COMPARISON OF DEGRADATION EFFICIENCY OF THE SULFAMETHOXAZOLE ANTIBIOTIC DRUG BY USING ACIDIC CONDITIONS FROM AQUEOUS SOLUTIONS WITH HETEROGENEOUS PHOTOCATALYTIC-OZONATION PROCESS

HETEROJEN FOTOKATALİTİK-OZONLAMA PROSESİ İLE ASİDİK ŞARTLAR KULLANILARAK SULU ÇÖZELTİLERDEN SÜLFAMETOKSAZOL ANTİBİYOTİK İLAÇLARIN BOZUNMA VERİMLİLİĞİNİN KARŞILAŞTIRILMASI

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ABSTRACT

The main sources of the antibiotics are; domestic wastes, hospitals, health centers (medical treatment, removal of unused medicine) poultry and livestock feeding processes and the pharmaceutical manufacturers. The entry of the pharmaceutical active substances into the environment occurs in the various ways. In this cycle which starts from humans and animals, drug active substances is the done reach wastewater, soil, groundwater and to our drinking water unless the adequate treatment. Pharmaceutical wastes in the sludge scattered around the environment as a result of rains reach in the aquatic medium by infiltration. High concentration of the sludge negatively affect soil organisms. It is also possible that the medicinal substances spread around in the environment may mineralize in the soil or reach underground waters. The main part of the antibiotic inlet is the caused by human practices through hospital exit waters or urban wastewater. For this reason, the development of the alternative treatment methods has gained importance in the recent years for the removal of antibiotic pollution which causes important problems in the environment. Advanced oxidation processes have been found to be effective in the purification of antibiotics. Heterogeneous photocatalytic ozonation process which is one of the advanced oxidation processes is an effective method used in the removal of antibiotics.

In this study, the degradation efficiency of the antibiotic drug sulfamethoxazole with acidic conditions (pH:3 and pH:5) the heterogeneous photocatalytic-ozonation process the was compared. Zinc-oxide/MMT nanocomposite was used as catalyst in the heterogeneous photocatalytic-ozonation process experiments.

Experimental conditions with the highest degradation efficiency of the pH:5 were obtained. Degradation efficiency in the acidic conditions were compared by using different parameters. These parameters are compared, amount of the zinc-oxide/MMT catalyst, SMX (Sulfamethoxazole) initial concentration, ozone inlet flow rate, reusability of the catalyst and organic and inorganic scavengers. The degradation efficiency of sulfamethoxazole in the different processes such as adsorption, photolysis, photocatalysis, ozonation, catalytic ozonation, photocatalytic-ozonation in ZnO/MMT catalyst are compared.

Keywords: Photocatalytic-Ozonation Process, Sulfamethoxazole, Acidic Conditions, Degradation Efficiency, Pharmaceutical Wastes.

ÖZET

Antibiyotiklerin ana kaynakları; evsel atıklar, hastaneler, sağlık merkezleri (tıbbi tedavi, kullanılmayan ilaçların uzaklaştırılması) kümes hayvanları, hayvan besleme süreçleri ve ilaç üretim atıklarıdır. Farmasötik aktif maddelerin çevreye girişi çeşitli yollarla gerçekleşir. İnsanlardan ve hayvanlardan başlayan bu döngüde ilaç aktif maddeleri, yeterli arıtma yapılmadıkça atık su, toprak, yeraltı suyuna ve içme suyumuza ulaşır. Çevreye yayılmış olan arıtma çamurlarındaki farmasötik atık maddeler yağmurlar sonucunda sızma yolu ile sucul çevreye ulaşır. Yüksek konsantrasyon arıtma çamurları toprak organizmalarını olumsuz etkiler. Çevreye yayılmış olan tıbbi maddelerin toprakta mineralize olmaları veya yeraltı sularına ulaşmaları da olasıdır. Antibiyotik girişinin temel kısmı, hastane çıkış suları veya kentsel atık sulardaki insan uygulamalarından kaynaklanmaktadır. Bu nedenle, son yıllarda çevre kirliliğinde önemli sorunlara neden olan antibiyotik atık kirliliğinin giderilmesi için alternatif geri kazanım yöntemlerinin geliştirilmesi önem kazanmıştır. İleri oksidasyon proseslerinin antibiyotiklerin saflaştırılmasında etkili olduğu bulunmuştur. İleri oksidasyon proseslerinden biri olan heterojen fotokatalitik ozonlama işlemi, antibiyotiklerin giderilmesinde kullanılan etkili bir yöntemdir.

Bu çalışmada, antibiyotik ilaç olarak kullanılan sülfametoksazolün asidik şartlarda (pH:3 ve pH:5) heterojen fotokatalitik ozonlama işlemi ile bozunma verimi karşılaştırılmıştır. Heterojen fotokatalitik ozonlama prosesi deneylerinde katalizör olarak çinko-oksit/MMT nanokompoziti kullanıldı.

En yüksek bozunma verimliliği pH: 5 olan deney koşullarında elde edildi. Asidik şartlarda bozunma verimliliği, farklı parametreler kullanılarak karşılaştırıldı. Bu parametreler, çinko-oksit/MMT katalizörünün miktarı, SMX (Sülfametoksazol) başlangıç ilaç konsantrasyonu, ozon giriş akış hızı, katalizörün tekrar kullanılabilirliği, organik ve inorganik temizleyicilerin bozunma verimliliği karşılaştırıldı. ZnO/MMT katalizörü ile adsorpsiyon, fotoliz, fotokataliz, ozonlama, katalitik ozonlama, fotokatalitik ozonlama gibi farklı proseslerde sülfametoksazolün bozunma verimliliği karşılaştırıldı.

Anahtar Kelimeler: Fotokatalitik-Ozonlama Prosesi, Sulfametoksazol, Asidik Şartlar, Bozunma Verimliliği, Farmasötik Atıklar.

1. INTRODUCTION

Medicines used by humans are excreted from the human body only in a slightly transformed or the unchanged form. Through urine they reach in the sewage and from there to the wastewater treatment plant. Pharmaceutical wastes reaching the treatment facility cannot be disposed of in the treatment facility (Sorensen et al., 1998). The ability of the antibiotics to affect bacteria changes with biological processes in the treatment plants. Polar antibiotics probably cannot to be eliminated. Because the active carbon adsorption used for in the removal works with hydrophobic interaction (Khataee et al., 2013). As a result receiving waters and other environmental medium may be contaminated. Some of the antibiotics that reach nature in this way can be found in the nature for many years due to their long half-lives (Topkaya, 2014; Kıranşan, 2015). Active compounds are discharged almost unchanged from the wastewater treatment plants to the receiving environment. If the metabolites are still biologically active, they affect the aquatic organisms in the environment and pose a real threat to the ecosystem and human health (Sorensen et al., 1998).

If a substance is not removed by any means it is may reach the environment with potential adverse effects on the aquatic and terrestrial organisms. From there it can be reach people by in the mixing with drinking water (Kemper, 2008). Antibiotics are designed to the affect microorganisms. Antibiotics are released into the environment with little or no it conversion and conjugated to the polar molecules (Kemper, 2008). Since antibiotics have low the biodegradability they accumulate in the different environments (Çelebi and Sponza, 2007). The availability of the antibiotics in the environment depends on physical and chemical properties, general climatic conditions, soil type and other environmental factors (Sorensen et al., 1998). The fate and behavior of antibiotics in soil is the defined as one of the important issues in the environmental chemistry. Antibiotics used for veterinary purposes are excreted by the animals and end up in the soil used as agricultural fertilizers (Jorgensen and Sorensen, 2000). In terms of their changing structural classes antibiotics are ionized as the amphiphilic or amphoteric and therefore antibiotics are absorbed as a result of the adsorption in the soil (Kemper, 2008). Sorption and fixation of the substances in the soil are different due to their physical and chemical properties such as the molecular structures, size, shape, solubility and hydrophobicity (Beltran et al., 2012).

2. MATERIALS AND METHODS

2.1 Mechanism of the Heterogeneous Photocatalytic-Ozonation Process

The heterogeneous photocatalytic-ozonation process consists of a series of complex reactions. These reactions take place in the 5 steps; (i) diffusion of reactants to the surface, (ii) adsorption of reactants to the surface, (iii) reaction at the surface, (iv) desorption of products from the surface, (v) diffusion of products from the surface (Pirkanniemi and Sillanpaa 2002; Al-Rasheed, 2005).

Having a higher absorption coefficient, ozone absorbs UV radiation below 320 nm wavelength, generating additional hydroxyl radicals and other oxidants with in the increased degradation efficiency (Augugliaro et al., 2006; Khataee et al., 2016). The basic mechanisms of the photocatalytic ozonation are shown in the equations below (Eq.1-4).

$$O_3 + h\nu\ (320\ nm) \rightarrow O\ (^1D) + O_2 \quad (1)$$

$$O\ (^1D) + H_2O \rightarrow H_2O_2 \quad (2)$$

$$H_2O_2 + h\nu \rightarrow 2.\ OH \quad (3)$$

$$O\ (^1D) + H_2O \rightarrow {}^{\cdot}OH + {}^{\cdot}OH \quad (4)$$

All possible reaction steps during the production of hydroxyl radicals can be summarized as follow. One of them, under UV irradiation, absorption of the photons with higher energy of ZnO nanoparticles band gap leads to oxidant positive hole formation on the valence band and electron migration to the conduction band as shown in Eq. (5-8) (Beltran et al., 2009; Ahmed et al., 2014).

$$ZnO + h\nu \rightarrow e^- + h^+ \quad (5)$$

$$O_3 + e^- \rightarrow O_3^{\cdot -} \quad (6)$$

$$O_3^{\cdot -} + H^+ \rightarrow HO^{\cdot}_3 \quad (7)$$

$$HO^{\cdot}_3 \rightarrow O_2 + {}^{\cdot}OH \quad (8)$$

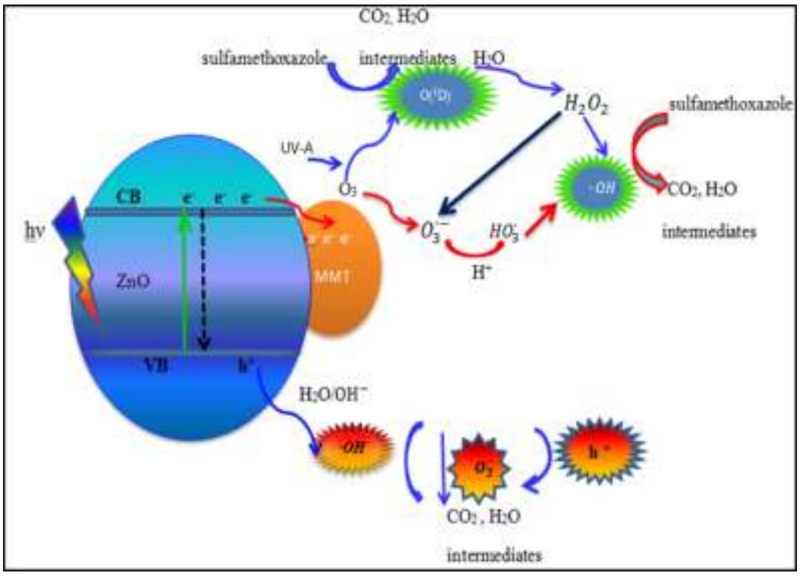

Figure 1. Schematic representation of SMX degradation during heterogeneous photocatalytic ozonation with ZnO/MMT as photocatalyst.

The formation of hydroxyl radicals (•OH) is the possible by direct electron transfer from ZnO to ozone molecule under UV light and the formation of ozonide radicals in the adsorption layer (Parrino et al., 2015; Fathinia et al., 2016).

3. RESULTS AND DISCUSSION

3.1 Effect of Initial Sulfamethoxazole (SMX) Concentration in the Acidic Conditions

In photocatalytic ozonation experiments with the initial sulfamethoxazole (SMX) drug concentration in the acidic conditions, the catalyst amount was determined as 0.1 g L^{-1} and the ozone inlet flow rate as 2 L h^{-1}. Sulfamethoxazole concentration was studied from 5 mg L^{-1} to 40 mg L^{-1} (Akyol et al., 2004).

As a result of the photocatalytic ozonation experiments under acidic conditions, the highest degradation efficiency was obtained at pH: 5 in the acidic conditions. In experimental conditions with the sulfamethoxazole concentration of 5 mg L^{-1}, degradation efficiency at pH: 3 was 87.16% and degradation efficiency at pH: 5 was 94.04% as a result of photocatalytic ozonation reactions for 30 minutes (Sakthivel et al., 2003).

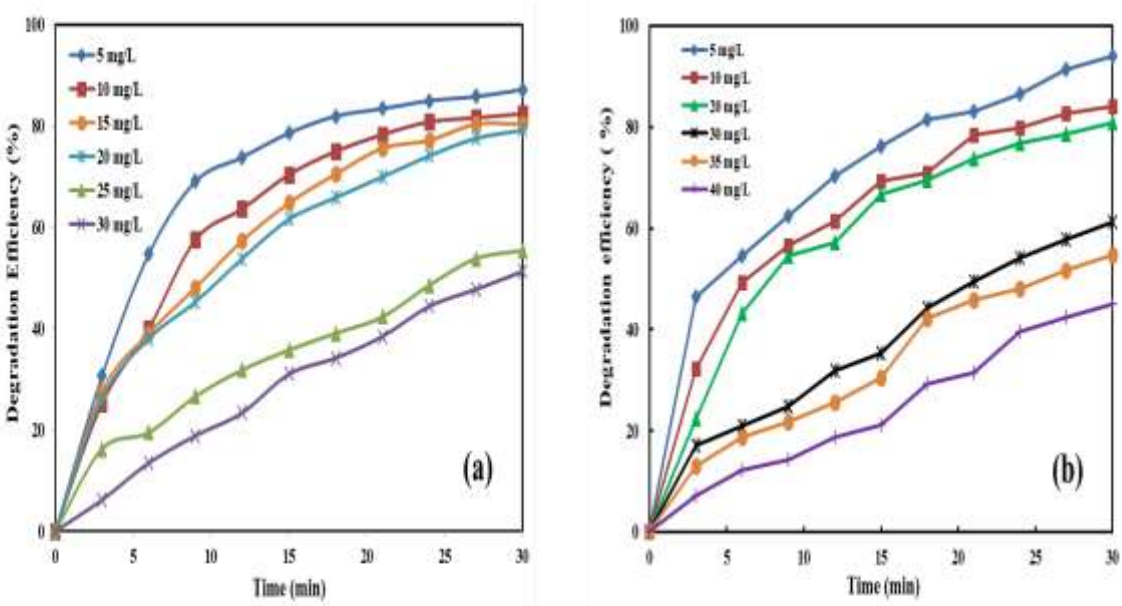

Figure 2. The effect of initial sulfamethoxazole concentration on the degradation efficiency by ZnO/MMT under photocatalytic ozonation process. Experimental conditions: $[ZnO/MMT]_0$: 0.1 g L^{-1}, ozone gas inlet flow rate: 2 L h^{-1}, (a) pH=3, (b) pH=5.

3.2 Effect of Ozone Inlet Flow Rate in the Acidic Conditions

In photocatalytic ozonation experiments performed with ozone flow rate under acidic conditions, sulfamethoxazole concentration was determined as 20 mg L^{-1}. Ozone flow rate concentration was studied from 1 L h^{-1} to 5 L h^{-1}.

As a result of the ozone flow rate experiments under acidic conditions, the highest removal efficiency was obtained in pH: 5 acidic conditions. In experimental conditions with sulfamethoxazole concentration of 20 mg L^{-1}, as a result of 30 minutes of ozonation reactions, the removal efficiency at pH: 3 at 5 L h^{-1} ozone flow rate was found to be 81.45% at 71.21% pH: 5 (Mehrjouei et al., 2014).

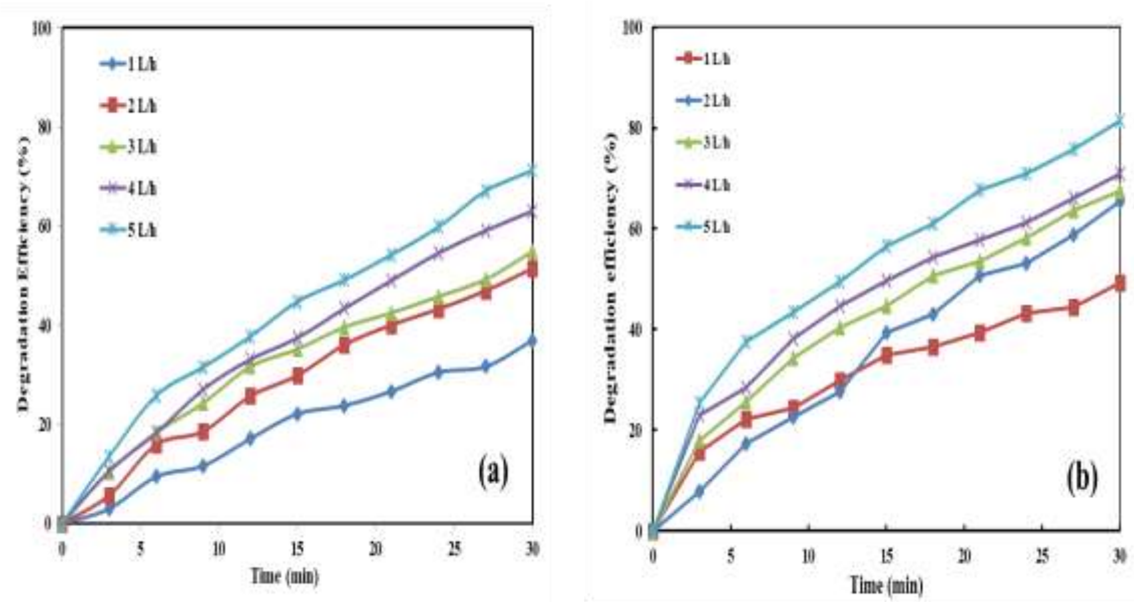

Figure 3. The effect of ozone gas inlet flow rate on the sulfamethoxazole degradation during ozonation process. Experimental conditions: $[SMX]_0$: 20 mg L^{-1} (a) pH=3, (b) pH=5.

4. CONCLUSION

The combination of heterogeneous photocatalysis and ozonation processes accompanied by ZnO/MMT photocatalyst was applied to remove sulfamethoxazole antibiotic from aqueous solution. To prepare ZnO/MMT catalyst, synthesized ZnO nanoparticles was immobilized onto MMT surface. The samples was characterized by the analytical tecniques of FT-IR, XRF, XRD, SEM, TEM. Characterization results confirmed the succesfull immobilization of ZnO onto MMT surface. The effect of the various operational parameters, such as catalyst dosage, initial SMX concentration, ozone gas flow rate and pH on the SMX degradation efficiency was investigated.

Based on the obtained results from the experiments it can be said that the treatment of wastewaters involving the pharmaceuticals by photocatalytic ozonation process under UV light irradiation accompanied with ZnO/MMT as an eccellent photocatalyst is a promising way. And also, this system should be a low-cost, efficient, and nontoxic technology for removal of similar contaminants in wastewaters.

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