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Treatability Studies on Organized Industrial District Wastewater with Chemical Treatment, Fenton and Fenton-Like Processes

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Organized industrial districts are established to carry out the industrialization by minimizing the environmental problems. For this reason, wastewater arises from different industries are treated by various treatment processes. In this study, the wastewater of organized industrial district which is situated in Bursa city of Demirtas district, Turkey is treated by chemical treatment with various coagulants and Fenton and Fenton-like processes. $Al_2(SO_4)_3{\cdot}18H_2O$, $FeSO_4{\cdot}7H_2O$ and $FeCl_3{\cdot}6H_2O$ were used in chemical treatment studies and 72, 78 and 78 % COD removal, 59, 41 and 50 % suspended solid removal were obtained, respectively. Fenton and Fenton-like processes showed high COD (> 60 %) and suspended solid (> 75 %) removal performance on evaluated effluents.

Key Words: Chemical treatment, Fenton and Fenton like oxidation, Organized industrial district wastewater.

INTRODUCTION

Organized industrial districts (OIDs) are models which have been used by State Planning Organization (SPO) in Turkey, to provide balanced development and regular urbanization, to build industries that do not cause environmental problems[1].

Today in Turkey, 261 organized industrial districts have been become a legal entity. While the completed organized industrial district projects were only 70 until the year of 2002. In the last 10 years, 77 organized industrial district projects were completed and the total number of organized industrial district projects increased to 147. The works on infrastructure and treatment plant lending of 65 organized industrial districts have been continued in the investment program of 2012. Also, it is planned to have been completed of 15 organized industrial districts projects by the end of 2012[2].

Rapid growth of organized industrial districts has increased the usage of water[3]. The discharged wastewater amount was 190 million m^3 in 2010, according to the results obtained from the 134 organized industrial districts directorate, *via* Water, Wastewater and Waste Statistics Survey of 2010. The total treated wastewater amount was 161 million m^3 and advanced, biological, physical or chemical treatment were applied on 58.5, 40.1 and 1.4 % of treated wastewater, respectively[4].

The applications of conventional treatment processes are not sufficient to obtain the discharge criteria of wastewater. Therefore, advanced treatment processes have been applied and thus, reclamation and reuse of wastewater is provided. Because reclaimed water is an alternative water supply for countries which suffer from water scarcity[5].

The main objective of this study is to investigate of treatability of organized industrial district wastewater by chemical treatment, Fenton and Fenton-like processes. For this purpose, various coagulants such as $Al_2(SO_4)_3{\cdot}18H_2O$, $FeSO_4.7H_2O$ and $FeCl_3.6H_2O$ were used in chemical treatment. The results of treatment studies are presented as a function of chemical oxygen demand (COD) and suspended solids (SS).

EXPERIMENTAL

Characteristics of Demirtas Organized Industrial District wastewater: Demirtas organized industrial district (DOID) is situated in Bursa, northwest of Turkey and provides employment opportunities for 37,529 people. It contains 414 factories from different industrial sectors such as textile, automotive and sub-industry, machine, electrical and electronic tools, furniture and forest products, metal, food, chemistry, packing, petroleum products and other industries (Table-1). The domestic and industrial wastewaters of the DOID are discharged to Nilufer river by open and closed canals[6]. Demirtas Organized Industrial District (DOID) wastewater treatment plant that meets the discharge criteria enforced by the Turkish Water Pollution Control Legislation[7] having a flow rate 70,000 m^3/day and the DOID wastewater is treated by physical and biological treatment.

Raw wastewater samples used in this study were collected from the homogenization tanks of DOID and analyzed in

TABLE-1
INDUSTRIAL CLASSIFICATION IN DOID[6]

Category	Number of firms
Textile	267
Automotive and sub-industry	49
Machine	10
Electrical and electronic tools	3
Furniture and forest products	6
Metal	12
Food	15
Chemistry	30
Packing	3
Petroleum products	2
Other industries	17
Total	414

accordance with Standard Methods[8]. Environmental characterization of DOID wastewater is given in Table-2. The experiments were carried out on the samples in order to remove COD and suspended solid.

TABLE-2
CHARACTERIZATION OF WASTEWATER

Parameter	Unit	Value
pH	–	8.96
COD	mg/L	1008
Suspended solid	mg/L	460
EC	mS/cm	4.82

Chemical treatability studies: Chemical treatability experiments were performed at room temperature (20 ± 1 ºC) with 1 L samples in a Jar Test apparatus (Velp Scientifica, Model FC6S, Italy). The pH of the samples was adjusted with the addition of H_2SO_4 and NaOH. Samples were left for precipitation for 1 h after 2 min of rapid mixing (120 rpm) and 15 min of slow mixing (20 rpm). Then, analytical analyses were carried out on chemically treated wastewater.

Fenton and Fenton-like experiments: Fenton and Fenton-like experiments were conducted at room temperature (20 ± 1 ºC) using varying $FeSO_4{\cdot}7H_2O$-H_2O_2 (for Fenton experiments) and $FeCl_3{\cdot}6H_2O$-H_2O_2 (for Fenton-like experiments) dosages at varying pH values in order to determine optimum dosages give better results in COD and suspended solid removal. The pH was manually adjusted to desired range (pH 2-6) using 1 N sulphuric acid and/or sodium hydroxide before starting the experiments. During the determination of optimum pH value, doses of $FeCl_3{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$ (supplied from Merck) and H_2O_2 (supplied from Merck, 35 %, w/w) were fixed at 200 mg/L. H_2O_2, $FeSO_4{\cdot}7H_2O$ and $FeCl_3{\cdot}6H_2O$ dosages, change between 100 and 350 mg/L were used to decide chemical dosages after the optimum pH was determined. Sedimentation over 2 h was applied following the pH adjustment (7.5-8.0) after 2 min of rapid mixing at 120 rpm and 20 min of slow mixing were applied at Jar Test setup. COD and suspended solid analyses were performed on wastewater supernatant, which was taken after 2 h precipitation.

Analytical procedure: To decompose residual H_2O_2, which interferes with the COD, the samples containing H_2O_2 were treated with MnO_2 powder[9,10]. The concentration of residual H_2O_2 in the test solution was measured using test strips (Merck Merckoquant Peroxide Test). Before each analysis, the samples were filtered on 0.45 µm Millipore membranes to remove MnO_2. The pH and conductivity values were measured with a pH meter (Sartorius, Model PB-11, Germany) and a WTW 315I conductivity meter (WTW, Germany), respectively. COD (closed reflux method) and suspended solid were measured in accordance with Standard Methods[8].

RESULTS AND DISCUSSION

Chemical treatment studies: The effect of pH with various coagulants ($Al_2(SO_4)_3{\cdot}18H_2O$, $FeSO_4{\cdot}7H_2O$ and $FeCl_3{\cdot}6H_2O$) on COD removal was shown in Fig. 1. In chemical treatment studies, the COD removal increased until the pH 7 and 9 whereas the removal of COD decreased beyond the pH 7 and 9, when $Al_2(SO_4)_3{\cdot}18H_2O$ and $FeSO_4{\cdot}7H_2O$ were used, respectively. When $FeCl_3{\cdot}6H_2O$ was used, the maximum COD removal was obtained at pH 4. The optimum pH values for the chemical treatment with $Al_2(SO_4)_3{\cdot}18H_2O$, $FeSO_4{\cdot}7H_2O$ and $FeCl_3{\cdot}6H_2O$ were determined as 7, 9 and 4, respectively.

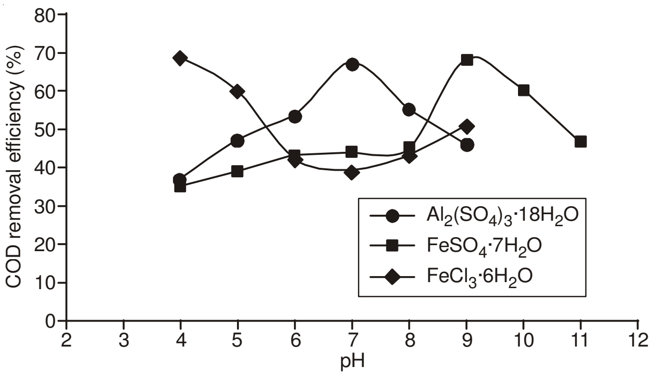

Fig. 1. Effect of pH on COD removal during chemical treatment studies

Fig. 2 shows the effects of $Al_2(SO_4)_3{\cdot}18H_2O$, $FeSO_4{\cdot}7H_2O$ and $FeCl_3{\cdot}6H_2O$ doses on COD removal. The optimum dose of $Al_2(SO_4)_3{\cdot}18H_2O$ and $FeSO_4{\cdot}7H_2O$ were determined as 300 mg/L whereas the optimum dose of $FeCl_3{\cdot}6H_2O$ was 350 mg/L. The dose of 300 mg/L of $Al_2(SO_4)_3{\cdot}18H_2O$ (at pH 7) and 300 mg/L $FeSO_4{\cdot}7H_2O$ (at pH 9) resulted in 49 % of suspended solid and 37 % of suspended solid removal efficiency, while $FeCl_3{\cdot}6H_2O$ removed 40 % suspended solid at a dose of 350 mg/L (at pH 4) (Fig. 3).

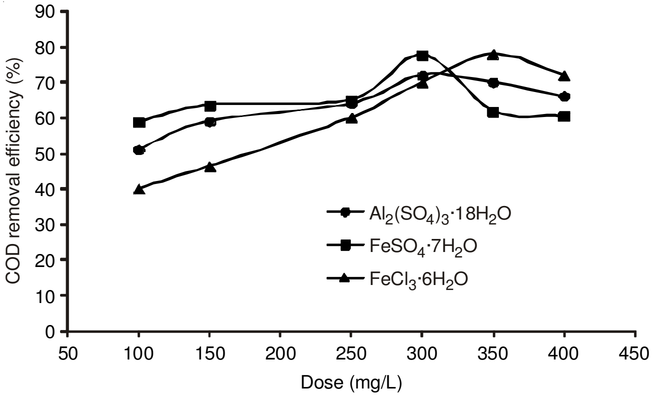

Fig. 2. Effects of coagulants dose on COD removal during chemical treatment studies

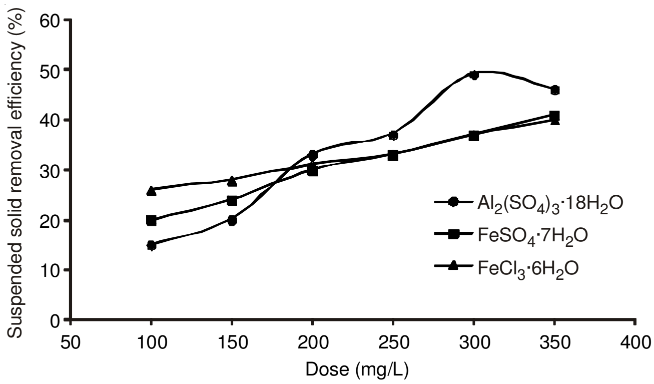

Fig. 3. Effect of coagulants dose on suspended solid removal during chemical treatment studies

Eker and Çiner [11] applied the chemical treatment with various coagulants, such as $Al_2(SO_4)_3 \cdot 18H_2O$, $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ to the wastewater of Sivas Organized Industrial District. They obtained 84 % COD and 55 % suspended solid removal at a dose of 400 mg/L $Al_2(SO_4)_3 \cdot 18H_2O$ at pH 7. When they used $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ at a dose of 250 mg/L at pH 8, 76 and 73 % COD, 52 % suspended solid and 37 % suspended solid removal were obtained, respectively. In another study done by Çiner and Eker[12], $Al_2(SO_4)_3 \cdot 18H_2O$, $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ were used in chemical treatment studies of Sivas organized industrial district and all these coagulants proved high COD removal (> 70 %), but relatively low TSS solid removal (around 50 %). Üstün *et al.*[13] removed 45-50 % COD and 84-96 % suspended solid with $Al_2(SO_4)_3 \cdot 18H_2O$, $FeCl_3$ and $Fe_2(SO_4)_3$ by adding anionic polyelectrolyte in chemical treatment studies.

Fenton and Fenton-like processes: The operating pH and the dosages of $FeSO_4$ and $FeCl_3$ are the parameters that affect the Fenton and Fenton-like processes. The optimum pH has been observed to be 3 in Fenton processes[14-16]. Also, the oxidation potential of hydroxyl radicals ($^{\bullet}OH$) is known to decrease with an increase in the pH[17].

In this study, the optimum pH value for the Fenton and Fenton-like processes was determined by adjusting the pH from 2-6. The resulting COD removal efficiencies were observed. As shown in Fig. 4, the maximum COD removal efficiency occurred at pH 3 for these two processes. The COD removal efficiencies for DOID wastewater at pH 3 (200 mg/L $FeSO_4 \cdot 7H_2O$, 200 mg/L $FeCl_3 \cdot 6H_2O$ and 200 mg/L H_2O_2 dosages) were 58 % for the Fenton process and 60 % for the Fenton-like processes, respectively.

Other important operational parameters of Fenton and Fenton-like processes are H_2O_2, $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ concentrations. In these two processes, a constant H_2O_2 concentration of 250 mg/L at pH 3 and dosages of $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ between 100 and 350 mg/L were used to determine the optimum concentrations. Fig. 5 shows the COD removal efficiencies at a constant H_2O_2 concentration and the varied $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ dosages. The optimum $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ dosages were determined as 250 mg/L for both Fenton and Fenton-like processes.

The other significant parameter in the Fenton and Fenton-like processes is the H_2O_2 dosage. The H_2O_2 dosage influences the degradation process and excess H_2O_2 interferes with COD

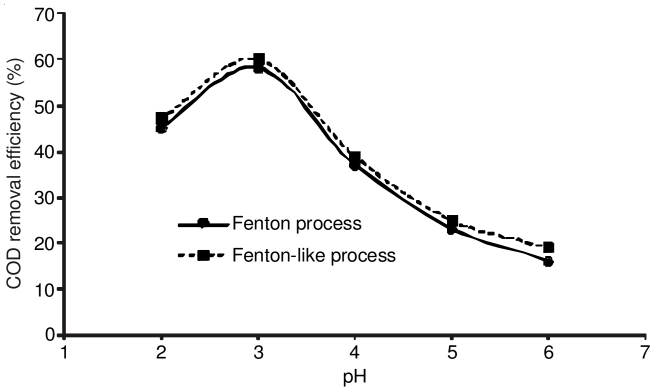

Fig. 4. Effect of pH on COD removal during Fenton and Fenton-like processes (C_{FeSO_4} = 200 mg/L, C_{FeCl_3} = 200 mg/L and $C_{H_2O_2}$ = 200 mg/L)

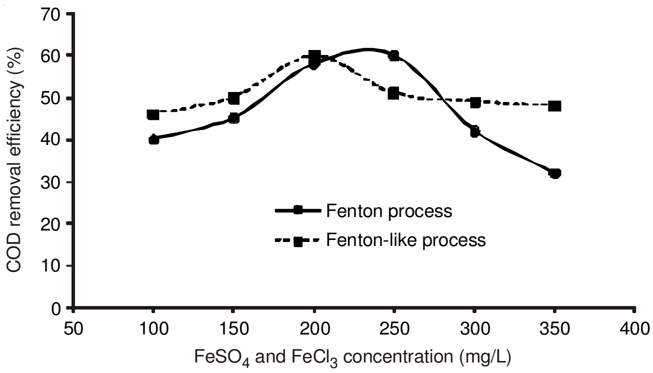

Fig. 5. Effect of $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ concentrations on COD removal efficiencies during Fenton and Fenton-like processes (pH = 3 and CH_2O_2 = 250 mg/L)

measurements. The residual H_2O_2 in the Fenton process can consume $K_2Cr_2O_7$, which leads to an increase in the inorganic COD[18]. Studies aimed at determining the optimum H_2O_2 dosage were conducted at the previously determined $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ dosages and pH values. Fig. 6 shows the COD removal efficiencies at different H_2O_2 dosages (between 100 and 350 mg/L) and constant $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ concentrations. According to the Fig. 7, the optimum pH value and the H_2O_2 and iron salt dosages for the Fenton and the Fenton-like processes were determined as follows: pH = 3, $C_{H_2O_2}$ = 250 mg/L and C_{FeSO_4} = 250 mg/L (61 % COD removal)

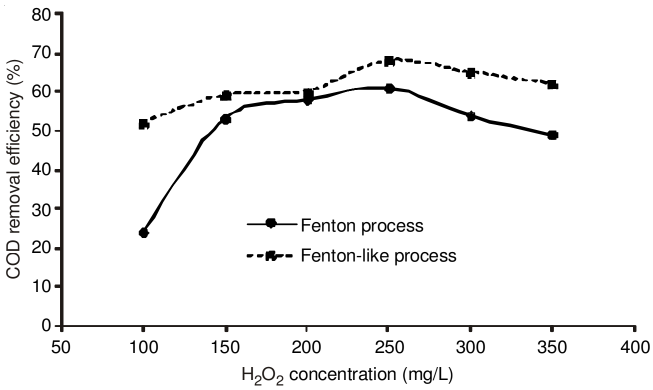

Fig. 6. Effect of H_2O_2 concentration on COD removal efficiencies during Fenton and Fenton-like processes (Fenton process (pH = 3 and C_{FeSO_4} = 250 mg/L) (61 % COD removal, 72 % suspended solid removal), Fenton-like process (pH = 3 and C_{FeCl_3} = 200 mg/L) (68 % COD removal, 76 % suspended solid removal))

TABLE-3
PROCESS RESULTS FOR DOID WASTEWATER TREATMENT

Process	pH	COD removal (%)	SS removal (%)	$C_{Al_2(SO_4)_3 \cdot 18H_2O}$ (mg/L)	$C_{H_2O_2}$ (mg/L)	$C_{FeSO_4 \cdot 7H_2O}$ (mg/L)	$C_{FeCl_3 \cdot 6H_2O}$ (mg/L)
Chemical treatment with $Al_2(SO_4)_3 \cdot 18H_2O$	7	72	49	300	–	–	–
Chemical treatment with $FeSO_4 \cdot 7H_2O$	9	78	37	–	–	300	–
Chemical treatment with $FeCl_3 \cdot 6H_2O$	4	78	40	–	–	–	350
Fenton process	3	61	72	–	250	250	–
Fenton-like process	3	68	74	–	250	–	200

and pH = 3, $C_{H_2O_2}$ = 250 mg/L and C_{FeCl_3} = 200 mg/L (68 % COD removal), respectively. The COD removal efficiencies obtained from Fenton-like process were higher than those obtained from Fenton oxidation process. Also, 72 and 74 % suspended solid were removed under these optimum circumstances in Fenton and Fenton-like processes, respectively.

The results of processes applied on DOID wastewater are summarized in Table-3 and consequently, the Fenton-like process generally resulted in higher COD and suspended solid removal efficiencies.

Conclusions

In this study, chemical treatment, Fenton and Fenton-like processes were applied on organized industrial district wastewater. The following conclusions can be drawn from this study.

1. The COD removal efficiencies were similar when $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ used in chemical treatment.

2. The most appropriate coagulant for chemical treatment is $FeSO_4 \cdot 7H_2O$. Because, the price of $FeSO_4 \cdot 7H_2O$ is less than $Al_2(SO_4)_3.18H_2O$ or $FeCl_3 \cdot 6H_2O$.

3. Fenton and Fenton-like processes have shown satisfactory COD and suspended solid removal performances on organized industrial district wastewater.

4. The COD and suspended solid removal efficiencies obtained from Fenton-like process are higher than Fenton process.

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