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Effect of eco-friendly production technologies on wastewater characterization and treatment plant performance

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ABSTRACT

Operating a wastewater treatment plant (WWTP) efficiently is a knowledge required key issue than the entity of treatment plant. In this study, efficiency of WWTP of a metal finishing industry was evaluated and optimized after the process renovation by means of a modern eco-friendly process application. Three processes intensively consuming water and producing wastewater are metal surface pre-treatment, painting, and enamel coating. Based on the characterization studies, it is observed that the process renovation resulted in an improvement in the quality of the raw wastewater leading low pollutant load. Chemical treatment experiment was performed to assess optimum dosages for the WWTP. Also respirometric analyses were conducted in order to evaluate biological treatability of wastewater. Similar results were obtained for all the coagulants tested, but sludge quality after flocculation as well as settleability was better for both commercial and pure $FeCl_3$ solutions. As a result of the observed low pollution load in the raw wastewaters and based on the respirometric analyses, biological treatment step of industrial wastewater was eliminated which was an important constituent of the overall energy requirement of the existing WWTP.

Keywords: Optimization; Wastewater characterization; Energy recovery; Cost saving; Respirometric analysis; Chemical treatment

1. Introduction

The improvements in the context of environmental friendly and cleaner production are the main target for most of the industries. The number of industries that apply cleaner production methodologies to diminish negative impact of their activities and their products on the environment keep increasing all over the world [1,2]. The Directive 2010/75/EU on industrial emissions (integrated pollution prevention and

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control) requires the integrated approach, where the whole environmental performance of the plant should be considered (e.g. emissions to air, water and land, generation of waste, use of raw materials, energy efficiency, noise, prevention of accidents, and restoration of the site upon closure) [3]. Additionally, in the vision of "Europe 2020," sustainable growth was highlighted as one of the three mutually reinforcing priorities. Under this framework, European Commission initiated act of "Resource Efficient Europe." Many factories have already started to do implementation to improve their resources (e.g. energy, water, and chemical) to reach "Resource Efficient Europe" [4]. Similarly, the achievement of the sustainable management and efficient use of natural resources is one of the 17 goals published in the 2030 UN Global Sustainable Development Goals [5]. Especially, changes in production processes to eco-friendly technologies have important effects on eco-footprint (e.g. carbon and water footprint) of facilities. Besides, technology shifting requires the assessment in whole facility to optimize conditions of resource consumption.

Metal coating industry, 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 product involve rapid 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 [6].

The primary environmental problems associated with metal finishing and electroplating operations are disposal of contaminated wastewater, 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 [2].

On the other hand, corrosion is an important problem for production process with 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 processes 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. Nanoceramic coating is one of these techniques [7]. Being eco-friendly, applications of nanocomposites offer new technologies and business opportunities for several sector of metal finishing industry [6]. 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 better performance [8].

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 (WWTP); (3) to optimize resource consumption and determine energy recovery in the WWTP after the improvements.

2. Materials and methods

2.1. Industry profile and process description

The metal finishing factory, where this study is conducted is located in Bolu, Turkey. The factory is one of the biggest white goods manufacturers in Turkey. The number of the staff working in the factory is 2,200 with an annual production capacity of 2,879,278 pieces of cookers (data of 2014).

The sheet metal parts coming from mechanical production or sub-industries used in the production have to be exposed to surface pre-treatment processes as degreasing, rinsing, nanoceramics coating, and deionization rinsing process, consecutively. Metal sheets were covered with oil film in order to prevent oxidation of metals. Firstly, the metal sheets have to be cleaned to increase the efficiency of coating process. The cleaning process is called degreasing process. In addition to degreasing process, enamel and painting processes are the other two wastewater generating processes. In the factory, there are two enamel coating units called as Enamel Process I and Enamel Process II to bring more thermal resistance to the product. In the painting process, product parts which are exposed to heat (200℃) are painted. The painting process varies according to paint color or specialty. Silver, white-black, and antifinger processes are the specific painting processes that are classified under the painting process. Silver and white-black process varies according to the paint colour, while antifinger process is related to the paint speciality. The products become stain proofed of fingerprint after antifinger stage. Stages of painting process is given in Fig. 1. The pieces after pre-surface treatment are painted under dried condition during 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.

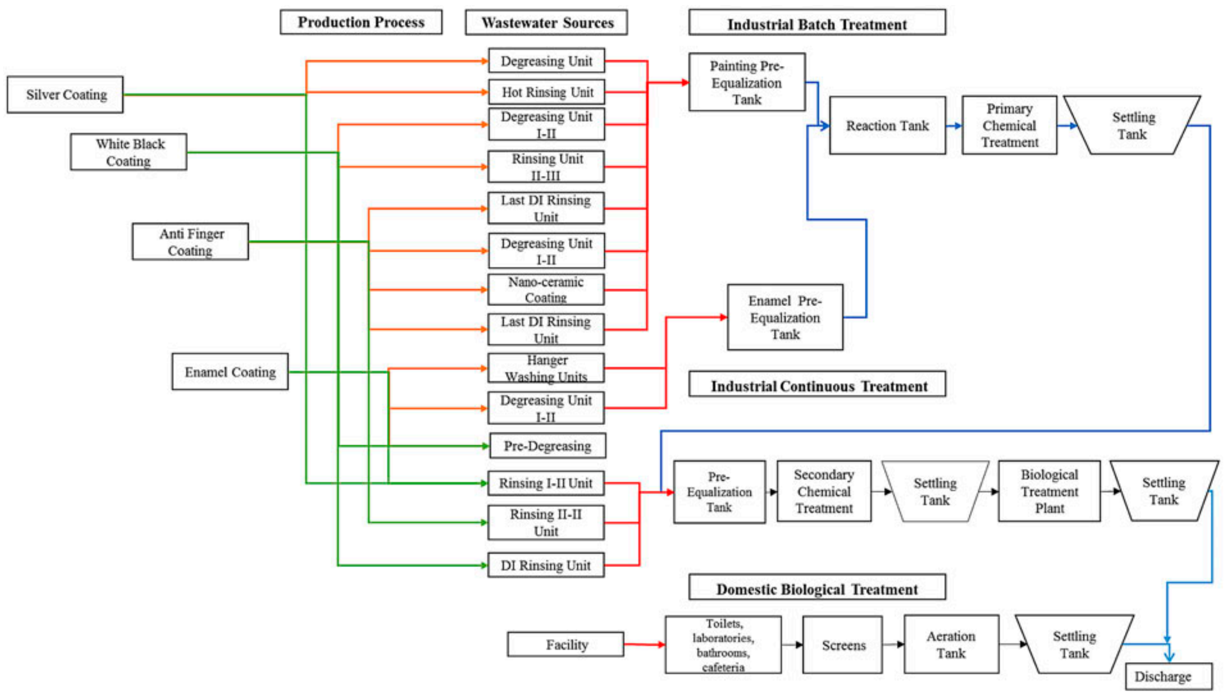

Fig. 1. Schematic of wastewater sources from processes reaching to the WWTP.

2.2. Wastewater sources and sampling

The main wastewater sources in the factory consist from domestic and industrial wastewater streams. While domestic wastewater is generated from toilets, cafeterias, and recreational facility, industrial wastewaters are originated from metal surface treatment, enamel coating, and painting processes. In addition, a small amount of wastewater is derived from cooler towers and chiller that generate 20 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. Continuous treatment unit receives both domestic and industrial wastes (Fig. 1). Highly polluted wastewaters are generated from painting, and enamel processes were treated chemically in a batch treatment unit. Whereas low-loaded rinsing wastewaters of these processes are treated in continuous treatment process in the industrial chemical treatment unit. Both industrial and domestic wastewaters are discharged into Bolu Kuruçay River after treatment. As the effluents of treatment plant are discharged to the river, pollutant level should comply with the water pollution and control regulation in Turkey [9].

Wastewaters originating from the degreasing process are treated in batch chemical treatment unit. Firstly, in order to homogenize the wastewaters, the painting and enamel wastewaters are collected in the equalization tank in the batch treatment process. In the reaction tank, HCl and $FeCl_3$ solutions are introduced for pre-oxidation. As the oil content of the wastewater was high, the wastewater was directed to the flotation unit after the reaction tank. On the other hand, the application of powder and nanotechnology coating methods resulted in an improvement in the wastewater character in terms of oil content, which leaded to the deactivation of the flotation unit in the treatment plant. In the chemical treatment unit, wastewater is exposed to neutralization, coagulation, and flocculation processes. Right after the batch treatment process, wastewater 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 separately in biological treatment unit.

In this study, the samples taken at different times from WWTP were analyzed and treatability studies were performed. During the first campaign, grab samples were collected from the determined points at the same hour during the day for four consecutive days. In addition to these samples, hourly composite samples were collected between 08:00 a.m. and 06:00 p.m.

2.3. Analytical methods

All conventional analyses were performed as described in Standard Methods [10]. The chemical treatability study was carried out using F105A0112 Velp Jar Test (Type FC6S; U.K). Different dosages of coagulant were added to the respective jars to determine the optimum dosage range. Jar test was performed in 500-ml glass flasks. Coagulant was added into the mixing sample until flocks started to occur to determine optimum dosage. Starting from minimum dosages seven different coagulant dosages were applied. The coagulant was added simultaneously after the rapid mixing was 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 reaching to the treatment plant. The mixing ratio of wastewater was 3:1 for painting:enamel wastewater. A commercial solution containing $FeCl_3$, alum and $FeCl_3$ was used in the Jar Test experiments for "Chemical Treatment Analysis." Additionally, pH of this solution was adjusted to 5.5 and 6.5–7 using HCl and NaOH solutions according to the type of coagulant. Finally, 400 μL/L anionic polyelectrolyte was used as a flocculent.

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 process. Also buffer solutions were added in the reactors to satisfy the requirement of trace elements for biological activity [11–12]. In respirometric analyses 1.5 L of sludge sample was used and the b_H level was monitored for at least 15 min and then 1 L of wastewater was added. In order to eliminate any confusion, the b_H 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 2.1e software [13].

Initial inert COD components of the three types of influent wastewaters generated from painting process, enamel process, and rinsing process were assessed. The sludge taken from industrial-activated sludge aeration tank was used in all the reactors. The inert COD fractions were assessed using the methods as defined in the literature [14].

3. Results and discussion

Domestic and industrial wastewater generation in the factory during the last six years is given in Table 1. The ratio of industrial and domestic wastewater streams were in the range of 45–60% reflecting that the annual production of domestic and industrial wastewater amounts were almost same. Similar results were also observed in the literature where the ratio of domestic wastewater streams to industrial streams has been reported as 40% [4]. Both industrial and domestic wastewater amount were increased in accordance with the production rate and worker number in the facility. Although an increase was observed in the total amount of wastewater generated, there was not a significant change in the amount of wastewater per equivalent product (Table 1). Water requirement of the same facility is reported as 244,830 m^3/year and 65% of consumed water reaches to the industrial WWTP [15].

The factory started to apply the nanotechnologic coating technology instead of zinc phosphating process in 2007. The raw wastewater characterization before 2007 is given in Table 2. After revisions in production process, a remarkable decrease in wastewater pollutant load was observed. However, optimization studies using detailed characterization of the generated wastewater were not performed. Therefore, it was necessary to perform a detailed characterization as well as treatability study that will lead to the effective operation of the current WWTP.

3.1. Wastewater generation and characterization

Generally, water resources such as tap water, well water, or well water subjected to the deionization using reverse osmosis (RO) are used in painting, degreasing, and rinsing processes. The wastewater generated from the processes contains oil, heavy metals, organic solvents, alkaline, and acidic solutions depending on the type of the process.

Wastewater characterization results after implementation of nanoceramic coating technology are presented in Table 3. COD values in painting, enamel, and rinsing wastewaters were determined as 190, 616, and 155 mg/L, respectively. The characterization results reflected significant improvement in the wastewater pollution load after the renovation of the coating technology. Also results indicated that COD concentration of raw enamel wastewater decreased approximately 80% while TSS concentration decreased 90%. Characterization studies also showed that heavy metal concentration of raw wastewater was very low (Table 3).

The COD concentration of three different wastewater sources is given in Table 4. The results showed that grab samples (especially enamel wastewaters)

Table 1
The annual industrial and domestic wastewater generation

Year	Industrial wastewater (m^3)	Total wastewater (m^3)	Total wastewater/product (m^3/equivalent product)
2009	68,000	135,002	0.07
2010	98,450	171,770	0.09
2011	114,500	190,940	0.08
2012	122,240	233,050	0.08
2013	144,110	262,220	0.07
2014	130,520	305,040	0.07

Note: Equivalent units/products are the units in production multiplied by the percentage of those units that are complete (100%) or those that are in process.

Table 2
Raw wastewater characterization before nanoceramic coating technology

Units	pH	COD (mg/L)	TSS (mg/L)	Oil and grease (mg/L)
Batch Painting Pre-equalization Tank	7.01	497	210	154
Batch Enamel Pre-equalization Tank	8.83	3,572	800	900

may also reflect particular situation in the production process. Although no change was occurred during the production processes, grab samples reflected some variety in the COD concentrations of the wastewaters with high fluctuation in the standard deviation. This fluctuation may be a result of the discharge of high-loaded painting and coating baths at different hours during the day. Low flow rate of enamel process wastewater is advantageous in terms of the probable pollutant dilution which will prevent shock loading.

Table 3
Average raw wastewater characterization

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

The COD concentrations and pH values for the similar industrial wastewaters have been reported between 75–5,905 mg/L and 1.35–9, respectively [16–18]. The results reflect that in this sector the COD concentrations may fluctuate significantly considering the differences in the applied processes and used technologies. Similarly, pH values of the generated wastewaters may range between acidic and basic content. Except from the characterizations results of Sthiannopka [17], metal concentration values have been indicated below 1 mg/L [16–18]. Approximately, 22 mg/L zinc and 8.2 mg/L nickel concentration generated from phosphating process has been stated for raw wastewater [18]. Heavy metal contamination observed for the similar type of industry in terms of zinc, total chromium, and iron concentration have been stated as 4.37, 1.91, and 7.49 mg/L, respectively, in the literature [19]. In a study conducted with the effluent wastewater of the brass and electroplating industries, the heavy metal contents (i.e. Cr, Zn, Cu, Ni, Cd, and Fe) of the wastewaters were reported in the range of 1.2–13.7 mg/L [20]. These reported concentrations were relatively higher than the concentrations observed in this study. The reason for the observed low concentrations can be explained by the renovation in the production process. As mentioned above, pollutant load of wastewater characterization has been decreased with new eco-friendly technologies. Heavy metal concentrations in the facility were detected below 0.2 and 0.3 mg/L which were under the limits reflected in the regulations.

Table 4
COD concentrations in the generated wastewaters from three different processes

Campaign no	COD (mg/L)		
	Painting wastewater	Enamel wastewater	Rinsing wastewater
1*	190 ± 70	615 ± 155	155 ± 85
2**	60	280	55
3**	155 ± 5	230 ± 5	90 ± 20
4**	265 ± 5	220 ± 5	80 ± 20

*Four grab samples at different days.
**Composite sample.

3.2. Optimization studies in the WWTP

3.2.1. Chemical treatment analysis

COD, TSS concentrations, and pH value of the wastewater mixture (enamel and painting) were measured as 253 mg/L, 65 mg/L, and 8, respectively. COD, pH, and turbidity results of chemically treated wastewater are shown in Table 5 for 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. It should be indicated that pH controls were required at 100 and 150 μL/L dosages.

Heavy metal concentration results for different coagulant types are given in Table 6. As a result of the chemical treatment of the wastewater mixture, aluminum, ferrous, zinc, and total chrome concentrations are complied with regulation limits.

In addition to the above-mentioned parameters, volume of produced sludge and the sludge settling properties were also determined. As all coagulant dosages were fulfilled, the required limits, amount of the sludge production and settling efficiency were also considered in order to determine optimum coagulant dosage. In the jar test analysis, more compact sludge character with better settleability quality was obtained above 50 mg/L coagulant concentration. Therefore, amount of optimum dosage was chosen as 50 mg/L $FeCl_3$ solution and 50 μL/L for the commercial solution.

3.2.2. Inert COD evaluation

Determination of particular and soluble inert COD fractions is an important step in order to design and operate a WWTP. At the beginning of the inert COD experiments the initial total COD concentration of enamel, painting, and rinsing wastewaters were measured as 230, 235, and 100 mg/L, respectively. Total inert COD in enamel, painting, and rinsing wastewaters were determined as 21, 17, and 12% of the total COD content, respectively. Details of inert COD fractions for process wastewater streams are presented in Table 7. Although organic COD content is high, COD concentration reaching to the biological treatment unit is very low. Thus, biological treatment unit is not an efficient and necessary technology for these wastewater streams. These results reflected that optimization can be performed for biological treatment unit of WWTP where the highest energy consumption occurs.

3.2.3. Respirometric studies and simulation

Acute toxicity effects as well as biodegradability potentials of industrial wastewater generated from the factory were assessed respirometrically using activated sludge obtained from the biological treatment unit of domestic wastewater. The effluent of chemically treated wastewater respirometrically analyzed in order to understand the treatment efficiency and to determine kinetic and stoichiometric constants.

In order to simulate the existing treatment plant, a sample of composite wastewater was prepared and treated by coagulation and flocculation method using determined optimum dosage (50 mg/L). Wastewater composition is prepared same as in the Jar test method. Supernatant of chemically treated wastewater is respirometrically analyzed using domestic activated sludge. Volume of sludge and wastewater were selected as 1.5 and 1 L, respectively. Initial TSS and VSS were 2,430 and 3,510 mg/L, respectively.

Organic matter content of the industrial wastewater after chemical treatment decreased considerably. Soluble COD concentration after chemical treatment is determined as 50 mg/L. As seen in Fig. 2, when the wastewater introduced into the reactor, oxygen uptake rate increased barely due to the very low biodegradable organic matter content of the wastewater. Kinetic and stoichiometric coefficients for respirometric analysis are presented in Table 8.

Table 5
Chemical treatment assay results

	Commercial solution				FeCl$_3$ solution					Alum solution			
		Supernatant					Supernatant				Supernatant		
Coagulant Dosage (μL/L)	TSS (mg/L)	pH (–)	COD (mg/L)	Turbidity (NTU)	Coagulant Dosage (mg/L)	TSS (mg/L)	pH (–)	COD (mg/L)	Turbidity (NTU)	TSS (mg/L)	pH (–)	COD (mg/L)	Turbidity (NTU)
1	66	6.1	115	23	1	50	6.04	100	15	72	7.4	100	15
10	95	6.2	50	5.5	10	55	6.08	50	5.5	86	7.2	50	5.5
25	95	6.2	45	5	25	80	5.97	50	4	87	7.15	50	2.5
50	96	6.3	45	4	50	86	6.01	50	3	117	7.17	50	2
75	100	6.2	40	3	75	118	6.34	45	2.5	113	7.05	45	2.5< × <2
100	123	5.6	40	3.5< × <4	100	163	6.00	45	3.5	120	7.22	45	1.5
150	129	5.8	40	3.5	150	180	6.02	45	3.5	185	7.24	40	1.5
Limit*	–	6–9	100	–		–	6–9	100	–	–	6–9	100	–

*Discharge limit, water pollution, and control regulation [9].

Table 6
Heavy metal concentrations of chemical treatment effluent by different coagulant

Heavy metals (mg/L)	Commercial solution optimum dosage: 50 μL/L	$FeCl_3$ solution optimum dosage: 50 mg/L	Alum solution optimum dosage: 50 mg/L	Limit* (mg/L)
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

*Discharge limit, water pollution, and control regulation [9].

Table 7
Inert COD fractions in process wastewater

Wastewater Stream	Soluble Inert COD (% in total wastewater)	Particulate Inert COD (% in total wastewater)	Total Inert COD (%)
Enamel	7	14	21
Painting	7	10	17
Rinsing	12	0	12

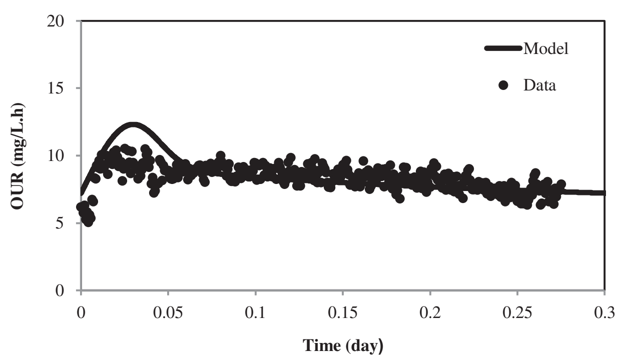

Fig. 2. Modeling results of respirometric assessment of chemically treated wastewater.

3.3. Possible effects of optimization studies

3.3.1. Energy recovery

Energy consumptions and individual costs of each process in the WWTP are given in Table 9. Aeration processes of biological treatment units are the most energy consuming constituents of WWTP. For this reason, necessity of the biological treatment unit after the chemical treatment is particularly studied in this study.

3.3.2. Sludge generation

The generated amount of the treatment sludge in the facility for the year 2011 was identified as 65,840 kg. Sludge disposal cost is approximately 0.066 €/kg (year 2012), while transportation cost is 0.21 €/kg (year 2012). According to coagulant type, variations in the amount of sludge, disposal, and transportation costs are shared in Table 10. In terms of sludge generation, alum solution was the most effective coagulant. However, alum solution had adverse effects on sludge characteristics (i.e. settleability, floc type).

Table 8
Kinetic and stoichiometric coefficients .

Coefficients	Unit	Value
Maximum specific growth rate for S_S, μ_H	1/d	2.5
Half saturation constant for S_S, K_S	mg/L	10
Maximum hydrolysis rate for X_S, k_{hx}	1/d	1
Hydrolysis coefficient for X_S, K_{XX}	gCOD/gcellCOD	0.15
Endogenous decay rate, b_H	1/d	0.24
Active biomass concentration, X_H	mgCOD/L	900

Table 9
Evaluation of energy cost in the WWTP

Units	Consumed energy/d			
	Before optimization (kWh/d)	After optimization (kWh/d)	Before optimization (%)	After optimization (%)
Batch treatment	284.9	80.8	20.9	9.4
Continuous chemical treatment	116.6	218.1	8.5	25.3
Industrial biological treatment	473.9	228.5	34.7	26.6
Domestic biological treatment	362.2	185.5	26.6	21.6
Others*	126.5	147.9	9.3	17.2
Total	1,364.1	860.7	100	100

*Others; sludge drying units, chemical preparation units, WWTP building, etc.

Table 10
Effect of coagulant type on sludge disposal*

Saving	Alum solution	$FeCl_3$ solution	Commercial solution
Amount of sludge	32,292 kg	41,223 kg	38,360 kg
Disposal cost	9,064 €/kg	11,571 €/kg	10,768 €/kg
Transportation cost	2,910 €/kg	3,716 €/kg	3,457 €/kg

*For year 2012.

4. Conclusion

The main objective of this study was the evaluation of the current situation of the WWTP in terms of resource and treatment efficiency to improve environmental performance for a metal finishing industry in Turkey.

Characterization results reflected that low pollution load was observed in the investigated factory compared to the other metal finishing industries. The application of the nanotechnologic coating technology instead of zinc phosphating process resulted in a remarkable decrease in wastewater pollutant load. All pollutant parameters of wastewater were complied with discharge regulation limits. All coagulant dosages used in this study reflected nearly same removal efficiencies. Considering economic conditions and sludge production, optimum $FeCl_3$ coagulant dosage was determined as 50 mg/L. In the light of the obtained results, operation of the biological treatment unit after chemical treatment was not necessary in the investigated factory. Re-evaluation of the treatment plant operation resulted in a considerable energy cost saving.

Beside environmentally sustainable production technologies, this study indicated that evaluation of WWTP also plays an important role for the resource efficiency as well as to interiorize standards set by European Commission.

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