Determination of the acute toxicities of physicochemical pretreatment and advanced oxidation processes applied to dairy effluents on activated sludge

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ABSTRACT

In this study, the acute toxicities of raw, physicochemical pre-treated, ozonated, and Fenton reagent applied samples of dairy wastewater toward activated sludge microorganisms, evaluated using the International Organization for Standardization's respiration inhibition test (ISO 8192), are presented. Five-day biological oxygen demand (BOD₅) was measured to determine the biodegradability of physicochemical treatment, ozonation, Fenton oxidation or no treatment (raw samples) of dairy wastewater. Chemical pretreatment positively affected biodegradability, and the inhibition exhibited by activated sludge was removed to a considerable degree. Ozonation and the Fenton process exhibited good chemical oxygen demand removal (61%) and removal of toxins. Low sludge production was observed for the Fenton process applied to dairy effluents. We did not determine the inhibitory effect of the Fenton-process on the activated sludge mixture. The pollutant-removal efficiencies of the applied processes and their associated operating costs were determined.

Key words: activated sludge inhibition, chemical pretreatment, Fenton process, dairy effluent, ozonation

INTRODUCTION

The dairy industry is the largest source of food processing (Britz et al., 2006); milk production and milk processing are also important agro-industries of Turkey. The amount of milk produced in Turkey is estimated to be approximately 17 million tonnes per year (sheep: 1,007,007 t; goat: 369,429 t; cattle: 15,978,837 t), and 60% of the milk produced is processed in dairy plants (www.tuik.gov.tr). All steps in the dairy chain, from production to marketing, affect the environment (Strydom et al., 1993), and, like most other agro-industries, dairy plant wastewaters are generally high-strength

wastes containing soluble, colloidal, and suspended solids at high concentrations, with several sources of chemical and biochemical oxygen demand (Samkuty and Gough, 2002; Turan, 2004; Demirel et al., 2005; Şengil and Özacar, 2006), but mainly of organic origin (Britz et al., 2006). The primary organic load of dairy industry effluents is contributed by carbohydrates, proteins, and lipids, which originate from milk (Kasapgil et al., 1994; Perle et al., 1995). Serious environmental problems can arise if dairy wastewater is not treated properly (Tocchi et al., 2013).

Dairy wastewaters are treated using several biological and physicochemical methods; for example, activated sludge process (Tawfik et al., 2008), aerated lagoons, trickling filters, upflow anaerobic sludge blanket reactors (Gavala et al., 1999; Kushwaha et al., 2013), sequencing batch reactors (Kushwaha et al., 2013), anaerobic filters (Omil et al., 2003), adsorption (Kushwaha et al., 2010), electrocoagulation (Tchamango et al., 2010), and reverse osmosis and ion exchange (Bickers and Bhamidimarri, 1998). These existing technologies are expensive or ineffective for the treatment of dairy wastewater. Furthermore, these processes only transfer pollutants from one phase to another rather than eliminating them from the water matrix (Solmaz et al., 2006).

Physicochemical pretreatment and advanced oxidation processes (AOP) are good pretreatment alternatives for dairy effluent. The application of AOP to different industrial wastewaters is widely studied. Glaze et al. (1987) established the concept of AOP and defined them as processes involving the generation of highly reactive oxidizing species able to attack and degrade organic substances (Quiroz et al., 2011). These processes work on the principle of the generation of free radicals. The hydroxyl radical (HO•), which reacts very rapidly with most organic compounds, is a powerful, nonselective chemical oxidant (Munter, 2001).

The Fenton process (Fenton, 1894) is a widely applied AOP. Fenton's reagent consists of H₂O₂ and ferrous ions, which produce highly oxidative species at lower pH values (Gu et al., 2013). However, ozone (O₃)

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is a well known and powerful oxidizing agent that can react with organic compounds at high pH values. Both O_3 and OH^- initiate chain reactions that subsequently produce free hydroxyl and other radical species (Steehelin and Hoigne, 1982; Gogate and Pandit, 2004).

A biological treatment process is the most common and economical approach for the treatment of contaminants in wastewater (Arslan-Alaton and Caglayan, 2006; Britz et al., 2006). However, these processes are only effective within a narrow range of these parameters; therefore, variations in flow rate and waste concentration affect biological processes. For these reasons, wastewater must be pretreated before it is discharged to ensure the efficiency of the subsequent biological step of wastewater treatment plants (Orupold et al., 1999; Guisasola et al., 2003; Ricco et al., 2004). Therefore, it is important to determine the acute toxicity of organic and inorganic pollutants in wastewater to be discharged into wastewater treatment plants to prevent damage to the treatment plant and the environment (Gutiérrez et al., 2002). Toxicity measurement of wastewater, sediments, and contaminated water bodies is important for the monitoring of environmental pollution; typically, aggregate parameters are used for pollution monitoring, such as dissolved oxygen level and chemical oxygen demand (COD; Parvez et al., 2006). Methods to determine the toxicity of pollutants or wastes toward activated sludge or aquatic organisms are widely described in the literature. The activated sludge respiration inhibition test is an adequate tool to determine respiration and toxicity. A standard has been established by ISO (1986; ISO 8192) involving an activated sludge inhibition test to evaluate the toxicity of chemicals or wastewater toward activated sludge bacteria (Gendig et al., 2003). Ozonation and the Fenton' process appear to have potential for the pretreatment process because the discharge flow from most dairy plants is not large; hence, these methods should be evaluated as good pretreatment alternatives for removal of toxins from effluents.

The main objective of this investigation was to determine the acute toxicities of untreated (raw) dairy effluent samples or samples pretreated using a physico-chemical method, ozonation, and Fenton oxidation on activated sludge microorganisms using the respiration inhibition test (ISO, 1986).

MATERIALS AND METHODS

Industrial Wastewater Samples

The wastewater samples used in this study were collected from the homogenization tanks of a dairy plant

Table 1. Environmental characterization of dairy wastewater

Item ¹	Value
pH	6.74
Suspended solids (mg/L)	840
Total N (mg/L)	98
Oil and grease (mg/L)	240
Total P (mg/L)	21
BOD ₅ (mg/L)	860
COD (mg/L)	6,300

¹BOD₅ = 5-d biological oxygen demand; COD = chemical oxygen demand.

in Bursa City, Turkey. Table 1 presents the characteristics of the dairy wastewater. This wastewater can be characterized as high-strength because of its high organic and inorganic contents.

Coagulation Experiments

Chemical treatment experiments were performed using a jar test apparatus (model FC6S, Velp Scientifica, Usmate Velate, Italy), along with reagents $Ca(OH)_2$, $Al_2(SO_4)_3$, $FeCl_3$, and $FeSO_4$ (all from Merck, Darmstadt, Germany) at dosages between 100 and 3,000 mg/L. All experiments were conducted at room temperature (20°C). The optimum pH and reagent doses were determined according to best COD removal efficiency for each chemical. The characteristics of the wastewater sample are listed in Table 1. The wastewater volume was 1 L, and different coagulants were used at varying concentrations. Before a 1-h sedimentation, 1 min of flash mixing (120 rpm in jar test apparatus) and 30 min of coagulation (20 rpm in jar test apparatus) were applied. At the end of sedimentation, the supernatants were collected for analysis.

Fenton Experiments

Fenton experiments were conducted at room temperature using different concentrations of $FeSO_4$ and H_2O_2 at varying pH values to determine the optimal conditions for COD removal. The pH was manually adjusted to the desired range (pH 2–7) by the addition of 1 N sulfuric acid or sodium hydroxide before starting the experiments. To determine the optimum pH, concentrations of $FeSO_4$ (Merck) and H_2O_2 (Merck, 35% wt/wt) were fixed at 400 mg/L. Then, H_2O_2 and $FeSO_4$ concentrations in the range of 100 to 1,000 mg/L were used to determine the chemical dose after the optimum pH was determined. The flocs that formed were allowed to settle for 4 h following pH adjustment (7.5–8). The wastewater was rapidly stirred for 2 min at 100 rpm and then stirred for 20 min in the jar test apparatus at

room temperature. The COD analyses were performed on 50 mL of the supernatant, which was collected after 2 h of precipitation.

Ozonation Experiments

The ozonation experiments were conducted in a closed cylindrical Pyrex glass reactor (2 L; Paşabahçe, İstanbul, Turkey). The reactor was connected to an Opal 200 model ozone generator (Opal Ozone, Ankara, Turkey) with an ozone production rate of 2 g/h. The bottom of the reactor was equipped with a sintered glass plate diffuser to produce fine ozone bubbles, which were produced by flowing high-purity (99.5%) oxygen at 2 L/min into the ozone generator. Teflon tubing was used to connect the ozone generator and the reactor. All experiments were performed at room temperature ($20 \pm 2^\circ\text{C}$) using 1.5-L samples. The inlet and outlet of ozone from the reactor were connected to the reactor filled with 2% KI to determine the ozone concentration. Ozone concentration was measured by iodometric method proposed by the International Ozone Association (IOA, 1987). The ozone gas flow rate was adjusted to 1,440 mg/h before all experiments. Ozone oxidation experiments were conducted at pH values of 7 to 12 and at different ozone doses. All analyses were performed on samples collected at specific times.

Activated Sludge Inhibition Tests

Inhibition tests of raw, pretreated (physico-chemical treatment applied), ozonation, and Fenton-processed wastewater samples were conducted in accordance with the test procedure described in ISO 8192 (ISO, 1986). The temperature of the testing area was kept constant ($20 \pm 2^\circ\text{C}$). Activated sludge used in toxicity tests was collected directly from the aeration tank of domestic wastewater treatment plant in Bursa, Turkey. After the sludge was allowed to settle, it was washed with tap water, and continuous aeration was applied to remove the impurities. Activated sludge biomass used in the inhibition tests, which was fed with synthetic municipal wastewater, was prepared as a 100-fold concentrate stock solution consisting of 16 g/L peptone, 11 g/L meat extract, 3 g/L urea, 0.7 g/L NaCl, 0.4 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.2 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and 2.8 g/L K_2HPO_4 . This synthetic domestic wastewater was diluted before use. The total suspended solids (TSS), volatile suspended solids, and sludge volume index values of domestic sludge were determined to be 2,980 mg/L, 2,840 mg/L, and 190 mL/g, respectively. 3,5-Dichlorophenol was used as a reference toxic chemical. During the tests, the following were used: a mix of activated sludge culture with distilled water, synthetic municipi-

pal wastewater (16 mL), and several concentrations of industrial wastewater (5–100% volumetric dilutions). The pH of the test mixture was adjusted to 7.5 ± 0.2 . The aeration test periods of the test mixtures were 30 and 180 min. Different diluted test mixtures of industrial wastewater samples (5 to 100%) were prepared for the activated sludge inhibition test procedure. Approximately 300 mL of the test mixture was transferred to the respiration vessel, and the respiration rate was determined using an oxygen electrode (WTW OXI 340i, Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany). The respiration tests were conducted at selected time intervals (5–10 s). The oxygen meter was connected to the computer through an RS-232 serial interface. MultiLab Pilot V4.4 (Wissenschaftlich-Technische Werkstätten GmbH) software was used for this application. The oxygen consumption rate (mg of $\text{O}_2/\text{h}\cdot\text{g}$) and the percentage inhibition were calculated at each test condition.

Analytical Procedure

Because of interference of ferrous ion and H_2O_2 with the analytical measurements, the pH of the supernatant increased to approximately >11 with the addition of NaOH for the precipitation of ferrous iron, as $\text{Fe}(\text{OH})_3$, and MnO_2 powders were added to destroy the residual H_2O_2 in the treated solution (Azbar et al., 2004; Yonar et al., 2005). The concentration of residual H_2O_2 in the test solution was controlled by use of test strips (Merckoquant Peroxide Test, Merck). Before each analysis, the samples were filtered using 0.45- μm Millipore membranes (Millipore, Billerica, MA) to remove $\text{Fe}(\text{OH})_3$ and MnO_2 . The analysis of COD (using closed reflux method), suspended solids, oil and grease, 5-d biological oxygen demand (**BOD**₅; mg of O_2 consumed per liter during 5 d of incubation at 20°C , indicating degree of pollution), total N, and total P were measured in accordance with standard methods (APHA-AWWA-WEF, 1995).

RESULTS AND DISCUSSION

Coagulation Experiment

The treatability studies consisted of 2 stages: chemical coagulation and Fenton oxidation processes. Different concentrations of $\text{Ca}(\text{OH})_2$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and FeSO_4 coagulants were used during chemical treatment experiments under different pH values and removal efficiencies, as listed in Table 2. Iron sulfate (FeSO_4) was found to exhibit higher performance, according to the COD parameter, for dairy wastewater. The optimum pH and chemical dosage

Table 2. Effect of coagulants on industrial wastewater samples

Coagulant	Optimal pH	Optimal concentration (mg/L)	COD ¹ removal efficiency (%)
Ca(OH) ₂	11	800	42
FeSO ₄	11	800	60
FeCl ₃	11	900	52
Al ₂ (SO ₄) ₃	8	800	46

¹Chemical oxygen demand.

were determined to be 11 and 800 mg/L (60% COD removal), respectively. Industrial wastewater aliquots were then used in the activated sludge inhibition tests.

Fenton Process

Several investigators have studied the Fenton process and the use of hydroxyl radicals to oxidize organic pollutants (Laine and Cheng, 2007). The main advantage of the Fenton process is the complete destruction of contaminants to stable compounds (Neyens and Baeyens, 2003). In the first step, the optimum pH of the process was determined for all wastewater samples separately. The pH was adjusted between 2 and 7, and the efficiencies of COD removal were determined for all industrial wastewater samples. Maximum COD removal efficiency was obtained at pH 3.5 (Figure 1) for the dairy effluent. At pH 3.5 (for 400 mg/L FeSO₄·7H₂O and 400 mg/L H₂O₂), COD removal efficiency for dairy effluent was 51% (Figure 2).

In addition to pH and H₂O₂, ferric salt concentrations are another important operating parameter for the Fenton process. Higher ferrous ion concentrations

Figure 1. Effect of pH on chemical oxygen demand (COD) removal during Fenton process (concentration of FeSO₄·7H₂O = 400 mg/L and concentration of H₂O₂ = 400 mg/L).

Figure 2. Effect of FeSO₄·7H₂O concentration on chemical oxygen demand (COD) removal during Fenton process (pH = 3.5 for dairy samples, concentration of H₂O₂ = 400 mg/L).

increase the unutilized quantity of iron salts, which is not permitted (Gogate and Pandit, 2004). To determine the optimum FeSO₄ concentration at a fixed pH (pH = 3.5 for dairy wastewater samples) and constant peroxide concentration of 400 mg/L, we applied concentrations of FeSO₄ between 100 and 1,000 mg/L. The efficiency of COD removal under a constant concentration of hydrogen peroxide and varied concentrations of FeSO₄ is illustrated in Figure 2. The optimum ferrous salt (FeSO₄) concentration was 700 mg/L (63% COD removal) for the dairy effluent used in this study.

The concentration of H₂O₂ also has an important influence in the degradation of organic contaminants. Excessive amounts of H₂O₂ reduce the degradation of organic compounds because H₂O₂ itself may act as a HO• scavenger at excessive levels (Lin and Lo, 1997; Kang and Hwang, 2000; Pera-Titus et al., 2004). We determined the optimum H₂O₂ concentration at the previously determined constant FeSO₄ concentration and pH value. We applied H₂O₂ in the range from 100 to 1,000 mg/L. The efficiencies of COD removal at different concentrations of H₂O₂ and a constant concentration of FeSO₄ are shown in Figure 3. The optimum conditions for dairy effluent treatment were determined to be pH 3.5, 800 mg/L H₂O₂ and 700 mg/L FeSO₄ (74% COD removal). Supernatants from the Fenton process experiments were used in the activated sludge inhibition tests.

Ozonation Experiment Results

At alkaline pH values, the efficiency of ozonation treatment was improved because the reactive radical oxidation dominated (Steahelin and Hoigne, 1982; Shu

Figure 3. Effect of H_2O_2 concentration on chemical oxygen demand (COD) removal during Fenton process (pH = 3.5 and concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ = 700 mg/L).

and Huang, 1995; Azbar et al., 2004; Gogate and Pandit, 2004; Solmaz et al., 2006; Yonar et al., 2005). To determine the optimum pH values that provide better efficiencies of COD and color removal, ozonation experiments were conducted at an ozone (O_3) dose of 2 g/h at varying pH (7–12) values. As can be observed in Figure 4, the highest removal efficiency was obtained at pH 12 for dairy wastewater. The reason for the enhance-

ment in COD removal in the samples is the accelerated ozone decomposition to free radicals at elevated pH (Arslan-Alaton and Caglayan, 2006). At the end of 3 h of ozonation, the COD removal efficiencies were 71% for dairy effluents (Figure 4). The COD removal efficiency of the ozonation process cannot reach that of the Fenton process, which can be explained by the presence of radical scavengers. In the presence of carbonates, bicarbonates, and organic substances, the chain reaction starting with ozone and hydroxide ions (OH^-) can be broken by trapping the hydroxyl radical ($\text{HO}^\bullet$) and by radical–radical coupling processes (Arslan, 2000). In addition, ozone reacts with oxidizable ions, such as S^{2-} , to form SO_3^{2-} and SO_4^{2-} oxyanions (Steahelin and Hoigne, 1982). These reactions are simple and the mechanisms only require contact of ozone with the ion. Therefore, inorganic compounds present in the medium, such as Cl^- , HCO_3^- , CO_3^{2-} , and S^{2-} , act as effective radical scavengers during the application of AOP (Yonar et al., 2005). To determine ozone consumption, the inlet and outlet of ozone from the reactor were analyzed using gas washing bottles, including 2% KI solutions. The ozone usage ratios varied in the range of 2% (pH 3) to 23% (pH 12) for the applied treatment period (for 240-min reaction times). As with the coagulation and Fenton process supernatants, the ozonation experiment supernatants were then used in activated sludge inhibition tests.

Figure 4. Chemical oxygen demand (COD) removal efficiencies at various pH values during ozonation (concentration of O_3 = 2 g/h, concentration of COD_0 = 6,300 mg/L, where COD_0 is the initial COD of raw wastewater).

Acute Toxicity Test on Activated Sludge

To evaluate toxicity in raw, physicochemically pretreated, and Fenton-processed dairy effluents, the activated sludge respiration inhibition test was applied, and the effective concentrations (EC_{20} , EC_{50} , and EC_{90} , indicating the concentrations resulting in 20, 50, or 90% inhibition of a toxic substance compared with blank control) values (in mg/L COD of wastewater samples) were determined. During the tests, oxygen uptake rate (**OUR**) values were determined by plotting dissolved oxygen concentration against time. Before the toxicity tests, the 3,5-dichlorophenol reference toxicant was used to determine the sensitivity of the activated sludge culture. The EC_{50} value of 3,5-dichlorophenol on the activated sludge mixture should be 5 to 30 mg/L according to ISO 8192 (ISO, 1986). The toxicity (EC_{50}) of this reference chemical on the activated sludge mixture was found to be 24 mg/L.

High organic loads of dairy effluents cause serious problems for conventional biological processes. Most dairy effluents are produced from cleaning operations of production lines, tank trucks, milk silos, and equipment malfunctions or operational errors (Demirel et al., 2005). The discharge of dairy effluents without treatment can cause serious environmental problems for water resources and centralized wastewater treatment plants.

Dairy wastewater containing raw, physicochemically pretreated, and Fenton-processed effluent was subjected to activated sludge toxicity assessment. The EC_{20} , EC_{50} , and EC_{90} values of the raw and treated samples of dairy wastewater were determined from the data plot of $\ln_{COD}$ versus I_{OUR} (%), as shown in Figure 5. The EC_{20} , EC_{50} , and EC_{90} values of raw ($EC_{20} = 3,630 \pm 25$ mg of COD/L and $EC_{50} = 6,050 \pm 40$ mg of COD/L; 90% inhibition not detected) dairy wastewater samples were determined from the data plots.

Another appropriate measure for the determination of biodegradability is the $BOD_5:COD$ ratio (Arslan-Alaton and Gurses, 2004). The $BOD_5:COD$ ratio of raw dairy effluent was determined to be 0.14. According to this result, the evaluated raw dairy wastewaters have toxic and inhibitory effects on activated sludge mixture, and these effluents almost cannot be treated by conventional biological processes. Effluents with $BOD_5:COD$ ratios exceeding 0.3 to 0.4 can be considered biodegradable (Arslan-Alaton and Gurses, 2004). Chemical precipitation, ozonation, and Fenton oxidation improved the biodegradability ($BOD_5:COD = 0.39$, 0.42, and 0.47, respectively) of dairy effluent. However, a simple $BOD_5:COD$ evaluation for the determination of biodegradability can be misleading (Arslan-Alaton

and Caglayan, 2006). Therefore, the inhibition test on activated sludge was performed on pretreated effluent samples. As shown in Figure 5, negative values of I_{OUR} were observed. A negative I_{OUR} value indicates that the exogenous nature of the activated sludge mixture is influenced by the applied sample. All the applied processes also eliminated toxins from dairy effluents. In other words, chemical precipitation, ozonation, and the Fenton process can be used as pretreatment alternatives for dairy effluents before discharge to a central wastewater collection system.

Cost Evaluation

The costs associated with the applied processes were analyzed and evaluated to determine the most suitable process. The main results of this study are presented in Table 3. The operating costs (on the basis of chemical requirements) and cost profiles of all processes were compared except for the sludge disposal cost (Table 4), and these were found to be affordable compared with usual treatment costs. Within this framework, this present investigation can be considered a feasibility study for the pretreatment of dairy wastewater before discharge to a sewage treatment plant.

CONCLUSIONS

In this study, we applied chemical treatments and the Fenton process to dairy effluents. The toxic nature of

Figure 5. Inhibition of oxygen uptake rate (I_{OUR}) for raw, chemical pretreated, ozonation, and Fenton-processed dairy effluent samples. COD = chemical oxygen demand.

Table 3. Results of studied processes on dairy effluent¹

Process	COD removal (%)	BOD ₅ :COD	pH	Concentration		
				H ₂ O ₂ (mg/L)	FeSO ₄ (mg/L)	O ₂ (g/h)
Chemical treatment	60	0.39	11	—	800	—
Ozonation	71	0.42	12	—	—	2
Fenton process	74	0.47	3.5	800	700	—

¹COD = chemical oxygen demand; BOD₅ = 5-d biological oxygen demand.

these wastewater samples inhibits degradation via activated sludge microorganisms. The acute toxicities of the samples on activated sludge microorganisms were determined using the respiration inhibition test. Raw dairy wastewaters have toxic and inhibitory effects on the activated sludge mixture, and this effluent cannot be treated by means of conventional biological processes. The removal efficiencies of coagulation experiments showed that FeSO₄ and lime resulted in the best COD removal for dairy effluent. Biodegradability and the inhibition of activated sludge were positively affected by chemical pretreatment. The efficiency of COD removal of the Fenton process was >69%. The inhibitory effect of Fenton-processed samples on activated sludge mixture was not determined. Ozonation is efficient but is not a practical solution for the pretreatment alternative before discharge. The Fenton process exhibited economical and satisfactory COD and toxicity removal performance.

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Table 4. Operating costs for the studied processes

Item	Basis	Cost (€)	Treatment cost ¹ (€/m ³)
Reagent			
FeSO ₄ ·7H ₂ O	kg	0.27	
H ₂ O ₂	kg	0.44	
Electricity	kW/h	0.05	
H ₂ SO ₄	kg	0.18	
NaOH	kg	0.17	
Ozone	€/kg	2.01	
Process			
FeSO ₄ coagulation			0.42
Fenton process			0.59
Ozonation			7.62

¹Cost of labor and sludge disposal not included.

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