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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 (BOD_5) 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 (Samkutty 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 ($HO^{\bullet}$), 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 H_2O_2 and ferrous ions, which produce highly oxidative species at lower pH values (Gu et al., 2013). However, ozone (O_3)

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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 (Steahelin 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 physicochemical 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 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.

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

[1] BOD_5 = 5-d biological oxygen demand; COD = chemical oxygen demand.

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