.S [mg/l]	97	62	301	169	280	207
Cl^- [mg/l]	158	63	750	36	617	58
SO_4^{--}[mg/l]	127	56	427	163	480	167
Total PO_4^{---} [mg/l]	0.4	0.11	0.955	0.08	680	1.6
COD [mg/l]	52.3	23	53	24	94	45
CN [mg/l]	0.001	0	0.003	0	0	0

were almost agreed with Ramadan[18] [2.3 mg/l].

In galvanizing waste, the results of Zn, Cr, Ni, and Fe [annual mean values of 32.959, 3.978, 2.253, and 55.46mg/l, respectively] showed high values. The Zn results were higher than that found by Baltpurvins et al.[19] [1 mg/l]. However, they were lower than that found by Rodenkirchen[10] and Gyliene et al.[3] [960 and 250 mg/l, respectively]. The results of Cr and Ni violated the limits [0.5 and 1mg/l] of decree 44/2000.[9] However, Cr results were lower than that has been found by Hall et al.[13] [7.6 mg/l]. Nickle results were lower than that found by Hall et al.[13] and Gyliene et al.[3] [6.2, and 180mg/l, respectively]. The results of copper [annual mean value of 1.409mg/l] were lower than that found by Hall et al.,[13] Gyliene et al.,[3] and decree 44/2000.[9] [4.45, 250, and 1.5mg/l, respectively].

In anodizing waste, Cu and Al concentrations [annual mean values of 1.707 and 16.715mg/l, respectively] showed high values. Copper violated decree 44/2000[9] limit [1.5mg/l]. However, aluminium results were very low compared with Brown et al.[20] [12 g/l].

2. Treatment of the wastewater of the different types

The end-of-pipe wastewater of the three types of metal finishing has been treated through two different methods: precipitation and adsorption.

2.1. Precipitation treatment

Lime has been used with different doses to adjust the pH at 8, 8.5, 9 and 9.5 for electroplating and galvanizing wastes, and 6.5, 7, 7.5 and 8.5 for anodizing waste. The treatment trials have been carried out on three samples per each type. The average results of physico-chemical analysis of the influent and effluent of each type are presented in table [3].

It has been noticed that pH of 9.5 for both electroplating and galvanizing and 8.5 for anodizing showed the best reduction of all the measured parameters except suspended solids and COD. However, their concentrations after treatment were low compared with their correspoding concentrations before treatment. For anodizing waste, sulfate and total phosphate have been reduced from 480 and 680mg/l to 167 and 1.6mg/l. The removal percentage of sulfate [65.2%] of the present study was not agreed with Brown et al.[20] [93%].

The average results of heavy metals analysis of the influent and effluent of the three samples treated by different doses of lime are presented in table [4].

All heavy metals concentrations have been decreased with pH increasing. The best reductions has been detected at pH of 9.5 where the high or violated concentrations of Cr, Ni, Pb, Cu, and Fe in electroplating waste; Zn, Cr, Ni, and Fe in galvanizing waste; and Al and Cu in anodizing waste have reduced. The reducation of heavy metals has been supported through hydroxides precipitates. The total heavy metals contents of the three treated types by lime [0.768, 1.689, and 1.121mg/l] were in compliance with decree 44/2000[9] limit [5 mg/l].

The reductions of heavy metals concentrations of the present study after treatment with lime agreed with Nurie[21] who found that Cr, Ni, and Cu concentrations

Table [4]: Results of heavy metals analysis of the final effluent of metal finishing factories treated by lime dose of 25mg/l, Alexandria, 2000

Factory	Electroplating		Galvanizing		Anodizing	
Parameter	Before Treatment	After Treatment	Before Treatment	After Treatment	Before Treatment	After Treatment
Zn [mg/l]	2.669	0.094	36.696	0.692	6.289	0.316
Cr [mg/l]	68.771	0.128	5.624	0.218	0.715	0.04
Ni [mg/l]	5.452	0.133	5.365	0.065	0.251	0.029
Cd [mg/l]	0.306	0.001	0.366	0.024	0.022	0.002
Pb [mg/l]	1.938	0.004	0.278	0.015	0.563	0.026
Cu [mg/l]	2.866	0.064	3.166	0.179	2.558	0.017
Fe [mg/l]	13.056	0.344	82.678	0.496	4.47	0.299
Al [mg/l]					12.812	0.392
Total		0.768		1.689		1.121

reduced to 1.5, 1, and 0.3 mg/l, respectively. The results also agreed with Srinivasan[17] work who found that Cu, Ni, and Zn were reduced into 3.17 mg/l, 2.80 mg/l and 1.79 mg/l, respectively. The results of the present study also complied with Cochran et al.[16] work who found that adjustment of pH at 9.5 reduced the concentrations of heavy metals less than 1 mg/l. UNEP et al.[11] showed that Cr, Cu, Ni, Fe, and Zn concentrations reduced into 0.02, 0.07, 2.34, 0.59, 0.31 mg/l, respectively which almost agreed with the results of the present study.

For galvanizing waste, the results of Zn in the treated galvanized waste were agreed with Graves[22] [0.34 mg/l]. The results of Ni, Cr, Zn, Cd, Pb, and Cu of the present study complied with Maruyama et al.[23] [0.012, 0.094, 0.584, 0.014, 0.019, and 0.352mg/l, respectively]. Also, the results of Zn, Cr, Ni, Cu, and Fe were almost within the range found by Lanouette[24] [0.5, 0.5, 0.5, 0.5, and 0.1mg/l, respectively].

For anodizing waste, the removal percentage of aluminum [96.93%] of the present study was higher than that found by Brown et al.[19] [70%].

2.2. Carbon adsorption treatment

The wastes have been treated at different pH's. Nitric acid and sodium hydroxide have been used to adjust the wastes pH at 4.5, 6, 7, and 7.5 whenever needed. Then, activated carbon dose of 10 gm/l has been used for each adjusted sample. The treatment has been carried out on one sample per each type only. The results of physico-chemical analysis of the influent and effluent of each sample treated by activated carbon dose of 10 gm/l are presented in table [5].

It is clear that with increasing in pH, all the measured parameters have been decreased except suspended solids. It has been noticed that pH value of 7.5 has been recorded the best reduction of all the measured parameters except suspended solids. However, their concentrations after treatment [54 for electroplating, 154 for galvanizing, and 200mg/l for anodizing] were lower compared with their corresponding concentrations before treatment [61, 220, 207mg/l, respectively]. In general the recorded values of all the parameters in the treated effluents agreed with decree 44/2000[9] limits.

The results of heavy metals concentrations analysis of the influent and effluent of each sample treated by activated carbon dose of 10 gm/l are presented in table [6].

The reduction of heavy metals have been increased with pH increasing. The highest efficiency of adsorption was at pH 7.5. At that pH the violated metals in the electroplating [Cr, Ni, Pb, Cu, and Fe], in galvanizing waste [Zn, Cr, Ni, and Fe], and in anodizing waste [Al and Cu] complied with the decree limits. The total heavy metals content of the treated types samples by activated carbon [0.869, 0.852, 1.29mg/l] agreed with decree 44/2000 limit [total heavy metals less than 5 mg/l]. The reduction of heavy metals in the present study was agreed with Netzer et al.[25] study who investigated that removal of heavy metals by activated carbon of Barney Cheney NL1266 type which has been used with the present study was superior. Their results

Table [5]: Results of physico-chemical analysis of the final effluent of metal finishing factories treated by activated carbon dose of 10gm/l, Alexandria, 2000

Parameter \ Factory	Electroplating		Galvanizing		Anodizing	
	Before Treatment	After Treatment	Before Treatment	After Treatment	Before Treatment	After Treatment
pH	6.08	7.5	9.3	7.5	1.9	7.5
Conductivity [uS/cm]	718	237	2597	1139	1869	559
TDS [mg/l]	411	107	2119	746	1436	224
S.S [mg/l]	61	54	220	154	207	200
Cl^- [mg/l]	180	55	475	15	150	10
SO_4^{--}[mg/l]	165	50	355	125	400	135
Total PO_4^{---} [mg/l]	0.7	0.3	1.7	0.3	550	0.91
COD [mg/l]	55	20	85	19	72	10
CN [mg/l]	0.002	0	0.003	0	0	0

Table [6]: Results of heavy metals analysis of the final effluen-t of metal finishing factories treated by activated carbon dose of 10gm/l, Alexandria, 2000

Factory	Electroplating		Galvanizing		Anodizing	
Parameter	Before Treatment	After Treatment	Before Treatment	After Treatment	Before Treatment	After Treatment
Zn [mg/l]	2.32	0.014	45	0.001	4.943	0.027
Cr [mg/l]	28.103	0.103	4.655	0.132	0.657	0.014
Ni [mg/l]	6.412	0.243	2.145	0.132	0.324	0.016
Cd [mg/l]	0.204	0	0.005	0	0.095	0
Pb [mg/l]	1.161	0.057	0.373	0.086	0.356	0.086
Cu [mg/l]	1.167	0.054	1.313	0.202	3.081	0.081
Fe [mg/l]	9.226	0.398	20.564	0.299	7.358	1.166
Al [mg/l]					75.314	0.9
Total		0.869		0.852		1.29

showed that at pH4 and above was efficient in metal removal through adsorption. Quki et al.[4] found that removal of 99% of Cr from electroplating wastewater on activated carbon can be achieved. This complied with the results of the present study [99.7%].

CONCLUSION AND RECOMMENDATIONS:

The following has been concluded based on the obtained results:

1- Most of the metal finishing wastes were violated the decree 44/2000 limits for some parameters such as pH, conductivity, TDS, total phosphates, and some heavy metals.

2- All the measured parameters of the samples whether treated by lime or activated carbon were agreed with decree 44 for 2000 standards.

3- The results of the treatment by lime of the three types samples showed that pH of 9.5 [8.5 in case of anodizing waste] have given the best reduction of all the measured parameters.

4- The results of the treatment by activated carbon of the three types samples showed that pH of 7.5 have given the best reduction for all the measures parameters.

6.2. Recommendations

1- Encouragement of keeping environmental registers, which will enforce them to continue monitoring of wastewater pollutants.

2- Establishment of an integrated environmental management through:

a- Movement of these activities to the nearest industrial area,

b- Enforcement of installing of wastewater treatment plant according to requirements of the regulation.

c- Establishment a centralized treatment plant based on precipitation, and encouraging them to establish neutralization treatment for pH adjustment within their enterprises,

d- Encouragement of substitution the toxic raw materials with non-toxic substances,

e- Encouragement of substitution of the old technologies with the clean technology, and

f- Encouragement of in-plant control.

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