EFFECTS OF ECOFRIENDLY PRODUCTION TECHNOLOGIES ON WASTEWATER CHARACTERIZATION AND TREATMENT PLANT PERFORMANCE

G. Yuksek[1*], D. Okutman Tas[1], E.Ubay Cokgor[1], G. Insel[1], B. Kirci[3], O. Erturan[2]

[1]*Istanbul Teknik Üniversitesi, İnşaat Fakültesi, Çevre Mühendisliği Bölümü*

[2]*Arçelik A.Ş, Enerji ve Çevre Departmanı*

[3]*Arçelik A.Ş, Bolu Pişirici Cihazlar İşletmesi*

E-mail: gulyuksek@itu.edu.tr, okutmand@itu.edu.tr, ubay@itu.edu.tr, inselhay@itu.edu.tr, betul.kirci@arcelik.com,ozge.erturan@arcelik.com

ABSTRACT

Operating the wastewater treatment plant efficiently is more sensitive issue than the entity of treatment plants. In this study, according to new wastewater characterization after modern eco-friendly process application, efficiency of wastewater treatment plant for a metal finishing industry was evaluated and optimized.Three processes in the facility that intensively consume water and produce wastewater are metal surface pre-treatment, painting and enamel coating processes.After determination of wastewater sources of the facility, samples are taken and characterization studies were performed during the year.Based onthe characterization studies, it is observed that after the process renovation the quality of the raw wastewater has changed positively leading low pollutant load and discharged wastewater is with the values of legal requirement. Chemical treatment experiment in Jar Test was performed to assess optimum dosages for the wastewater treatment plant. Also respirometric analyses were done in order to detect treatability of wastewater biologically. The results showed that treated water characterization were nearly same for all the coagulants tested but sludge quality of flocculation and settleability were better for commercial and pure $FeCl_3$ solutions (Optimum 50 µL/L.& 50 µg/L dosage).The amount ofbiodegradable COD coming to the industrial activated sludge unit after chemical treatment was very low. As a result of the observed low pollution load in the raw wastewatersand based on therespirometric analyses, biological treatment step of industrial wastewater canceled which was constituting a significant percentage of the overall energy requirement of the wastewater treatment plant.

Keywords: Optimization, wastewater characterization, energy recovery, cost saving, respirometric analysis, jar test

HIGHLIGHT

- Alteration in production process requires the optimization of the WWTP.
- Optimization of WWTP was done in frame of Water Quality and Control Regulation.
- 50 µL/L $FeCl_3$solution was chosen as a optimum coagulant dosage.
- High energy consuming industrial biological treatment was not necessary.

1. Introduction

The improvements in the context of environmental friendly and cleaner productionis the main target for most of the industries. The number of industries that apply cleaner production methodologies to weaken the negative impact of their activities and their products on the environmentkeep increasing all over the world [2,6]. According to the Council Directive 96/61/EC IPPC (IPPC Directive, 1996) concerning integrated pollution prevention and control, it is important to perform efficient raw material, energy and water usage, to substitute toxic substances by less harmful substances, and tominimize recover and recycle wastes and wastewaters [15].

Metal coating industry which is usually categorized under the metal finishing industry is one of the industries that consume high amount of chemicals (i.e., solvents, dyes etc.)energy and water. Increased metal ware usage and the need for more long-lasting productinvolverapid and eco-friendly production to meet both customers' request and environmental expectations.The processes applied in the metal coating industry are metal coating, anodizing, heat processes, metal treating, sand spraying, polishing, plastic coating, enamel coating, varnishing and hardening of metals [5].

The primary environmental problems associated with metal finishing and electroplating operations are disposal of contaminated cleaner, recovery of metals from the rinse water, and the treatment of wastewater before discharge to the local discharge channel. In addition, the business must also address the problem of disposing of solid wastes generated by metal finishing/electroplating processes.In terms of raw material consumption, the chemicals used have the potential to cause environmental harm particularly to surface waters, groundwater and soil[14].

Corrosion is the main problem which has a high influence on economics and safety for metals. In order to improve corrosion protection and adhesion to the next layer, surface pretreatments are used on metallic substrates. One of these common pretreatment is the phosphating technique. But this technique has several limitations especially in terms of environmental problems (i.e., detrimental effects on ground and surface water ecology). Beside this technique, nowadays a new surface pretreatment technique(i.e., ceramic based coating)replaced phosphating. Nano ceramic coating is one of these techniques [8-9]being eco-friendly, applications of nanocomposites offer new technologies and business opportunities for several sector of metal finishing industry [3]. In addition, this process has been also applied to many different metals and alloys (e.g., Al, Cu, Ti, Zn, Mg, and stainless steel) and showed superior performance [4].

The objectives of this study were(1) to evaluate the wastewater characterization profile after eco-friendly process application (2) to improve the performance of the existing wastewater treatment plant (3) to determine energy recovery in the factory after the improvements.

2. Materials and Methods

2.1. Industry Profile and Process description

The metal finishing factorywhere this study is conducted is located in Bolu, Turkey. The factory is one of the biggest white-goodsmanufacturers in Turkey. The number of the staff working in the factory is 2200 with an annual production capacity of 2879278 pieces of cookers in 2014.

The sheet metal parts coming from mechanical production or sub-industries used in the production have to be exposed to surface pre-treatmentprocesses asdegreasing process, rinsing, nanoceramics coating and deionization rinsing process, consecutively.Metal sheets were encased in oil film in order to prevent oxidation of metals in the enamel and painting process. Firstly, the metal sheets had to be cleaned to increase the efficiency of coating process. This process was called degreasing process. In addition to degreasing processthere are two wastewater generating processes in the industry namely enamel and painting processes. In the factory there are two enamel coating unit called as Enamel Process 1 and Enamel Process 2 to bring more thermal resistance to the product. There are no major different between two Enamel1& 2 processes, but in case of necessity second process is worked to support another Enamel processStages of enamel process including two degreasing and two rinsing stage were schematized in Figure 1.In the painting process, product parts which are exposed to heat (200°C) are painted. The painting process varies according to paint color or speciality. Silver process, white-black process and antifinger process are classified under painting process. Silver and white-black process varies according to the paint color, while antifinger process is related to the paint speciality. The products become stain proof of fingerprintafterantifinger stages.Stages of painting process were given in Figure 1. The pieces after pre-surface treatment are painted under dried condition in powder coating process. In the facility, powder painting is performed by paint guns automatically and it has been implemented as a zero wastewater producing process.

2.2. **Wastewater sources and sampling**

The main wastewater sourcesin the factory consist from domestic and industrial wastewater streams. While domestic wastewater was generated from toilets, cafeterias and recreational facility wastewaters, industrial wastewater wereoriginated from metal surface treatment, enamel coating, and paintingprocesses. In addition,a small amount of wastewater was derived from cooler towers and chiller that generate 20 m^3/year and 15 m^3/year wastewater, respectively.

There are two wastewater treatment units in the facility as a biological treatment unit and a continuous treatment unit for domestic and industrial wastes, respectively (Figure 1). Painting and enamel wastewater were treated by batch chemical treatment process followed by effluent of batch treatment process and rinsing wastewaters were treated together by continuous treatment process in the industrial chemical unit. After industrial and domestic wastewaters were treated separately they were discharged into BoluKuruçay River together. As the effluents of treatment plant were discharged to the river, pollutant level should comply with Water Quality and Control Regulation [11].

Wastewaters coming from the degreasing process were treated in batch treatment unit. Firstly, in order to homogenize the wastewaters, the painting and enamel wastewaters are collected in the equalization tank in batch treatment process. In the reaction tank, HCl and $FeCl_3$ solutions were added into the mixed wastewater for pre-oxidation. Because oil concentration of that type wastewaters is very high, the wastewater was send to the flotation unit after the reaction tank. The amelioration by selecting powder and nanotechnology coating methods, a decreasein the gress concentration in wastewater was observed and flotation unit was cancelled. Then, the wastewater was exposed to neutralization, coagulation and flocculation processes. The wastewater that is treated at batch treatment process, is directed to continuous treatment process and then to the industrial biological treatment process. The industrial biological treatment process is composed of activated sludge system. Domestic wastewaters are treated by biological activated sludge process.

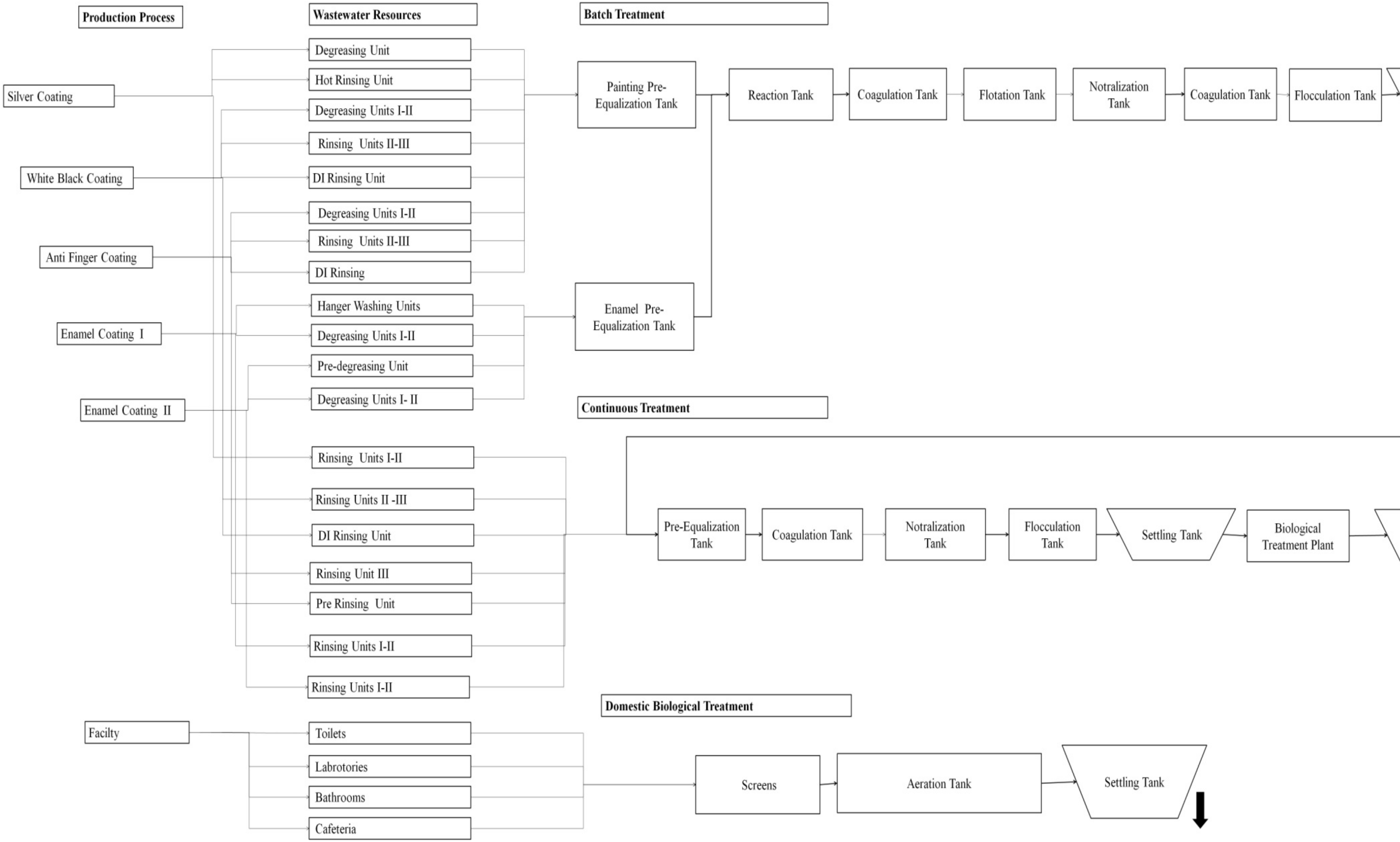

Fig. 1. Simple plan of wastewater treatment plant

The samples, which were taken in different times from wastewater treatment plant, were analyzed and treatability studies were practiced. Details about sampling points, sampling time and sample type were shared in Table 1 and Table 2.

In the first sampling, grab sampleswere collected from determined seven points at the same time during four days. In addition to these samples, sludge samples were also monitored.

Table 1 Sampling points.

Sample Points	Units	Sample
1	Rinsing pre-equalization tank	Water
2	Painting pre-equalization tank	Water
3	Enamel pre-equalization tank	Water
4	Effluent water of batch treatment unit	Water
5	Influent water of domestic wastewater treatment plant	Water
6	Effluent water of domestic wastewater treatment plant	Water
7	Effluent water from discharge point	Water
8	Domestic Biological Treatment Activated Sludge Unit	Sludge
9	Industrial Biological Treatment Activated Sludge Unit	Sludge

Table 2 Details about sampling period and type.

Sample No	Day	Time	Sample Type
1	09.12-15.2012	14:00-14:25	Grab (4 days)
2	01.18.2012	08:00-18:00	Composite
3	03.07.2012	11:00-17:00	Composite
4	04.25.2012	09:00-17:00	Composite

2.3. Analytical Methods

All conventional analyses were performed as described in Standard Methods [1]. The chemical treatability study was carried out using F105A0112 Velp Jar Test Type FC6S (U.K). Different dosages of coagulant are added to the respective jars to determine the optimum dosage range. Jar test was performed in 500 ml glass flaks. Coagulant was added into the mixing sample until flocks started to occur to determine optimum dosage. Starting from minimum dosages 7 different coagulant dosages were applied. The coagulant was added simultaneously after the rapid mixing is started. First the samples were mixed rapidly for 3 min at 100 rpm and then about 15-20 min slow mixing to simulate flocculation followed by 30 min settling. The wastewater used in the jar test experiments were prepared by mixing painting and enamel wastewater according to the flow rates coming to the treatment plant. The mixing ratio of wastewaters was 3:1 for Painting: Enamel wastewater. Commercial solution which contained $FeCl_3$, alum and $FeCl_3$ was used in the Jar Test for “Chemical Treatment Analysis”. In addition to this, pH of this solution was adjusted to 5.5 and 6.5-7 by HCl and NaOH, according to the type of coagulant. Finally, 400 µL/L anionic polyelectrolyte as a flocculant was used.

AppliTek Ra-Combo respirometer was used for the respirometric analyses. Nitrification inhibitor (Formula 2533TM, HACH Company) was introduced to prevent any possible interference induced by nitrification.

Also buffer solutions were added in the reactors to satisfy the requirement of trace elements for biological activity[14]. In respirometric analyses 1.5 L of sludge sample was used and the bH level was monitored for at least 15 minutes and then 1 L of wastewater was added. In order to eliminate any confusion the bH data in the respirometric analysis results section were given as diluted by the factor of 1.5:2.5. Respirometric results were modeled using Activated Sludge Model (ASM 1) with Aquasim.

Initial inert COD components of the three types of influent wastewaters generated form painting process, enamel process and rinsing process were assessed. The same sludge taken from industrial activated sludge aeration tank, was used in all the reactors. The inert COD fractions were assessed using the methods defined by Orhon et al. (1994) [10].

3. Results & Discussion

Domestic and industrial wastewater production in the factory for the last five years were given in Table3. Both industrial and domestic wastewater amount were increased in accordance with the production rate and worker number. In contrast to increase in total amount of wastewater, the change in amount of wastewater per product was not considerably major.

Table 3: The annual industrial and domestic wastewater production.

Year	Domestic Wastewater (m^3)	Industrial Wastewater (m^3)	Total (m^3)	Total (m^3/product)
2009	67,002	68,000	135,002	0.07
2010	73,320	98,450	171,770	0.09
2011	76,440	114,500	190,940	0.08
2012	-	-	110,810	

The factory started to apply the nano-technologic coating technology instead of zinc phosphating process in 2007. The raw wastewater characterization before 2007 was given in Table 4. After revisions in production process, a remarkable decrease inwastewater pollutant load in was observed.Therefore, in it became necessary to perform a detailed characterization study that will leadto an optimization study in the treatment plant operation.

Table 4 Raw wastewater characterization before nano-ceramic coating technology.

Units	pH	COD mg/L	TSS mg/L	Gress mg/L
Batch Painting Pre-equalization Tank	7.01	497	210	154
Batch Enamel Pre-equalization Tank	8.83	3572	800	900

3.1. Wastewater Generation and Characterization

The results of wastewater characterization were presented in the Table 5and 6. COD values in painting, enamel and rinsing wastewaters were analyzed as 190, 616 and 155 mg/L respectively.

Table 5. Raw wastewater characterization.

Wastewater Type / Parameters	Enamel	Painting	Rinsing
pH (-)	8.5 ± 0.6	8.1 ± 0.2	7.7 ± 0.7
TSS(mg/L)	146 ±13	37 ± 18	19 ± 11
VSS (mg/L)	101 ± 11	28 ± 12	10 ± 8
Total COD (mg/L)	615 ± 155	190 ± 70	155 ± 85
Soluble COD (mg/L)	300 ± 70	65 ±10	50 ± 5

Characterization studies showed that heavy metal concentration of raw wastewater was very low (**Table 6**).

Table 6. Heavy metal concentrations in industrial wastewater stream

Wastewater Type	Cu	Zn	Cd	Pb	Mn	Al	T. Cr	Cr^{+6}	Fe	Ni
	(mg/L)									
Painting	<0.2	1.2	<0.05	<1	<0.1	<1	<0.2	<0.2	1.06	<0.3
Enamel	<0.2	0.2	<0.05	<1	0.3	<1	<0.2	<0.2	<1	<0.3
Rinsing	<0.2	1.1	<0.05	<1	0.2	<1	<0.2	<0.2	<1	<0.3

COD concentration of three different wastewater sources were shared in Table7. The results showed that grab samples (especially enamel wastewaters) may also reflect particular situation in the production process. When first grab samples were taken, although production processes were the same, COD concentrations have shown variety. This situation may be because of the day off in the production or discharging of painting and coating baths.Comparing COD concentration of other wastewater sources for first sampling, the most fluctuation was observed for enamel wastewater. But also, enamel wastewater had leastflow rate load in all three wastewater sources, and this feature gave advantage to dilution pollutant load in order to prevent shock loading.

The COD concentrations andpH values for the similar industrial wastewaters have been reported between 75-5905 mg/L and1.35 to 9, respectively[7,13,16]. Except of characterizations results of Sthiannopka (2009), metal concentration values are stayed under 1 mg/L in results of Wahaab (2001) andGabaldón (2007) [7,13,16]. Approximately 22 mg/L zinc and 8.2 mg/L nickel concentration as a heavy metal load is originated from phosphating unit to raw wastewater [16]. As mentioned before, pollutant load of wastewater characterization have been decreased with new eco friendly technologies.

Table 7. Changes in COD concentrations.

Sampling Date	**COD**(mg/L)		
	Painting Wastewater	**Enamel Wastewater**	**Rinsing Wastewater**
12-15.09.2011	190± 70	615± 155	155± 85
18.01.2012	60	280	55
07.03.2012	155± 2	230± 6	90± 18
25.04.2012	265± 3	220± 5	80± 22

3.2. Performance Improvement Studies in the Wastewater Treatment Plant

3.2.1. Chemical Treatment Analysis

COD and TSS concentrations of mixed wastewater were 253 mg COD/L and 65 mg/L, respectively. pH of the mixed wastewater was 8.

COD, pH, turbidity results of chemical treatment was seen in Table 8, 9 and 10for different coagulant types and dosages. In terms of COD concentration, except 1 µL/L dosage, the COD concentrations have been complied with regulation limits at all coagulant dosages. Also pH controls were required at 100 and 150 µL/L dosages.

Table 8. Commercial solution assay results.

Coagulant Dosage (µL/L)	**Mixed Sample** **TSS** (mg/L)	**Supernatant** **pH** (-)	**COD** mg COD/L	**Turbidity** NTU
1	66	6.1	115	23
10	95	6.2	50	5.5
25	95	6.2	45	5
50	96	6.3	45	4
75	100	6.2	40	3
100	123	5.6	40	3.5<x<4
150	129	5.8	40	3.5
Discharge Limit* [11]	-	6-9	100	-

***Water Quality and Control Regulation (2004)

Table 9. $FeCl_3$ solution assay results.

Coagulant Dosage (mg/L)	**Mixed Sample** **TSS** (mg/L)	**Supernatant** **pH** (-)	**COD** mg COD/L	**Turbidity** NTU
1	50	6.04	100	15
10	55	6.08	50	5.5
25	80	5.97	50	4
50	86	6.01	50	3
75	118	6.34	45	2.5
100	163	6.00	45	3.5
150	180	6.02	45	3.5
Discharge Limit*[12]	-	6-9	100	-

***** Water Quality and Control Regulation (2004)

Table 10. Alum solution assay results.

Coagulant Dosage (mg/L)	**Mixed Sample** **TSS** (mg/L)	**Supernatant** **pH** (-)	**COD** mg COD/L	**Turbidity** NTU
1	72	7.4	100	15
10	86	7.2	50	5.5
25	87	7.15	50	2.5
50	117	7.17	50	2
75	113	7.05	45	2.5<x<2
100	120	7.22	45	1.5
150	185	7.24	40	1.5
Discharge Limit*[11]	-	6-9	100	-

Heavy metal concentration results for different coagulant types were givenin Table 11. As a result of chemical treatment, aluminum, ferrous, zinc and total chrome concentration was complied with regulation limits.

Table11. Heavy metal concentrations of chemical treatment effluent by different coagulant.

Heavy Metals (mg/L)	**Commercial Solution Optimum Dosage: 50 mg/L**	**$FeCl_3$ Solution Optimum Dosage: 50 mg/L**	**Alum Solution Optimum Dosage: 50 mg/L**	**Discharge Limit* (mg/L)**[11]
Al	<1	<1	<1	2
Fe	0.5	0.5	0.2	3
Zn	1.3	0.6	1	2
T. Cr	<0.2	<0.2	<0.2	2

In addition to mentioned parameters, volume of produced sludge and settling properties were determined. As all coagulant dosages were supplied the required limits, amount of sludge production and settling efficiency were considered to determine optimum coagulant dosage. In the jar test analysis, produced sludge was more compact and settleableabove 50 mg/L coagulant concentration. For this reason, amount of optimum dosage was chosen as 50 mg/L $FeCl_3$ solution& 50 µL/L commercial solution.

3.2.2. Inert COD Evaluation

Determination of particular and soluble inert COD fractions was important in order to design and operate a treatment plant. For this purpose, inert COD concentrations were evaluated with three different industrial raw wastewater. At the beginning of the study, total COD concentration of enamel and painting wastewater were 230 mg/L and 235 mg/L, respectively while total COD concentration of rinsing wastewater was 100 mg/L. Total inert COD in enamel, painting and rinsing wastewaters were determined as 21%, 17% and 12% of the total COD content respectively.

3.2.3. Respirometric Studies and Simulation

Acute toxicity effects as well as biodegradability potentials of industrial wastewaters generated from the factory were assessed using two types of activated sludges obtained from the treatment plant of the same factory. Industrial wastewater respirometrically analyzed using industrial activated sludge in order to understand the treatment efficiency. In the wastewater treatment plant, because of low organic substances the amount of sludge production is not sufficient and the sludge requirements of industrial biological treatment have been supplied by domestic activated sludge. Because of this, industrial wastewater respirometrically analyzed using domestic activated sludge in order to determine the acute effect of industrial wastewater on the domestic sludge. Organic matter concentration of industrial wastewater was not very high. And industrial wastewater respirometrically was analyzed using industrial activated sludge in order to understand the treatment efficiency.

3.3. Possible Effects of Optimization Studies

3.3.1. Energy Recovery

Energy consumptions and individual costs of each processes in the wastewater treatment plant are shared in Table 13.Beause of aeration processes, biological treatment units are the most energy consuming part in both situations. For this reason, requrement of bioogical treatment is especially studied in this study.

Table1. Evaluation of cost of energy in the Wastewater Treatment Plant (WWTP)

Units	Consumed Energy/day (kWh/day)		Cost of Energy (TL/year)		Total Consume Energy in WWTP (%)	
	Before	**After**	**Before**	**After**	**Before**	**After**
Batch Treatment	284.88	80.8	19,942	5,656	20.9	9.39
Continuous Chemical Treatment	116.58	218.08	8,161	15,266	8.5	25.34
Industrial Biological Treatment	473.98	228.48	33,179	15,994	**34.7**	**26.55**
Domestic Biological Treatment	362.2	185.5	25,354	12,985	26.6	21.55
Sludge Drying Unit	7.25	131.75	174	3,162	0.5	15.31
Chemical Preparation	1.11	1.11	77,7	77.7	0.1	0.13
Others	118.1	15	8,267	1,050	8.7	1.74
Total	1,364.1	860.72	**95,155**	**54,191**	100	100

3.3.2. Chemical Consumption

During the jar tests, as previously mentioned, nearly all the coagulant type and dosage of the water discharge limits after treatment is provided. However, in terms of sludge density quality and settlability, sludge formation is started to observe after 50 mg/L and µL/L dosages.

Considering the total amount of chemical consumption and treated wastewater in the sampling period 82 µL solution consumption is seen to treat one liter wastewater. In addition to this, 227 µL solution consumption is observed annually.This amount of change in annual wastewater why it is so much variability in the formation, in the year of evacuation of the bathroom, cleanliness, and are the pause period.

Effects of coagulant type on expenses in the sludge management of wastewater treatment plant are showed in Figure 6. The most expensive solution is $FeCl_3$.

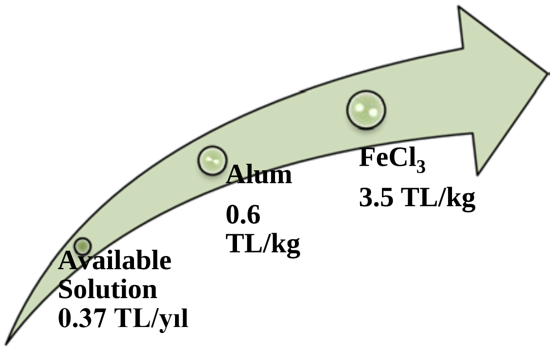

Figure 6. Effects of coagulant type on expenses in the wastewater treatment plant.

3.3.3. Sludge Generation

The amount of sludge in the facility for the year 2011 has been identified as the 65,840 kg. Sludge disposal cost is approximately 0.218 TL/ kg, while transportation cost is 07 TL/ kg. According to coagulant type, variations in the amount of sludge, disposal&trasnportation costs are shared in Table 14.In terms of sludge management, alum solution is shown most effective, but alum solution has some reverse effects on sludge characteristics (settleability, floc type).

Table 14. Effects of coagulant type on sludge disposal.

Saving	Alum Solution	$FeCl_3$Solution	Available Solutioni
Amount of Sludge	32,292 kg	41,223 kg	38,360 kg
Disposal Cost	7,040 TL/kg	8,987 TL/kg	8,363 TL/kg
Transportation Cost	2,260 TL/kg	2,886 TL/kg	2,685 TL/kg

4. Conclusion

Characterization results, when compared to the other raw wastewater in the metal finishing sector, low pollution load was observed for investigated industry. In year period, the COD parameter of wastewater was changed between 300-600 mg/L. Also, all pollutant parameter of wastewaterwere complied with discharge regulation limits.In chemical treatment assays, because of low pollutant concentration in wastewater, all coagulant dosages used in this study reflected nearly same removal efficiency. Considering economic conditions and sludge production, optimum $FeCl_3$ coagulant dosage is determined as 50 mg/L and 50µg/L. In the light of the results, the application of biological treatment methods after chemical treatment isnot proper for the studied industrial wastewaters because of the low COD concentration and inhibitory effect. Also for industrial wastewater, only chemical treatment is sufficient to comply with discharge regulation. Savings in the use of energy, chemical and cost is expected to achieve by removing unnecessary biological treatment units and adjusting optimum coagulant dosage in the wastewater treatment plan.

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