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THE EFFECT OF IMMOBILIZED ENZYME ON TEXTILE WASTEWATER

İMMOBİLİZE ENZİMİN TEKSTİL ATIK SULARINA ETKİSİ

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ABSTRACT

Textile wastewater has a complex composition characterized by high dye content and chemical oxygen demand. Therefore, textile wastewaters have serious environmental impacts, such as aesthetic degradation, and carcinogenic properties. Treatment and the recovery of textile wastewater are important due to their high volume and toxicity. The effects of peroxidase enzyme immobilized on magnetic chitosan-clay beads of synthetic textile wastewater were investigated in a batch reactor. System performance was determined by chemical oxygen demand (COD) and color. The batch reactor was operated in three different pH (5, 7, 10), temperatures (25, 35, 45 °C), and reaction times (0-5-10-20-30 min.) with synthetic textile wastewater. As a result, COD and color removal efficiencies were determined as 44% and 56%, respectively, corresponding effluent concentrations are 1442 mg/L, 450 Pt-Co. The results of this study show that using the enzyme immobilization process is an effective method to remove color and COD concentration from textile wastewater.

Keywords: enzyme, immobilization, textile wastewater

ÖZET

Tekstil atıksuları, yüksek boya içeriği ve kimyasal oksijen ihtiyacı ile karakterize edilen karmaşık bir bileşime sahiptir. Bu nedenle tekstil atıksuları estetik bozulma ve kanserojen özellikler gibi ciddi çevresel etkilere sahiptir. Tekstil atık sularının arıtılması ve geri kazanılması, yüksek hacimleri ve toksisiteleri nedeniyle önemlidir. Sentetik tekstil atıksularının manyetik kitosan-kil tanecikleri üzerine immobilize edilen peroksidaz enziminin etkileri kesikli reaktörde araştırılmıştır. Sistem performansı kimyasal oksijen ihtiyacı (KOİ) ve renk ile belirlendi. Kesikli reaktör, sentetik tekstil atıksuyu ile üç farklı pH (5, 7, 10), sıcaklık (25, 35, 45 °C) ve reaksiyon süresinde (0-5-10-20-30 dk.) çalıştırılmıştır. Sonuç olarak KOİ ve renk giderme verimleri sırasıyla %44 ve %56 olarak belirlenmiş olup, buna karşılık gelen atık su konsantrasyonları 1442 mg/L, 450 Pt-Co' dur. Bu çalışmanın sonuçları, enzim immobilizasyon prosesinin tekstil atıksularından renk ve KOİ konsantrasyonunu gidermek için etkili bir yöntem olduğunu göstermektedir.

Anahtar Kelimeler: enzim, immobilizasyon, tekstil atıksuyu

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INTRODUCTION

With the rapid population growth in the world, the demand for textile products is increasing. This increase brings with it the resulting wastewater, creating one of the most important industrial wastewater in the world. The textile industry which has the most complex structure among production industries, consists of dyes, suspended solids matter, inorganic salts, and other chemicals (Han et al., 2018; Sun et al., 2015). Textile wastewater is a serious source of pollution due to its high organic load (Bhimani, 2011). The most important pollutant parameter of such wastewater is that it contains dye components. Most organic dyes have carcinogenic and mutagenic properties (Weisburger, 2002). In addition to having negative environmental impacts, these dyes wastewater are toxic and have serious dyeing effects on water streams (Imtiazuddin et al., 2012). These are harmful pollutants that must be treated before being discharged into the environment. Treatment methods vary depending on the characteristics of the textile wastewater. The physical methods such as adsorption, sedimentation, flotation, flocculation, coagulation, ultrafiltration, photoionization, and incineration, as well as the chemical methods (e.g., neutralization, reduction, oxidation, electrolysis, ion exchange, wet-air oxidation) and biological methods (stabilization ponds, aerated lagoons, trickling filters, activated sludge, anaerobic digestion, and various types of microbial strains) have been widely used to removal color from textile wastewater (Darwesh et al., 2019).

Enzymes as biological catalysts could be used in free or immobilized forms, and are more advantageous compared to other methods. Immobilized enzymes are preferred for many reasons such as long-term operational stability, easy recovery, reuse, and being easier to separate from the product in textile wastewater. Immobilized enzymes are prepared by different physical and chemical methods, which affect the properties of the resulting enzymes and therefore their use in certain processes (Abid, et al., 2016; Sheldon, 2007; Cao, 2005; Adamczak and Krishna, 2004; Bommarius and Riebel-Bommarius, 2004). Peroxidase, laccase, lignin peroxidase, horseradish peroxidase, and tyrosinase enzymes were generally used in studies for color removal. A support material is required for the immobilization of enzymes. The support material should be cheap, and biocompatible. Chitosan has many interesting properties such as biocompatibility, hydrophilicity, mechanical stability, renewability, and ease of preparation in different geometric configurations suitable for a chosen biotransformation (Aydemir et al., 2015). Magnetic nanoparticles (MNPs), one of the support materials, increase immobilization efficiency by providing a large surface area for enzyme binding. MNPs are generally made from biocompatible materials such as Fe_3O_4, as they reduce the risk of particles aggregating (Shaw and Murthy, 2011). Therefore, MNPs are commonly used together including enzymes (Mohamed et al., 2017; Sarno et al., 2017; Wu et al., 2008; Kouassi et al., 2005).

This study aimed to investigate the color and COD removal performances (temperature, pH, and reaction time) of peroxidase enzyme attached to magnetic chitosan clay beads in synthetic textile wastewater.

MATERIAL AND METHOD

Simulated Textile Wastewater

Synthetic textile wastewater fed into the reactor contained nutrients required for microbiological growth. The synthetic textile wastewater content is given in Table 1.

Table 1. Synthetic Textile Wastewater (Cırık, 2010)

Nutrients (mg/L)	
NH_4CI (80)	$FeCI_3.6H_2O$ (5)
H_3BO_3 (0.04)	$NiCI_2.6H_2O$ (0.092)
$MnCI_2.4H_2O$ (0.5)	$CoCI_2.6H_2O$ (1)
$ZnCI_2$ (0.05)	$Na_2MoO_4.2H_2O$ (0.265)
K_2HPO_4 (35)	NaCl (127)
KH_2PO_4 (30)	EDTA (5.4)
$CaCI_2.2H_2O$ (367)	Glucose (1000)
$MgCI_2.6H_2O$ (500)	Remazol brilliant violet 5R (100)
$CuCI_2.2H_2O$ (0.038)	

Reactor Setup and Experimental Design

The schematic diagram of the reactors used in the study is shown in Figure 1. The reactors consisted of 100 mL of three different vessels. The peroxidase enzyme immobilization used in the study was according to Ayranpınar, (2022). HCl or NaOH was used to adjust the pH of wastewater.

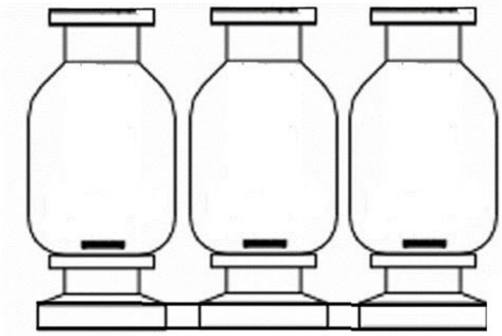

Figure 1. The Experimental Setup

Table 2. Experimental Plan

Parts	pH	Temperature (°C)	Reaction Time (min.)
I	5 7 10	25	0-5-10-20-30
II	Opt.	25 35 45	0-5-10-20-30

In this study, the system performance was evaluated in two different parts, and the experimental plan is shown in Table 2. In the first part of the study, the effect of different pH (5-7-10) and reaction times (0-5-10-20-30) at 25 °C was investigated in synthetic textile wastewater. In the remaining part of the study (part II), the system was operated under varying temperatures (25-35-45 °C) and reaction times (0-5-10-20-30) at the optimum pH.

Analysis

The pH and temperature were measured by a pH meter (WTW Multi 340i, Weilheim, Germany). All samples were centrifuged at 4000 rpm for 5 min (Labortechnic, Wehingen, Germany) and then, were filtered using a sterile syringe 0.45µm filter (Sartorius AG, Gottingen, Germany). The COD measurements 1.5 ml of disintegration solution (15,324 g of $K_2Cr_2O_7$, 49.95 g of $HgSO_4$ and 250.5 g of H_2SO_4 was added to the flask and made up to 1000 ml) on top of the 2 ml sample, and 3.5 ml of sulfuric acid-mercuric sulfate solution (10,12 g Ag_2SO_4 was added to 1000 ml (complete with H_2SO_4) in a flask and left in a thermoreactor (ECO 16 Thermoreactor, Velp Scientifica, Milan, Italy) for 2 hours at 150ºC, then at 600 nm in the HACH-DR 5000 brand spectrometer (Hach-Lange, Dusseldorf)., Germany). Color analyses were performed with a HACH DR 5000 (Loveland, CO., USA) spectrophotometer.

RESULTS AND DISCUSSION

Effect of pH on COD and Color Removal

In this study, the effect of different pH (5-7-9) and reaction times (0-5-10-20-30 min.) using an immobilized peroxidase enzyme on COD and color removal was investigated in textile wastewater. The effect of pH on COD and color removal is shown in Figure 2. The influent COD and color values of synthetic textile wastewater were around 2556 mg/L and 1030 Pt-Co, respectively. The maximum color removal efficiency as Pt-Co was obtained at 400, corresponding to 61% at 10 pH and 5. min. This was an indication that the immobilized peroxidase was more stable under alkaline conditions (Darwish et al., 2019). Sekuljica et al. (2015), obtained 94.7% color removal efficiency at pH 4 and a reaction time of 15 min using horseradish peroxidase enzyme. Han F. et al. (2020) observed in their activities that the pepsin enzyme had max. color removal efficiency at pH 2. They obtained higher results compared to our study. COD removal efficiency remained relatively unchanged at 5. min. at all pH values. The maximum COD removal efficiency was obtained at 1614 mg/L, corresponding to 37% at 5 pH and 5. min.

Effect of Temperature on COD and Color Removal

The effect of different temperatures (25-35-45°C) and reaction times (0-5-10-20-30 min.) using an immobilized peroxidase enzyme is shown in Figure 3. When evaluated in terms of COD and color, the treatment efficiency was 44% and 56% at 35ºC temperature at 5. min and 5 pH, while the corresponding COD and color values were observed as 1442 mg/L and 450 Pt-Co. Sökmen et al. (2018) studied the effect of temperature on immobilized tyrosinase enzyme and observed that the treatment efficiency reached 47% at 35°C. Çelebi et al. (2013) investigated the removal efficiency of R-active Blue 19 dye for 60 minutes at different temperatures using immobilized peroxidase enzyme and concluded that the maximum dye removal efficiency was at 30°C.

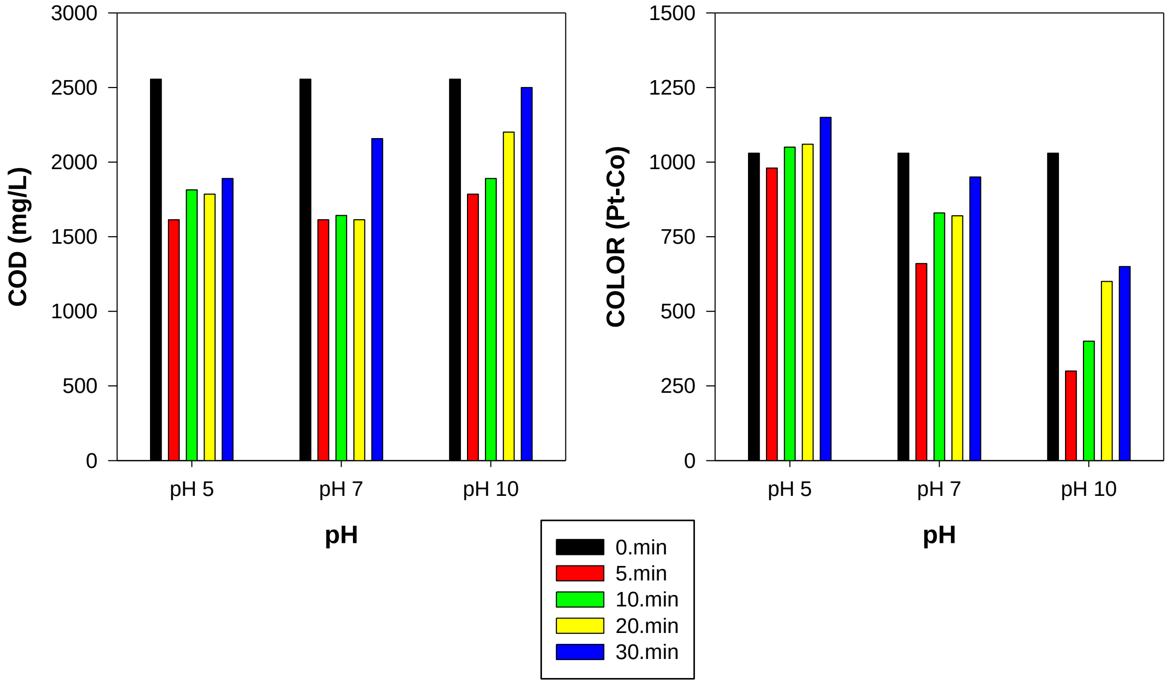

Figure 2. The Effect of pH on DOC and Color Removal

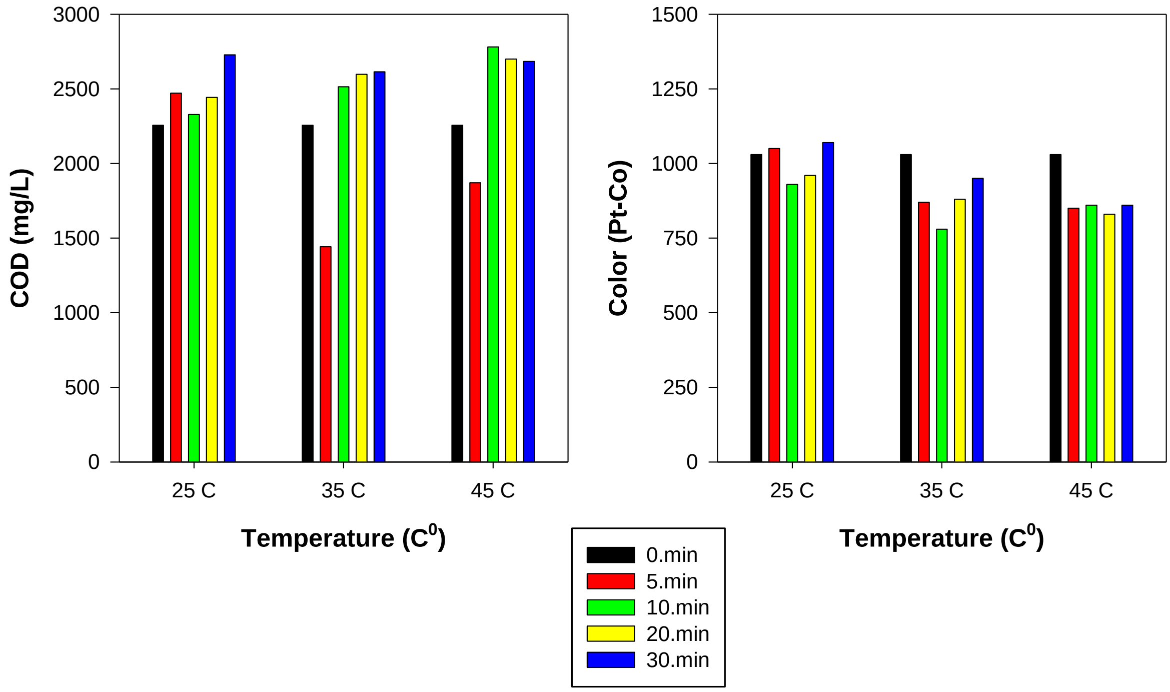

Figure 3. The Effect of Temperature on DOC and Color Removal

CONCLUSION

This study investigated different pH, temperatures (°C), and reaction times (min.) with an immobilization process using synthetic textile wastewater. The optimum pH, temperature, and reaction time were found as 10, 35, and 5, respectively. At optimum pH, temperature, and reaction time 56% color removal efficiency, while COD removal was 44%, corresponding to effluent Pt-Co and COD values of 1442 mg/L and 450 Pt-Co, respectively. This study showed that enzyme-by-immobilizing processes were an effective strategy for COD removal. However, the temperature parameter was ineffective in terms of color removal efficiency as observed. Effluent color and COD values still do not meet the discharge standards of 280 Pt-Co and 700 mg COD/L in the Water Pollution Control Regulation of Turkey. Therefore, the treatment performance of the immobilization process to meet the discharge standards can be improved by integration.

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