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Physico-Chemical Studies of Enamel Cover Industry Wastewater

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The enamel plating industry wastewater has a reputation for being a major pollutant. Plating has become a major industry and is one of the fastest growing sectors of the world economy. Enamel industry is typically associated with detrimental environmental effects. There was not exactly a study source of enamel cover wastewater and characteristics in Turkey. This study has been made for completing this subject and to solve available problems. To achieve the objectives of the study, the samples taken from metal plating wastewater, were analyzed in the laboratories. Wastewater produced plating unit in enamel have high chemical oxygen demand (394 mg L^{-1}) and suspended solid (486 mg L^{-1}) concentrations. In this study, physico-chemical properties were also evaluated in enamel plating industry wastewater. The optimum polielectrolyte dose with lime addition was determined as 1660 mgL^{-1} in order to obtain 86 % COD, 94 % TSS removal effiency at pH 9.

Key Words: Enamel plating wastewater, COD, TSS, Removal.

INTRODUCTION

Some of the wastewater metal products and machinery industries are aerospace, electronic equipment, ordinance and hardware industries. Metal products and machinery include electroplating, metal enameling and coil coating[1]. The Metal Finishing Industries have been considered to be the fourth most polluting industries in South Africa and is a major industrial source of heavy metals in wastewater. The waste generated from the industry has been found to be hazardous to the environment and humans. This emanates from the fact that the raw materials used are usually highly toxic, flammable and the acid and alkali solutions used in the processes are both corrosive and reactive[2]. Contact of the compound with acids liberates a poisonous gas which leads to burning of the skin, eyes and respiratory tract. Sodium cyanide is also flammable and is toxic to aquatic and terrestrial life[3].

The depletion of essential resources and the deterioration and destruction of natural processes is of major concern in the world today. These changes are mainly a result of poor agricultural practices, industrialization and urban growth[2]. The mixes used in enamel industry are toxic and/or acidic. Considering its metal groups included and variable pH range, discharging it without refining will cause crucial problems in receiving medium. Copper, nickel, cadmium, silver and zinc are the metals that are expected in this stream. The effluent is treated with sodium metabisulphite ($Na_2S_2O_3$), sodium hypochlorite (NaOCl), caustic soda or soda ash (Na_2CO_3). An effluent treatment plant has been built on site to comply with legal discharge limits. Solids are effectively removed by filtration[4].

Enamel industry wastewater has variable character depending on operating sensitivities of the plants. The plates coming to process in packets, after mechanical operations, for cleaning surfaces, being filled in the tanks of oil trap; acid and base, respectively, are treated at 70 ºC. Then, immersing in pre-coating tank, they are pre-coated and pre-coat is dried at 83 ºC. The dried material, with immersing in enamel tanks, is subjected to final enamel plating treatment. The wastewater from industry is 'after use waste water' forming in the tanks above mentioned. The tanks are emptied in batch system and some differences occur in terms of pH (with emptying caustic and acid tanks separately, pH varies between 3 and 11). This industry use a number of hazardous chemicals including sulphuric acid, metal salts, chromic acid and phosphoric acid[5].

Laboratory and pilot testing was conducted using numerous coagulants, reducing agents, polyelectrolyte and pH adjustment systems and schemes. Individual, joint, batch and continuous treatment schemes for all the wastewaters identified were investigated and evaluated. The final system design utilizes automated batch neutralization of spent solutions, anodizing and washer and enameling wastewater. Ferrous sulfate addition for hexavalent chromium reduction, pH adjustment and polyelectrolyte addition occurs prior to an inclined plate clarification unit[6]. The waste minimization options implemented that cascade and counterflow rinsing has been introduced to this line and a saving of 50 % in water use was achieved.

EXPERIMENTAL

The sample used was taken from wastewater of Avsar Enamel Plant. Wastewater of the plant contains high amount of solid material, which are able to precipitate. The first stage of refining plant is pre-decantation pull. The solid materials, can precipitate here, are removed *via* sedimentation. The sample used during study was taken from stabilizing pull ahead of decantation pull. The properties of the sample are given in Table-1.

In refining system used during the tests, are oil trap with vents (barrier system), chemical refining, decantation, neutralization, sand filter (anthracite), respectively (Fig. 1). During chemical refining, commercial $Ca(OH)_2$ and polyelectrolyte were used. $Ca(OH)_2$ solution used was prepared by 20 g of $Ca(OH)_2$ + 1000 mL of water; while the poly electrolyte solution was prepared 10 g of polyelectrolyte + 1000 mL of water.

TABLE-1
PROPERTIES OF THE SAMPLE TAKEN FROM WASTEWATER AND STABILIZING PULL IN THE PLANT FORMING DIFFERENT PROCESSES

Parameter	Rinsing outlet	Cleaning water	Acid tank water	Sample used
pH	6.95	7.22	1.80	6.5
TSS (mg/L)	465	621	75.42	486
COD (mg/L)	561	170	82.54	394
Oil-Grease (mg/L)	30	80	62	49
F^- (mg/L)	1.38	1.38	1.57	1.43
NH_4^- (mg/L)	0.00	0.00	0.00	0.00
NO_2^-, (mg/L)	0.0	0.0	0.0	0.00
Al^{3+} (mg/L)	0.1010	1.6729	5.7308	1.98
Cd^{2+} (mg/L)	0.1052	0.3478	0.0155	0.1946
Cr^{3+} (mg/L)	0.0000	0.0004	4.6772	0.9874
Cr^{6+} (mg/L)	0.0000	0.0000	0.0000	0.0000
Cu^{2+} (mg/L)	0.0000	0.0000	0.5679	0.0051
Fe^{2+} (mg/L)	2.7077	0.2794	280.52	87.4
Ni^{2+} (mg/L)	0.1027	0.1472	2.7769	0.68
Pb^{2+} (mg/L)	0.0000	0.0000	0.0462	0.0110
Zn^{2+} (mg/L)	0.0424	0.0053	0.9111	0.039

The values indicated, as 0.0 are the values being under the measurement limit of analysis device.

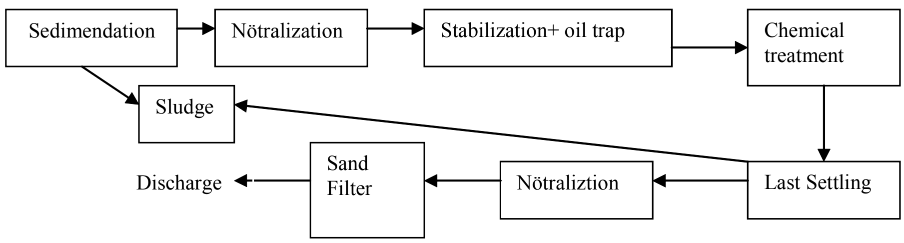

Fig. 1. In enamel industry, refining plant flowsheet for physico-chemical refining

During refining studies, 500 mL of raw wastewater and different doses 250, 500, 750, 1000, 1250, 1500, 1750, 2000 mg L^{-1} of $Ca(OH)_2$ were added. After subjecting to 2 min of fast mixing, adding 1 mL of polyelectrolyte, it was subjected to 4 min of slow mixing. After mixing operation finished, wait for 15 min, taking necessary amount of sample from the upper part of the beakers for TSS and KOI tests, analysis was carried out. TSS tests were measured by gravimetric method, while KOI tests by UV visible spectrometry (Dr Lange Cadas 200). After stabilizing high pH (6.5-7.5) due to $Ca(OH)_2$, increasing of the efficient was aimed by passing through sand filter.

RESULTS AND DISCUSSION

Wastewater sample (500 mL) was taken and added $Ca(OH)_2$ in doses of 250, 500, 750, 1000, 850, 900, 950, 1000, 1050, 1100, 1250, 1500, 1750, 2000 mg L^{-1} in it and finally 1 mL of polyelectrolyte was also added at the beginning of slowly mixing. The values of TSS and COD and per cent efficiencies were shown in Table-2.

TABLE-2
COD AND TSS RESULTS IN THE STUDY PERFORMED WITH $Ca(OH)_2$ AND % EFFICIENCY

$Ca(OH)_2$ dose (mg L^{-1})	Outlet COD (mg L^{-1})	Efficiency (%)	Outlet TSS (mg L^{-1})	Efficiency (%)
250	168.3	57.3	176.6	63.6
500	157.3	60.1	173.8	63.9
750	131.4	66.7	154.6	68.2
1000	128.5	67.4	122.5	74.8
1250	122.2	69.0	110.9	77.2
1500	99.3	74.8	87.7	81.9
1550	84.4	78.6	69.5	85.7
1600	71.0	82.0	60.3	87.6
1650	63.9	83.8	43.3	91.1
1670	61.9	84.3	48.6	90.0
1685	62.7	84.1	53.7	89.6
1700	67.4	82.9	64.7	86.7
1750	72.5	81.6	83.2	82.9
2000	93.5	77.3	108.8	76.3

In this stage, any treatment was not performed on pH of the samples. However, the fact that pH is crucial in such studies made necessary for us to carry out the works given its results as follows. When examining the values given in Table-2, the highest COD removal is corresponding to 1670 mg L^{-1} $Ca(OH)_2$ of dose and the highest TSS 1650 mg in $Ca(OH)_2$ L^{-1} of dose were obtained. As seen in Fig. 2, the works after dosing 1650 mg L^{-1} of $Ca(OH)_2$, the efficiency has begun to decrease. In this study, the flakes in beakers have shown floating tendency rather than precipitation tendency in higher doses.

For the studies above, adopting as a reference the dose provided the best efficiency (1660 mg L^{-1} of $Ca(OH)_2$), the tests were carried out in different pH ranges (pH = 4-9) and pH range was determined for operating conditions. In pH range worked on, it was again focused on the efficiencies of COD and TSS.

The highest COD and TSS removal have been obtained in the dose of 1660 mg $Ca(OH)_2$ L^{-1} and at pH = 9 (Table-3). In addition, the higher pH accompanying $Ca(OH)_2$ forming has contributed for this system to work efficiently. As shown in Fig. 3, at lower pH values, for refining wastewater of enamel industry by $Ca(OH)_2$, appropriate efficiency cannot be achieved.

TABLE-3
COD AND TSS RESULTS AND % EFFICIENCIES IN THE TESTS PERFORMED FOR DIFFERENT pH

pH	Outlet COD (mg L^{-1})	Efficiency (%)	Outlet TSS (mg L^{-1})	Efficiency (%)
4	182.8	53.6	300.3	38.2
5	132.7	66.3	160.3	67.0
6	111.8	71.6	145.3	70.1
7	98.1	75.1	129.7	77.3
8	78.8	80.0	35.4	92.7
9	55.1	86.0	30.1	93.8

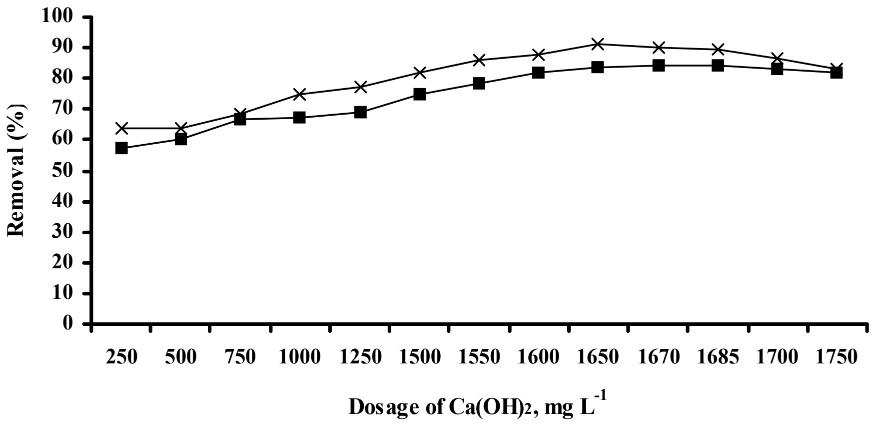

Fig. 2. Per cent of COD and TSS removal *vs.* $Ca(OH)_2$ dose (× TSS, ■ COD)

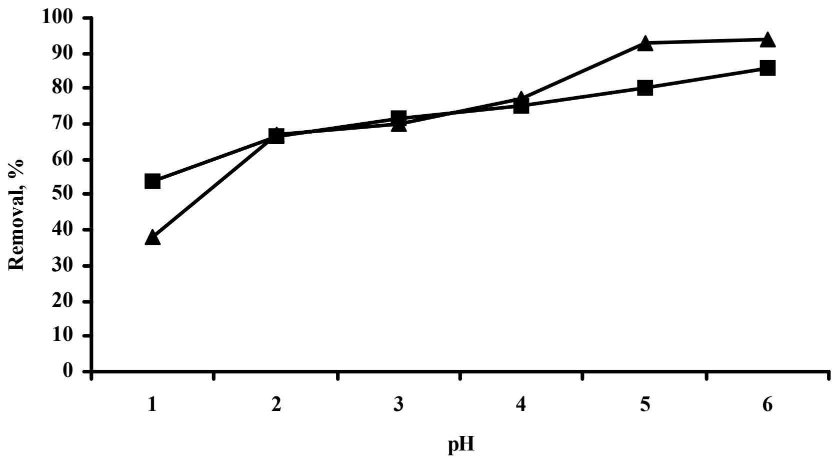

Fig. 3. Per cent of COD and TSS removal *vs.* different pH ranges (▲ TSS, ■ COD)

$Ca(OH)_2$ dose achieved the best efficiency was determined as 1660 g L^{-1} of $Ca(OH)_2$ and pH = 9. The wastewater (55.1 mg L^{-1} for COD, 30.1 mg L^{-1} for TSS) obtained in marked conditions was subjected to neutralization process and brought into higher pH levels (pH = 6.5-7.5). Then, the wastewater being passed a tower, whose packing material is anthracite sand, provided extra efficiency 48 % in COD value and 61 % in TSS value after chemical refining outlet. However, final outlet water quality obtained in study of enamel wastewater refining was found as pH; 6.5-7.5, COD; 28.6 mg L^{-1}, TSS; 11.6 mg L^{-1}.

The generation of waste is inevitable from the manufacture of a product or the application of a process. While the 'zero waste' concept has been mentioned as a goal at times, it often refers to zero waste disposed of to landfill[7]. Mostly, in manually operated enamel industries, there are possibilities to control the wastes in their sources.

It has been taken a look the importance and place in Turkey of the metal plating industry and plating forming stages and the wastewater from the plating plant have been examined. By means of chemical precipitation, COD and TSS removal of enamel plating industry have been investigated. Consequently, it has been observed that there was a quite good refining visually in the tests carried out. However, a limited number of data has been obtained from these efforts. Therefore, the data belonging to precipitating with $Ca(OH)_2$ and pH dependent values were obtained. In order to identify the best refining efficiency, it is necessary to determine the parameters sufficiently such as chemical, medium conditions, the pollution condition of the wastewater. As a result, it was concluded that, by means of chemical precipitation method of enamel plating industry wastewater, COD and TSS could be removed. In the tests performed, the effects of the parameters have been given as follows:

As a result of treating efforts, optimum dose of $Ca(OH)_2$ has been determined as optimum 1660 mg L^{-1}. In the doses over 1700 mg L^{-1} $Ca(OH)_2$, the rate of suspended matter and a decrease has been observed in TSS efficiency. Additionally, in the studies over this dose, it has been argued that, by means of the method applied to, the lime was not fully dissolved and it also decreased the efficiency.

Especially for production plants, minimization of the wastes must be provided. (i) Drainage boards have been installed between tanks to reduce dragout, thus saving water and chemicals. (ii) Emphasis has been placed on educating workers with respect to waste minimization. (iii) Chemical consumption is being monitored and controlled. (iv) The company has begun monitoring water consumption. (v) Excessive amount of water is used for manual rinsing purposes. (vi) Insufficient time is allowed for the drainage of articles. As a result, there is a lot of carryover of solution to subsequent tanks. (vii) Introduce drainage boards between tanks to allow solutions to drain back into their tanks. (viii) Install overhead draining bars to increase drainage. (ix) Adjust overflowing rinse water to the minimum flow rate required for adequate rinsing. (x) Fix all leaks in tanks and pipes. (xi) Rinse water flowrates have been adjusted to the minimum required for adequate rinsing. (xii) Rinse water is being reused. (xiii) Unused taps are shut off. (xiv) More water meters have been installed. (xv) Workers are not restricted with respect to the amount of water used during spray rinsing (hose connected directly to water mains). It was suggested that the flow rate by restricted to an adequate setpoint, that allows effective rinsing. (xvi) Analysis of tanks are done fortnightly by the manager. Control measures should be implemented to allow quantification of chemical usage. (xvii) Barrels should be redesigned to facilitate better drainage. (xviii) Install spray rinses. (xix) Install air operated return pumps. (xx) Investigate the possibility of installing wall hanging rinses and (xxi) Undertake an energy audit.

As a result of experimental studies carried out for determining the pH influence, as seen from the values obtained, the pH values decrease, the less COD and TSS removal decrease. The best efficiency was achieved at pH = 9. pH value of raw water is about 9. In this case, it has been concluded that there is no extra chemical for the variation of pH.

During the investigations and experimental studiers performed, for wastewater having sensible pollution load such as enamel plating wastewater, it has been seen that chemical refining has been successfully applied to. The removal in enamel plating wastewater was 1660 mg L^{-1} for optimum $Ca(OH)_2$ dose and pH value was 9. It has been expressed that COD removal efficiency was 80-86 % and TSS removal efficiency was 93.8 %.

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