REMOVAL OF ORGANIC MATTER FROM DAIRY INDUSTRY WASTEWATER USING MICROWAVE RADIATION

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Abstract

The dairy industry meets basic needs and has high production volumes. It cannot be ignored in terms of its potential for water pollution. Dairy industry wastewaters contain significant amounts of organic matter. Wastewater from the Pınar Milk Plant in Eskişehir Organized Industrial Zone was controlled by chemical oxygen demand, oil and grease, suspended solids and pH parameters. Microwave (MW) treatment involves a combination of MW irradiation, an adsorbent (as catalyst) and an oxidant. The effects of radiation power and time, and adsorbent and oxidant dosages on removal efficiency were investigated. Bentonite, limestone and pumice were used as adsorbents, with hydrogen peroxide as oxidant. The best organic matter removal (41.4%) was obtained with limestone, while 49% oil and grease removal was achieved with pumice. The best suspended solids removal (67%) was obtained with limestone.

SÜT ENDÜSTRİSİ ATIKSUYUNDAN MİKRODALGA IŞINIM YÖNTEMİNİ KULLANARAK ORGANİK MADDE GİDERİMİ

Anahtar Kelimeler

Süt endüstrisi
Atıksu
Mikrodalga ışınım
Adsorban

Öz

Süt endüstrisi temel ihtiyaçları karşılar ve yüksek üretim hacimlerine sahiptir. Su kirliliği potansiyeli açısından göz ardı edilemez. Süt endüstrisi atık suları önemli miktarda organik madde içerir. Bu çalışmada, Eskişehir Organize Sanayi Bölgesi'ndeki Pınar Süt Fabrikası'ndan gelen atık su, kimyasal oksijen ihtiyacı, yağ ve gres, askıda katı madde ve pH parametreleri ile kontrol edildi. Mikrodalga (MW) işlemi, MW ışıması, bir adsorban (katalizör olarak) ve bir oksidan kombinasyonunu içerir. Atıksuyun arıtımı üzerine ışınım gücü ve ışınım süresi, adsorban ve oksidan dozajlarının etkileri araştırıldı. Bentonit, kireçtaşı ve pomza adsorban olarak, hidrojen peroksit ise oksidan olarak kullanılmıştır. En iyi organik madde giderimi (% 41,4) kireçtaşı ile elde edilirken, yağ ve gres giderimi pomza ile %49 gerçekleştirildi. En iyi askıda katıların uzaklaştırılması ise (% 67) kireçtaşı ile elde edildi.

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1. Introduction

One source of organic pollutants in the environment is the wastewater from milk and dairy products. The dairy industry generally uses processes like homogenization, pasteurization, bottling, and condensation, to produce cheese, cream, butter, milk, yoghurt, and ice cream, etc. The main raw material in the industry is milk, but water is also essential.

The organic load in milk industry wastewater comprises carbohydrates, proteins and fats (Qasim and Mane, 2013). Most dairy industry wastewater arises from cleaning equipment, lines and silos, and/or equipment faults (Demirel, Yenigün and Onay, 2005; Al-Shammari, 2018). When the wastewater's organic load is high, the consumption of dissolved oxygen in the receiving environment is also high, affecting natural life. Continuous consumption, without renewal, of oxygen leads to anaerobic and septic conditions in the receiving environment, and the release of gases like methane and H_2S.

As for any industry, the quantities and characteristics of dairy industry wastewater vary greatly depending on the processes used and the product types. The most

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important parameters for characterizing wastewaters are biological oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), pH, oil and grease, and temperature. All of these may vary diurnally and through the seasons.

In Turkey, following the promulgation of environmental laws and regulations, businesses have started to establish wastewater treatment plants. Biological treatment is generally preferred for treating organic solutes due to its low cost and environmental impact, but has limited applicability in wastewaters containing recalcitrant organics and high organic loads (Yazıcı and Dervişoğlu, 2003; Çiner and Tüfekçi, 1997; Değermenci, Bayhan and Değermenci, 2014).

The Pınar Milk Factory is in Eskişehir Organized Industrial Zone, Turkey. The factory produces long-life, pasteurized, and flavored milks, as well as yoghurt, ayran and butter, and fruit juices. At the plant, environmental management programs are being applied for the efficient use of natural resources, minimization of the environmental impacts of wastes, the environmental performance of processes, and waste management. The plant's partially treated wastewater is sent on for further treatment at the wastewater treatment plant of the Organized Industrial Zone.

Numerous works have been done for organic matter removal from dairy wastewater. The feasibility of using upflow anaerobic sludge blanket (UASB) reactors for the treatment of dairy wastewaters was explored. The maximum COD reduction was 95.6% (Ramasamy, Gajalakshmi, Sanjeevi, Jithesh and Abbasi, 2004), Şengil and Özacar (2006) studied COD reduction from dairy wastewater was electrocoagulation (EC). The overall COD removal efficiencies reached 98%. In the another work deals with investigation of electrochemical technique for the treatment of milk liquid fractions. the removal efficiency of COD attained 80% (Bensadok, Hanafi and Lapicque, 2011). Dessai and Prasanna (2016) presented adsorption method for COD from dairy wastewater. Gravel, charcoal and Laterite adsorbents showed more than 75% COD.

Since about 2000, more effective wastewater treatment methods have been investigated as a result of the failure of traditional methods to reach the wastewater discharge limits and the increasing costs of wastewater treatment. Microwave (MW) irradiation has been used to remove various organic pollutants, its principal advantages being fast heating and high energy efficiency. The non-ionizing electromagnetic waves used in MW are in the 300 MHz to 300 GHz frequency range. Breaking the chemical bonds of many organic compounds is difficult using these wavelengths alone MW treatment efficiency can be increased using an adsorbent catalyst and an oxidant (Lin, Yuan, Chen, Xu and Lu, 2009; Lin, Yuan, Chen, Wang, Wan and Lu, 2010; Lai, Lee, Wu, Shu and Wang, 2006; Wang, Zheng, Jiang, Lung, Miao and Wang, 2014; Yılmaz, 2015; Demiral, Bektaş and Şamdan, 2019).

In this study, bentonite, limestone and pumice were used as catalysts to help remove organic matter from wastewater by MW radiation. The wastewater came from Eskişehir Pınar Milk Factory. The effects were investigated of radiation power and time, and adsorbent and oxidant dosages on removal efficiency.

2. Materials and Methods

As shown in the Figure 1, the milk industry wastewater is discharged with a different COD value each day according to the process done at the factory. The wastewater used is characterized in Table 1. The oxidant was hydrogen peroxide. Bentonite consists mainly of the clay mineral montmorillonite, which has a layered crystal structure – the material was obtained from the Balıkesir area, in Marmara, Turkey. Bentonite consists of hydrated aluminum silicates containing iron or magnesium as well as sodium or calcium. Limestone consists mostly of calcium carbonate ($CaCO_3$) and the raw material was obtained from Eskişehir Cement Factory. Pumice is a natural pozzolan produced by gas release during the cooling and solidification of lava. It comprises primarily silicon dioxide (amorphous aluminum silicate) and some aluminum oxide, with traces of other oxides. That used in the study was obtained from Nevsehir, Turkey. All chemical materials used were of analytical grade. The MWs were generated in a domestic microwave oven (750 W, 2450 MHz, Turkey) with several power settings. COD concentrations were determined with a Lovibond MD200 Vario spectrophotometer, and SS and oil-grease using standard methods (APHA, AWWA and WPCF, 1967).

Table 1

Wastewater Sample Characterization

COD (mg/L)	SS (mg/L)	Oil and grease (mg/L)	pH
5760	948	161.2	6.26

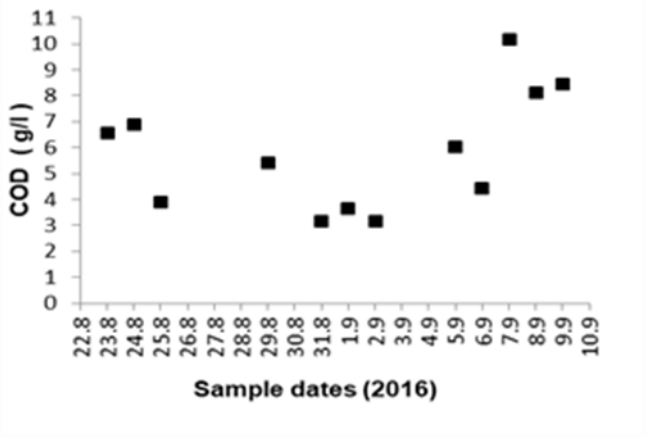

Figure 1. COD Values of Wastewater Samples Taken From The Factory on Different Dates

COD removal, oil and grease content, suspended solids were calculated by the following equations.

$$\%COD = \frac{COD_{final} - COD_{initial}}{COD_{initial}} x100 \quad (1)$$

$$OilGres(mg/L) = \frac{(A-B)x1000}{V} \quad (2)$$

A: Oil+tare (mg)

B: Tare (mg)

V: Sample volume (mL)

$$SS(105^{\circ}C, mg/L) = \frac{(A-B)x1000}{V} \quad (3)$$

A = Filter paper + weighing of dry residue (mg)

B = Weighing of filter paper (mg)

V: Sample volume (mL)

In the study, fixed amounts of adsorbent and oxidant were mixed with 250 mL aliquots of wastewater in capped volumetric glass flasks, and irradiated with MW under varying conditions. All samples were filtered after irradiation and the COD values determined spectrophotometrically. Operating conditions were optimized to achieve the maximum COD reduction by MW radiation. Four parameters were investigated: microwave power (336 or 595 W), irradiation time (3 or 8 minutes), adsorbent mass (2.5, 5.0 and 7.5 g/250 mL), and the amount of hydrogen peroxide (analytical grade, 2.5, 5.0 and 7.5 ml/250 mL).

Eskişehir Pınar Milk Factory approved this study with its decision numbered 407 dated 21/01/2016. In this study, research and publication ethics were followed.

3. Results and Discussion

3.1. Effect of MW Power and Radiation Time

Irradiation power and time are the important parameters in microwave processing. Their effects were investigated using 2.5 g of bentonite, limestone or pumice together with 2.5 ml oxidant for 250 ml of wastewater. According to Table 2, COD removal efficiencies of adsorbents decreased or increased slightly with time and power changes. Microwave radiation produces hydroxyl radicals from hydrogen peroxide. Hydroxyl radicals partially react with high molecular weight organic materials and convert to smaller molecular weight structures. These molecules are removed from the wastewater by adsorbent. Microwave heating varies depending on the strength of the microwave, the specific temperature, shape, surface area and temperature of the material to be heated.

Table 2

Effect of MW Power and Radiation Time an COD Removal (%)

Irradiation time / Adsorbents (2.5 g)	3 min		8 min	
	336 W	595 W	336 W	595 W
Bentonite	24.9	39.4	26	29.5
Limestone	41.4	36.5	27	25
Pumice	29.7	28	29	32.7

3.2. Effect of Adsorbent and Oxidant Dosage

Tables 3 and 4 show the effects of adsorbent and oxidant dosage on organic matter removal. COD removal was decreased with increasing amounts of adsorbent and oxidant. Doses of 2.5, 5.0 or 7.5 g/250 mL of adsorbent was combined with a constant oxidant dose (2.5 mL/250 mL) at initial pH 6.26. The best COD removal efficiency was achieved with 2.5 g of adsorbent and 2.5 mL of hydrogen peroxide for all adsorbents. Although the increasing amounts of adsorbents and oxidants were theoretically sufficient to oxidize all organic matter in wastewater, the conversion of hydroxyl radical to off-target compounds due to its selective properties reduced COD removal efficiency. For example, carbonate ions in limestone react with OH^- radicals to form carbonate radicals. The SS and oil-grease removal

efficiencies were also determined, and the wastewater's pH measured at the best adsorbent and oxidant dosages observed – Table 5.

Table 3

Effect of Adsorbent Dosage on COD Removal (%)

Adsorbent dosage (g)	Bentonite (595 W, 3 min)	Pumice (595 W, 3 min)	Limestone (336 W, 3 min)
2.5	39.4	36.5	41.4
5.0	25.3	32.3	21.3
7.5	20.4	30.8	19.9

Table 4.

Effect of Oxidant Dosage on COD Removal (%)

Oxidant dosage (mL)	Bentonite (595 W, 3 min)	Pumice (595 W, 3 min)	Limestone (336 W, 3 min)
2.5	39.4	36.5	41.4
5.0	17.3	28.4	29.5
7.5	6.4	15.5	18.4

Table 5

Other Parameters Determined

Adsorbent	SS removal (%)	Oil and grease removal (%)	pH
Bentonite	42	9	7.2
Pumice	So light, unavailable	49	6.9
Limestone	67	40	11.2

4. Conclusions

In this study, the possibility of treatment of the milk industry wastewater containing organic matter by using the catalytic and oxidative effective microwave irradiation method was investigated. The characteristics of the dairy wastewater vary throughout the day. Wastewater samples were taken daily for 1 month. The COD values of this wastewater samples were changed between 3000-10000 mg/L. At the end of the studies, quite different COD removal efficiencies were obtained depending on the character of wastewater. Therefore, no comparison of adsorbent performances could be made. The results of experiments performed on different days should be interpreted differently in terms of comparison of the adsorbents. The dissolved organic matter in dairy industry wastewaters consists mainly of protein, carbohydrates, and oils and fats. The adsorbents and oxidant enhanced organic matter removal from dairy industry wastewater by MW radiation. Clay minerals are materials used in wastewater treatment due to their high ion exchange, absorption and catalysis properties as well as their natural and low cost. In this study it was investigated as an alternative to chemical availability of natural material obtained from different regions of Turkey. In traditional, heat-treatment methods, heat is transmitted from the surface of the material to the interior. When MWs are used, the heating rate is high because the heat is generated within the material, so processing time is short. The MW technology reduces the reaction time, decreases the activation energy, improves the reaction rate, reduces the equipment size and waste and increases the yield and purity of the products.

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Contribution of Researchers

In this study; Tijen Ennil Bektaş has contributed to the project on consultancy, design of experiments, application of experiments, scientific publication research, and the creation of the article. Sevgi Can Gönül contributed to project management, experimental work, and transferring it to the computer. Fazilet Çoker and Handan Öztel contributed to experimental studies.

Conflict of Interest

No conflict of interest was declared by the authors.

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