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APPLICATION OF TITANIUM DIOXIDE(TiO₂) NANOPARTICLE MATERIALS ON DOMESTIC WASTEWATER: REMOVAL OF POLLUTANTS

TİTANYUM DİOKSİT(TiO₂) NANOPARTİKÜL MADDELERİN EVSEL ATIKSULAR ÜZERİNE UYGULANMASI: KİRLETİCİLERİN GİDERİMİ

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ABSTRACT

Titanium is a very valuable element and is also the ninth most abundant element on earth and is commonly found in minerals such as rutile, ilmenite, and sphene. Adsorption, photocatalysis, and advanced oxidation processes are used in wastewater treatment. Among these processes, photocatalysis has emerged as a safe, efficient, and environmentally friendly process for wastewater with high pollutant content. Titanium dioxide (TiO₂) is usually used as a photocatalyst and adsorbent. Titanium dioxide nanoparticle material has been applied in various fields, including environmental water and wastewater treatment. In this study, treatment performance was investigated by using TiO₂ nanoparticles for the removal of pollutants in domestic wastewater. System performance was evaluated in terms of chemical oxygen demand (COD), dissolved organic carbon (DOC), and total nitrogen (TN). Different adsorbent concentrations (50-200 mg/L) and reaction times (15-90 min) were investigated at pH 7.2 to determine optimum conditions. Optimum adsorption concentration and reaction time were found to be 50 mg TiO₂/L and 60 minutes, respectively. COD, DOC, and TN removal efficiencies were observed as 80%, 30%, and 35%, respectively. The obtained results showed that the removal efficiency of COD and DOC from domestic wastewater of TiO₂ nanoparticles is high.

Keywords: Titanium dioxide, domestic wastewater, adsorption, nanoparticles

ÖZET

Titanyum, yer kabuğunda en bol bulunan dokuzuncu elementtir ve genellikle rutil, ilmenit ve sfen gibi minerallerde bulunur. Su ve atık su arıtımında adsorpsiyon, fotokataliz ve ileri oksidasyon prosesleri kullanılmaktadır. Bu prosesler arasında fotokataliz, kirletici içeriği yüksek atık suların arıtılması için güvenli, verimli ve çevre dostu bir arıtma prosesi olarak ortaya çıkmıştır. Titanyum dioksit (TiO₂) fotokatalizör ve adsorban olarak yaygın kullanılmaktadır. Titanyum dioksit nanoparçacık malzemesi, çevresel su ve atık su arıtımı dahil olmak üzere çeşitli alanlarda uygulanmıştır. Bu çalışmada, evsel atıksularda kirleticilerin giderilmesi için TiO₂ nanopartikülleri kullanılarak arıtma performansı araştırılmıştır. Sistem performansı, kimyasal oksijen ihtiyacı (KOİ), çözülmüş organik karbon (DOC) ve toplam nitrojen (TN) açısından değerlendirilmiştir. Optimum koşulları belirlemek için pH 7.2'de farklı adsorban konsantrasyonları (50-200 mg/L) ve reaksiyon süreleri (15-90 dakika) araştırılmıştır. Optimum adsorpsiyon konsantrasyonu ve reaksiyon süresi sırasıyla 50 mg TiO₂/L ve 60 dakika olarak

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belirlenmiştir. KOİ, DOC ve TN giderim verimleri sırasıyla %80, %30 ve %35 olarak gözlenmiştir. Elde edilen sonuçlar, TiO₂ nanoparçacıklarının evsel atık sularından KOİ ve DOC giderim verimi açısından yüksek olduğunu göstermektedir.

Anahtar Kelimeler: Titanyum dioksit, evsel atıksu, adsorpsiyon, nanopartiküller

INTRODUCTION

Wastewater treatment plants (WWTPs) are principal for treating domestic and industrial wastewater (Soares, 2020), and are significant in domestic wastewater treatment (Jin et al. 2014). The source of the domestic sewage plant mainly originates from human activity and industrial activity, which includes organics, bacteria, chemical oxygen demand (COD), dissolved organic carbon (DOC), and total nitrogen (TN). Removal of COD, DOC, and TN in domestic wastewater is considered to be a crucial and intractable problem. Over the years, various kinds of techniques for removing COD, DOC, TN, and ammonia nitrogen from domestic wastewater have been widely studied including photoelectrocatalytic (Ji et al. 2017), anammox (Yang et al. 2019), ion-exchange (Jorgensen and Weatherley, 2003), chemical precipitation (Chai et al. 2017), biological treatment process (Abu Hasan et al. 2013), air stripping (Sotoft et al. 2015), and adsorption method (Tu et al. 2019). The adsorption process is considered to be the most feasible method to remove from water since stable, and low-cost method for contaminants removal from wastewater. In recent years, nanoparticles have been used in wastewater treatment applications with the development of nanoscience and nanotechnology. Some nanoparticles are commonly used in much water and wastewater treatment. Among these nanoparticles, zinc oxide (ZnO), silver (Ag), copper oxide (CuO), and titanium dioxide (TiO₂) are widely used (Otero-González et al. 2014a; Ana Garcia et al. 2012; Li et al. 2017; Otero-González et al. 2014b; Demirel, 2016). TiO₂ nanoparticles have many advantages such as high stability, corrosion resistance, easy to obtain, inexpensive, surface activities, and photocatalytic properties. Therefore, it is among the most preferred nanoparticles. They reported that it is widely used for wastewater treatment because of these advantages (Burke, et al. 2008; Nakata, K., et al. 2013; Chiarello, et al. 2017; Zhou, et al. 2014; Xing, et al. 2018). At the same time, TiO₂ nanoparticles have been used in many technological fields such as solar cells, memory devices, and industrial and commercial applications (Liu et al., 2014; Lu et al., 2017). Recently, however, TiO₂ nanoparticles have been reported to be remarkable in wastewater treatment (Dariania et al. 2016; Lin et al. 2018; Tijani et al. 2019).

This study aims to use nanoparticles (TiO₂) as an adsorbent to remove contaminants (COD, TOC, and TN) from domestic wastewater.

MATERIALS AND METHOD

Characteristics of the Domestic Wastewater

The wastewater was collected from Kahramanmaraş Wastewater Treatment Plant(WWTP) in Kahramanmaraş, Turkey. Then, domestic wastewater was using lab-scale adsorption experiments. Domestic wastewater treatment performance was evaluated in terms of COD, TN, and DOC removals. The characteristics of domestic wastewater used in this study are largely variable and the mean values of treated wastewater are shown in Table 1.

Table 1. Characteristics of the Domestic Wastewater

Parameters	Concentration*
pH	7,2
Temperature	Room Temperature (25°C)
Chemical Oxygen Demand (COD)	517
Dissolved Organic Carbon (DOC)	141
Total Nitrogen (TN)	34

*Values are average of triplicate measurements

Experimental Operation

This study is to investigate the adsorption of pollutants removal in domestic wastewater by titanium dioxide at an adsorbent concentration (50-100-150-200mg/L) and contact time (15-90min). The schematic diagram of the experimental operation used in the study is illustrated in Table 2.

Table 2. Experimental Operation

PART	TiO ₂ Concentration (mg/L)	Reaction Time (dk)	pH	Temperature (°C)
Effect of Titanium Dioxide (TiO ₂) Concentration	50	15	7	Room Temperature (25°C)
		30		
		60		
		90		
	100	15		
		30		
		60		
		90		
	150	15		
		30		
		60		
		90		
	200	15		
		30		
		60		
		90		

Analyses

All samples were centrifuged at 4000 rpm for 5 minutes (Eppendorf Centrifuge 5415R, Hamburg, Germany) and then filtered using a 0.45 µm syringe filter (Sartorius AG, Göttingen, Germany). DOC, and TN concentrations were analyzed using the DOC-TN instrument (Shimadzu TOC-VCPN, Kyoto, Japan). pH was measured with a pH meter (Thermo, Orion 4 Star, Indonesia). COD measurements were made according to the dichromate-colorimetric method described in Standard Methods (Standard Methods, 5220 D).

RESULTS AND DISCUSSION

The COD Removal Performance of Domestic Wastewater

The adsorption process has long been used to remove simultaneous TN, DOC, and COD from municipal and industrial wastewater. It is known that COD concentration plays an important role in the adsorption process of nanoparticles, which directly affects removal efficiency. In this part of the study, system performance was evaluated in terms of COD removal efficiency at an adsorbent concentration and reaction time. COD influent, effluent concentrations and removal efficiency are demonstrated in Fig 1.

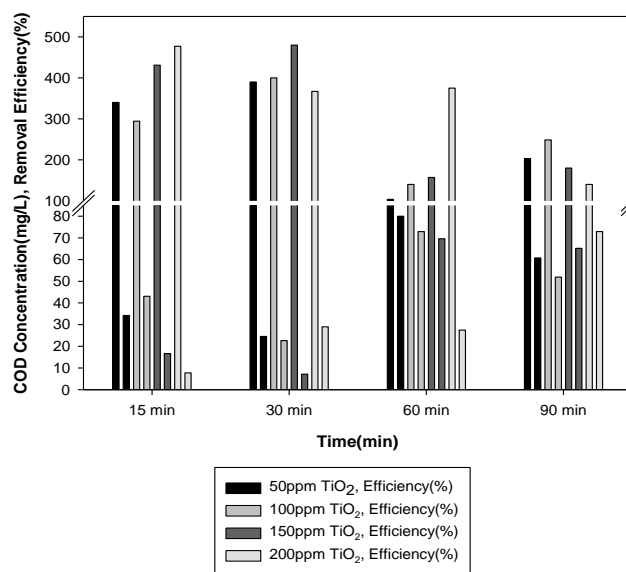


Figure 1. Chemical Oxygen Demand (COD) Removal Performance

The influent COD concentration throughout this study was an average of 517 mg/L. In this part of the study, the effect of TiO₂ concentration and reaction time on the adsorption process used in domestic wastewater was investigated by increasing the TiO₂ dosage from 50 mg/L to 200 mg/L. pH was kept stable at 7.2, and reaction times were adjusted to 15-90 min respectively. The effluent COD concentration was prominently increased by increasing the TiO₂ dosage from 50 mg/L to 200 mg/L. The high COD removal efficiency of 80% was obtained at a TiO₂ dosage of 50 mg/L and reaction time of 60min, corresponding effluent DOC concentration of about 103 mg/L (Figure 1). When TiO₂ dosage was increased to 50 mg/L and 200 mg/L, COD removal efficiencies of an average of 50% and 30% were obtained, respectively; which were average maximum values obtained in this part (Figure 1). When the reaction time increased from 15 min to 60 min at 50 mg/L TiO₂ concentration, it was observed that the COD removal efficiency reached the highest value and the corresponding COD removal efficiency was observed as 80%. While the TiO₂ concentration increased, no increase was observed in the COD removal efficiency. This situation was determined as the precipitation of TiO₂ NPs that can occur in the presence of cations (Xu, 2018; Lin et al. 2012). Mustafa, et al. (2021), in their study, investigated the effect of kaolin and kaolin/TiO₂ nano adsorbent on the removal of pollutants in tannery wastewater. According to the results they obtained, they observed that the COD removal efficiency was approximately 91%. Our studies are similar to the literature. Increasing nanoparticle concentration did not affect COD removal efficiency. These results indicated that TiO₂ concentration of 50 mg/L and reaction time of 60 min was favorable for the adsorption process of domestic wastewater and thus, the subsequent study parts were continued at this concentration.

The DOC and TN Removal Performance of Domestic wastewater

In this part of the study, adsorption system performance was evaluated in terms of DOC and TN removal at an adsorbent concentration (50-200mg/L) and reaction time (15-90min). The variations of DOC and TN concentrations and removal efficiency are demonstrated in Fig 2-3. The influent DOC concentration was an average of 141 mg/L. DOC removal efficiency was 30%, 5%, 7%, and 8% at an adsorbent concentration of 50, 100, 150, and 200mg/L, and optimum reaction time 60, respectively (Fig 2). The DOC removal efficiency reached over 80% at 50 mg/L TiO₂ concentrations and a reaction time of 60 min. In addition, when the TiO₂ concentration was increased to 200 mg/L and the reaction time to 60 minutes, the DOC removal efficiency decreased to 8%. A comparison was carried out between the present work and reported work in literature with the similar photocatalyst applied for real wastewater treatment with good interest for DOC removal efficiency, as illustrated in Fig 2. Pang, et al. (2013) in their study, on the effect of Fe-doped titanium dioxide (TiO₂) nanotubes by investigating the treatment of real textile wastewater. As a result, the color, COD, and DOC removal efficiency have obtained at 79.9%, 59.4%, and 49.8%, respectively. The results showed different TiO₂ forms, pollutant types, reaction times, and light sources that were sometimes contradictory based on the initial concentration of pollutants in the effluent. In addition, the forming of TiO₂ material is a key factor in the effectiveness of wastewater treatment on photocatalytic oxidation. It can be seen that TiO₂ coated on mesh showed higher performance of pollutant removal than TiO₂ powder (Wongaree, M., et al., 2022).

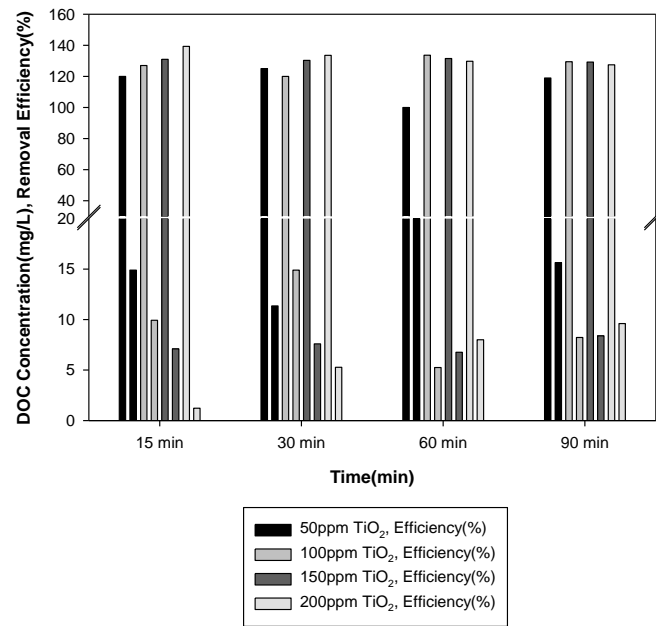


Figure 2. Dissolved oxygen demand (DOC) removal performance

The variations of TN concentrations and removal efficiency are demonstrated in Fig 3. The influent TN concentration was an average of 34 mg/L. At increasing adsorbent concentrations from 50 to 200mg/L and reaction time 15 to 90 min the TN removal efficiency was decreased from 35% to %14. The highest TN removal efficiency was observed at an adsorbent dosage of 50mg/L TiO₂ and the corresponding removal efficiency was 35% (Fig 3). According to TN removal efficiency, the optimum TiO₂ dosage and reaction time were determined to be 50mg/L and 60 min, respectively.

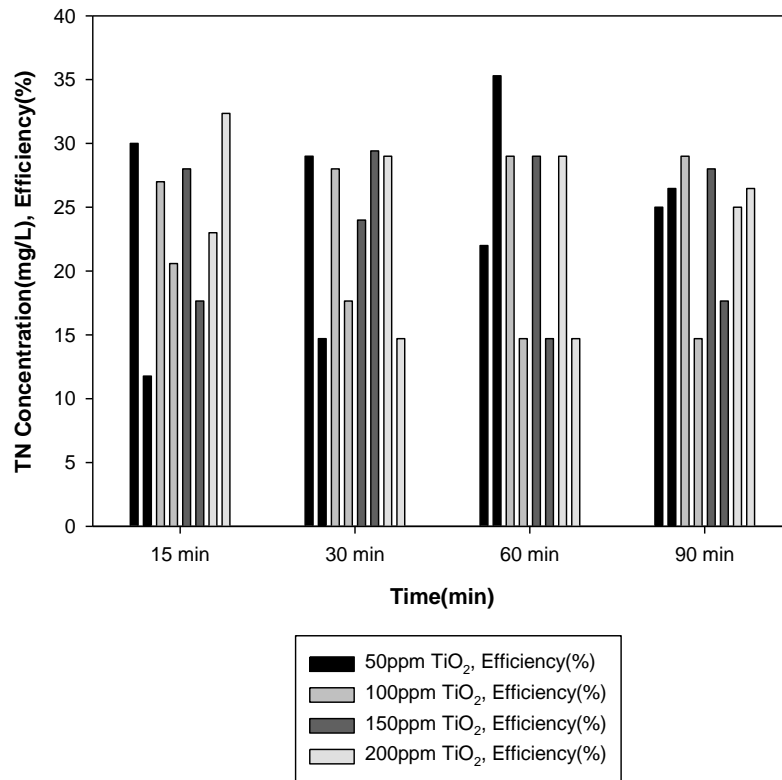


Figure 3. Total nitrogen(TN) removal performance

CONCLUSION

In this study, DOC, COD, and TN removal using the adsorption process from domestic wastewater were investigated under operating conditions including different adsorbent concentrations and reaction times. This study showed that adsorbent concentration and reaction time play a remarkably role in residual COD, DOC, and TN removal using the adsorption process; however, adsorbent concentration and reaction time had no significant effect on DOC and TN removal. According to COD removal efficiency the adsorbent concentration and reaction time were found optimum for 50mg/L TiO₂, and 60min for high system performance. At optimum adsorbent concentration, COD removal efficiencies were 80%, while DOC removals were 30%, and TN removal was 35%. In a conclusion, the effluent DOC, COD, and TN concentration of the adsorption process at TiO₂ concentration of 50mg/L and reaction time of 60 min were 100, 103, and 22mg/L, respectively. The study shows that nanoparticles matter (for pre-treatment) can be effectively used for domestic wastewater treatment. In this study, although the positive effects of nanoparticles on wastewater treatment have been noted, they have been used as pretreatment for the treatment of domestic wastewater. For this reason, more research is required related to the effect on the biological treatment of nanoparticles.

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