




Environmentally Friendly Approach for Decolorization Textile Wastewater by Nanobubble Water Technology and Enzymes

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ABSTRACT

One of the most important issues about textile industry is its negative environmental impacts because of the pollution produced. Herein, decolorization processes of different-colored reactive dyeing baths using eco-friendly ways; nanobubbles and enzymes, was discussed. Decolorizations were evaluated by examining the transmittance and chemical oxygen demands of the treated wastewater baths were measured. The results showed that nanobubbles could be used in decolorization while laccase and peroxidase enzymes increased the decolorization effect of nanobubbles. In addition to the decolorizing effect of nanobubbles, it was an important environmental advantage that the corresponding process provided lower chemical oxygen demand than that in the untreated wastewater. The results of the study reveal that it is possible to use nanobubble in decolorization and this technology is an important wastewater treatment technology in protecting the environment by reducing the chemical oxygen demand of wastewater.

ARTICLE HISTORY

Received: 19.12.2022

Accepted: 20.05.2023

KEYWORDS

Sustainability, cleaner production, textile wastewater, transmittance, chemical oxygen demand

1. INTRODUCTION

The history of nanobubbles (NBs), which are fine bubbles less than 1 μm in diameter [1], began in 1950 with the Epstein-Plesset theory [2]. Research studies and discussions about NBs still continue today. Examples of these are the longevity of NBs in water and short-life paradox predicted in Epstein-Plesset theory [3–6]. A successful theoretical model was developed by Epstein and Plesset in 1950 that explained the dissolution of gas bubbles in liquids using Laplace equation and diffusion theory [7]. According to this theory, which seems to deny the stable existence of nanoscale gas bubbles in liquids, a 100 nm radius bubble with an internal pressure of approximately 14.4 times atmospheric pressure cannot stay for less than 1 μs [2]. Many studies have been conducted on this subject in the following years. The concept of nanobubbles was

reproposed [8]. The aim of this proposal was to provide an explanation about the long-range attractive forces between two hydrophobic surfaces in aqueous solution. In the 2000s, direct observations of surface NBs were conducted [9,10] and they were found to be quite stable on surfaces in water solutions [11–13]. NBs are characterized by mass transfer efficiency, high zeta potential, producing high dissolved oxygen concentration, and large specific surface area [1,14,15]. The nanobubble (NB) technology has been used in health protection, mineral flotation, aquaculture, agricultural cultivation, and many other fields in recent years [16–20]. It is generally used in wastewater treatment in textile [21–24] because NBs decompose organic substances by generating free radicals, such as hydroxyl ($\bullet\text{OH}$) [25]. Their high oxidizing power can degrade even pollutants that do not readily decompose under normal

To cite this article: Anis P, Toprak-Cavdur T, Şardağ S, İncekara B. 2024. Environmentally friendly approach for decolorization textile wastewater by nanobubble water technology and enzymes. *Tekstil ve Konfeksiyon*, 34(3), 231-243.

conditions [26]. In addition, NBs have recently been used in dyeing and finishing processes [27–29].

The increasing demand for dyes derived only from natural sources before 1856 and the exorbitant costs of extracting dyes led to the discovery of the first synthetic dye in 1856 [30]. Since then, the industries depended on synthetic dyes have expanded, producing approximately 8×10^5 tons of dye per year [31,32]. Textile has an approximate share of 75% in this market and contains about ten thousand different dyes [30,33].

Reactive dyes, as the most popular dye class for cotton dyeing [34], due to the variety of brilliant shades, ease of application, excellent color fastness, and low price [35–37], are used in more than 50% of cotton dyeing [38]. In reactive dyeing, exhaustion agents are used to overcome the repulsion between dye - fiber [39,40]. Dye molecules that form covalent bonds with the hydroxyl groups of the cellulose under alkaline conditions provide high wet fastness [41,42]. In reactive dyeing performed in alkaline conditions, fixation and hydrolysis of reactive dyes are in competition, and a high fixation/hydrolysis ratio is required for efficient dyeing [43]. Hydrolyzed dyes that lose their power to react with the fiber are loosely held on the fiber. If these dyes and superficial dyes are not removed during soaping and washing, involving various rinses and washings [44], low washing fastnesses are obtained [45]. The wastewater from the reactive dyeing process of cotton contains 20-50% of the applied dyes in hydrolyzed forms, which cannot be recovered [41]. That is, reactive dyeing is characterized not only by high electrolyte and alkali concentrations [46,47], but also by color [48,49]. In addition, dyeing cotton with reactive dyes consumes the highest volume of water per kilogram of any fiber [50]. Consequently, in terms of environmental impact, reactive dyeing is a water-intensive dyeing and its wastewater discharged is highly polluted.

Dye-containing wastewater in textile industries is a major threat to humans and the environment due to the complex chemical structures of dyes, high pH, biological and chemical oxygen demands, and their presence in all kinds of complex matrices [51,52]. Recently, reuse, recovery and decolorization of dyeing wastewater has attracted great attention due to water scarcity in addition to these reasons. Textile dye wastewater treatment techniques have been categorized as chemical, physical, biological and their combinations [53,54]. While the physical treatment of industrial wastewater is oxidation, ion exchange, adsorption, and filtration [55]; chemical treatment includes various processes, including ozonation, coagulation, flocculation and chemical oxidation [56]. The biodegradation process occurs naturally through various microorganisms found in wastewater [57] and enzymes [58].

The motivation of this study is to examine the decolorization of reactive dyeing wastewater generated in the industry as one of the four important stakeholders (consumers, retailers, industry, and policymakers) for a more sustainable textile production by various methods. In this context, the decolorization of dyeing wastewater with NBs, as a new water technology, and enzymes, as a completely environmentally friendly technology, were examined. The effects of the decolorization processes on the wastewater of the dyeings carried out in three different shades with different colors were evaluated by transmittance measurements. Chemical oxygen demand measurements of some bathrooms were used to analyze decolorization methods from an environmental perspective.

2. MATERIAL AND METHOD

2.1 Material

The hydrogen peroxide (H_2O_2 -50%) used in decolorization has a concentration of 50% and was obtained from Akkim. Sodium hydroxide (NaOH) and acetic acid (CH_3COOH) were also obtained from the same company. Two different enzymes used for decolorization, laccase (Novalite Cold) and peroxidase (Denilite Cold), were purchased from Alfa Kimya. It has been suggested that laccase should be used at pH 4.5–5.5 at 65°C–70°C and peroxidase at pH 4.5–5 at 20°C–55°C. Names and content of dyes are given in Table 1. Everzol, which was one of the reactive dyes, was obtained from İlteks Boya ve Kimyevi Maddeler San. ve Tic. A.Ş. (Istanbul, Turkey), Synazol and Kimsoline from Eksoy Kimya (Adana, Turkey) and Itofix from İTK Tekstil Kimya Ltd. Şti. (Istanbul, Turkey).

Nanobubble generator was obtained from BSTWATER company. In the generator, the air flow was 3 L/min, the water flow was 5 m³/hour, the water pressure was 2-2.2 bar and the air pressure was 7-8 bar. Air and water flow rates were controlled by flowmeters, and air and water pressures were controlled by manometers.

2.2 Method

The temperature-time diagram of the reactive dyeing of cotton products is given in Figure 1, and that of the reactive washing process is shown in Figure 2.

Composite wastewater samples (C) were prepared by taking 10 ml from each of the dyeing bath and subsequent washing baths, that is, the ratio of each bath in the composite sample was 12.5%. The decolorization processes applied to these composite samples were nanobubbles (NBs) and nanobubbles+enzymatic (NBs-E) processes. In the NBs process, composite samples were passed through the NB generator at 30' (NBs-30'), 60' (NBs-60') and 90' (NBs-90'). NBs-E decolorization of the composite wastewater samples prepared by passing 60 minutes through the NB generator was performed with laccase (NBs-E-L),

peroxidase (NBs-E-P) and hydrogen peroxide+peroxidase (NBs-H₂O₂-E-P). In the NBs-E-L and NBs-E-P processes, laccase and peroxidase enzymes were added at the concentrations of 1 g/L, 2 g/L and 4 g/L to NBs-60' and composite wastewater sample baths whose pH was adjusted to 4.5 with acetic acid. These baths were treated with laccase and peroxidase enzymes for one hour at 65°C and 50°C, respectively. The only difference of the NBs-H₂O₂-E-

P from the NBs-E-P was the addition of 3g/L H₂O₂ to the baths as well as the enzyme. For comparison, all decolorization processes were performed with the addition of enzymes/hydrogen peroxide at similar concentrations to the composite sample without NBs applied (C-E-L, C-E-P, C-H₂O₂-E-P). Wet treatments were carried out in ATAC HT-16 sample dyeing machine at a liquor ratio of 50:1.

Table 1. Details of colors

Color	Shade	Content of the color	% Dye conc.
Fuchsia	Light	Synazol Red HF-3B Kimsolin Red HF 6BN %150 (Reactive Red 195)	0.032
Navy blue		Everzol Yellow ED-R Everzol Red ED7BN Everzol Navy ED (Reactive Blue 222)	
Green	Medium	Synazol Yellow HF 4 GL %150 (Reactive Yellow 160) Synazol Blue K BR Itifix Turq Blue G (N) 266% (Reactive Blue 21)	1.64
Purple		Everzol Yellow ED-R Everzol Red ED-3B (Reactive Red 195) Everzol Blue L-ED (Reactive Blue 221)	
Red	Dark	Everzol Yellow ED-R Everzol Red ED-3B (Reactive Red 195)	2.97
Blue		Everzol Yellow ED-R Everzol Red ED7BN Everzol Navy ED (Reactive Blue 222)	
Black		Everzol Yellow ED-R Everzol Red ED7BN Everzol Black ED-G	2.66

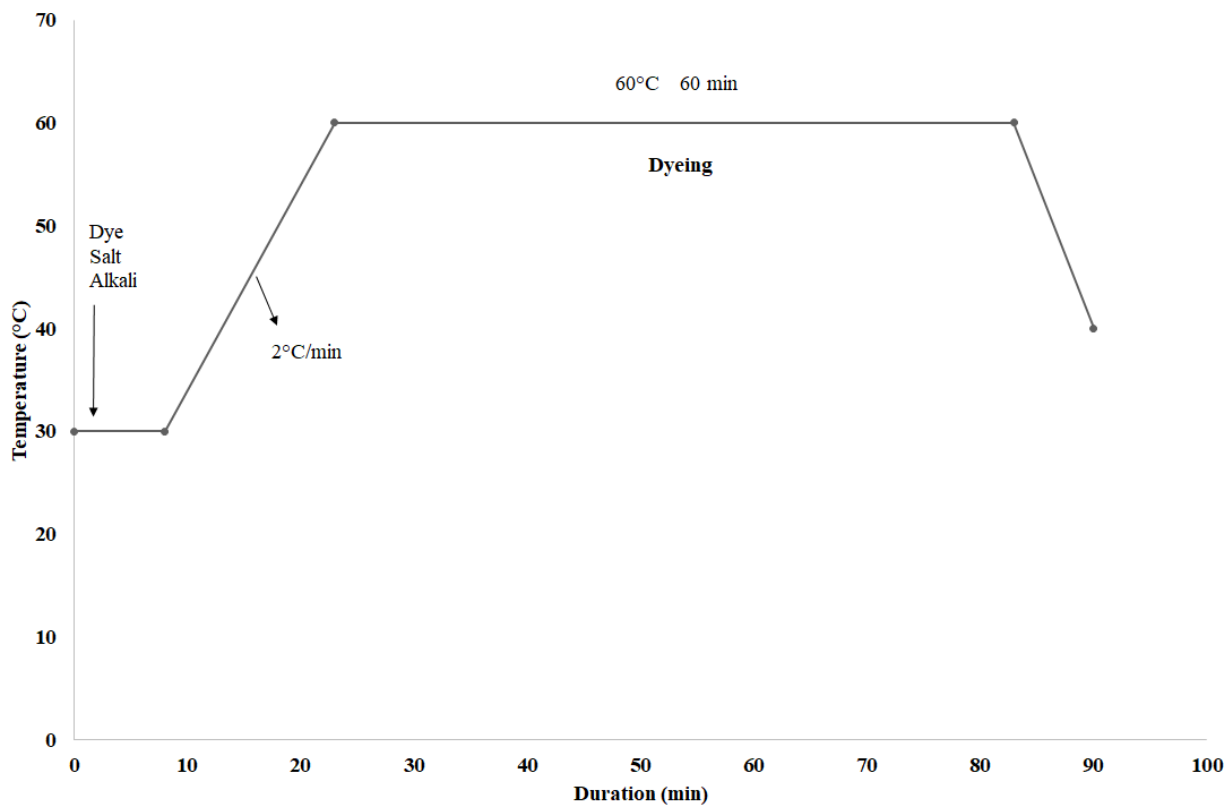


Figure 1. Temperature-time diagram of reactive dyeing

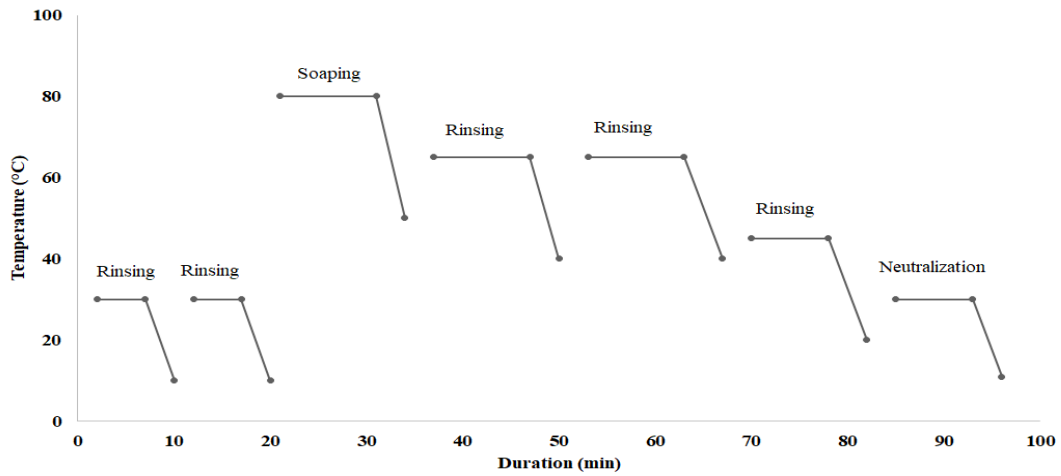


Figure 2. Temperature-time diagram of reactive washing

The transmittance measurements of the samples after decolorization processes were measured in the wavelength range of 400-700 nm using the Datacolor 800 L spectrophotometer. Measurements were recorded at 5 nm intervals. The differences between the transmittance values of the baths were calculated according to Equation (1).

$$\% \Delta T = [(T_2 - T_1) / T_1] \times 100 \quad (1)$$

In this equation, T_1 and T_2 were transmittance values before and after decolorization processes, respectively.

Chemical oxygen demand (COD) measurements of some wastewater samples after decolorization processes were conducted using Merck Millipore COD cell test, WTW CR 2200 thermoreactor, and photoLab S12 photometer.

3. RESULTS AND DISCUSSION

3.1 Decolorization

3.1.1 Decolorization of light shade dyeings

Transmittance values and baths images of the decolorization processes performed with different methods after the light shade dyeings are shown in Figure 3 and Figure 4, respectively. The wavelengths at which the maximum absorbance values of baths were taken in this study were 520 nm and 410 nm, for fuchsia and navy blue, respectively.

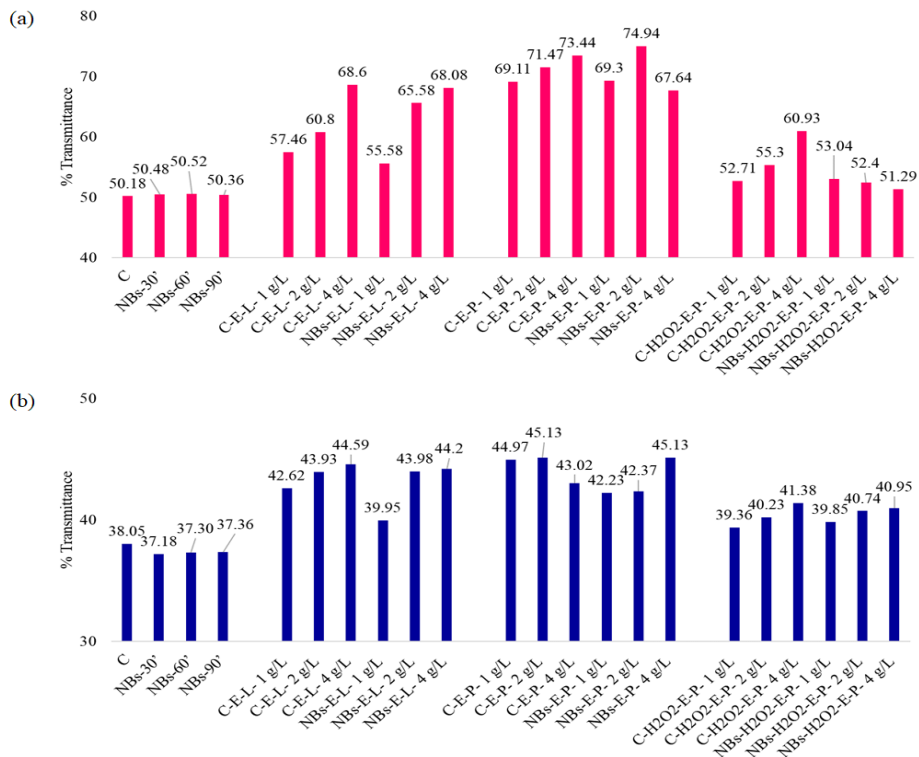


Figure 3. Transmittance values of the decolorization processes of light shade dyeings: (a) fuchsia, (b) navy blue



Figure 4. Images of the decolorization processes of light shade fuchsia (top) and navy blue (bottom) dyeings: (a) NBs, (b) C/NBs-E-L, (c) C/NBs-E-P, (d) C/NBs-H₂O₂-E-P

All of the decolorization methods performed after fuchsia and dark blue dyeing increased the transmittance values compared to the C. The effectiveness of nanobubbles in color removal increased with their use with enzymes. Especially, enzymes increased the transmittance values of the baths in which they were used. Peroxidase enzymes were more effective in color removal than laccases. There was information in the literature that higher decolorization levels were achieved with peroxidases than with laccases [59]. The highest transmittance values were obtained from treatments with peroxidase (C/NBs-E-P-). Hydrogen peroxide added to the decolorization baths along with the

peroxidase enzyme produced lower transmittance than the process in which enzyme was used alone. It was seen that hydrogen peroxide could have inactivated peroxidase enzyme as stated in literature [60,61]. In addition, increasing concentrations of enzymes generally increased bath transmittance. Transmittance values obtained from C-E- and NBs-E- processes were generally similar. Comparison of decolorization by color showed that overall higher transmittance values were obtained from fuchsia compared to navy blue. The color removal effect of enzymes at different level for two colors could have explained by the substrate specificity of the enzymes [62].

It was thought that the chemical structure of fuchsia was more compatible with the substrate on which the peroxidase enzyme was effective. In fuchsia, especially after decolorization with peroxidase, it was observed that the colors of the baths were almost completely removed (Figure 4). The highest transmittance value in fuchsia 74.94 was obtained from the bath treated with 2 g/L peroxidase in the presence of NBs. For dark blue, it was interpreted that NBs could not effective in decolorization, which was evaluated according to transmittance, due to the color shifts that occurred especially after decolorization with NBs-. Overall, 60 minutes would be sufficient for decolorization with NBs.

3.1.2 Decolorization of medium shade dyeings

Transmittance values and baths images of the decolorization processes performed with different methods after the medium shade dyeings are shown in Figure 5 and Figure 6, respectively. The wavelengths at which the maximum absorbance values of baths were 420 nm and 540 nm for green and purple, respectively.

All of the decolorization methods performed after dyeing increased the transmittance values of both colors compared to C. The use of NBs- with enzymes (NBs-E-) on the decolorization efficiency was more effective than the process in which NBs used alone. It has been stated in the

literature that NBs increase enzyme activity because they are very effective in oxygen mass transfer in the liquid phase [63]. It was also thought that the color removal efficiency would be higher if NBs were used with a positive charge[21]. Similar to the decolorization processes carried out with enzymes in light shade dyeings (Figure 3), the highest transmittance values of medium shade dyeings were obtained from the decolorization with peroxidase. This case could have been explained by the substrate specificity of the enzymes [62]. This result suggested that the chemical structure of green and purple were more suitable to the substrate of the peroxidase enzyme compared to those of laccase. Moreover, it was thought that the activity of laccase and even peroxidase could have been further improved in the presence of a mediator [59]. The bath images in Figure 6 showed that NBs/C-E-P 4g/L treated bath had the lowest colorfulness. With hydrogen peroxide+peroxidase (C/NBs-H₂O₂-E-P-), lower transmittance values were obtained compared to the decolorization in which peroxidase (C/NBs-E-P-) was used alone. Hydrogen peroxide could have effected peroxidase by inactivating [60,61]. Increasing concentrations of enzymes generally increased the bath transmittance of both colors. Although, the transmittance data of NBs-E- and C-E- processes were comparable, higher values were obtained from the NBs-E- process than that of the C-E- in the decolorization of green.

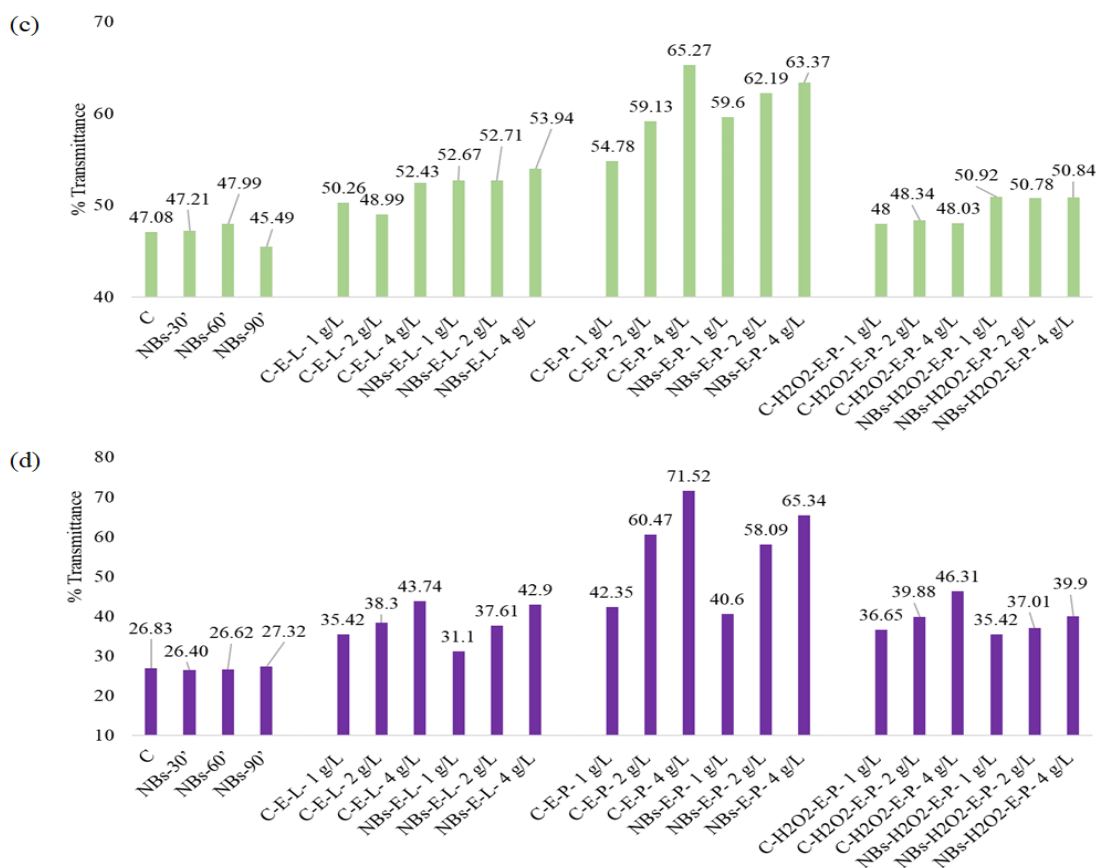


Figure 5. Transmittance values of the decolorization processes of medium shade dyeings: (c) green, (d) purple

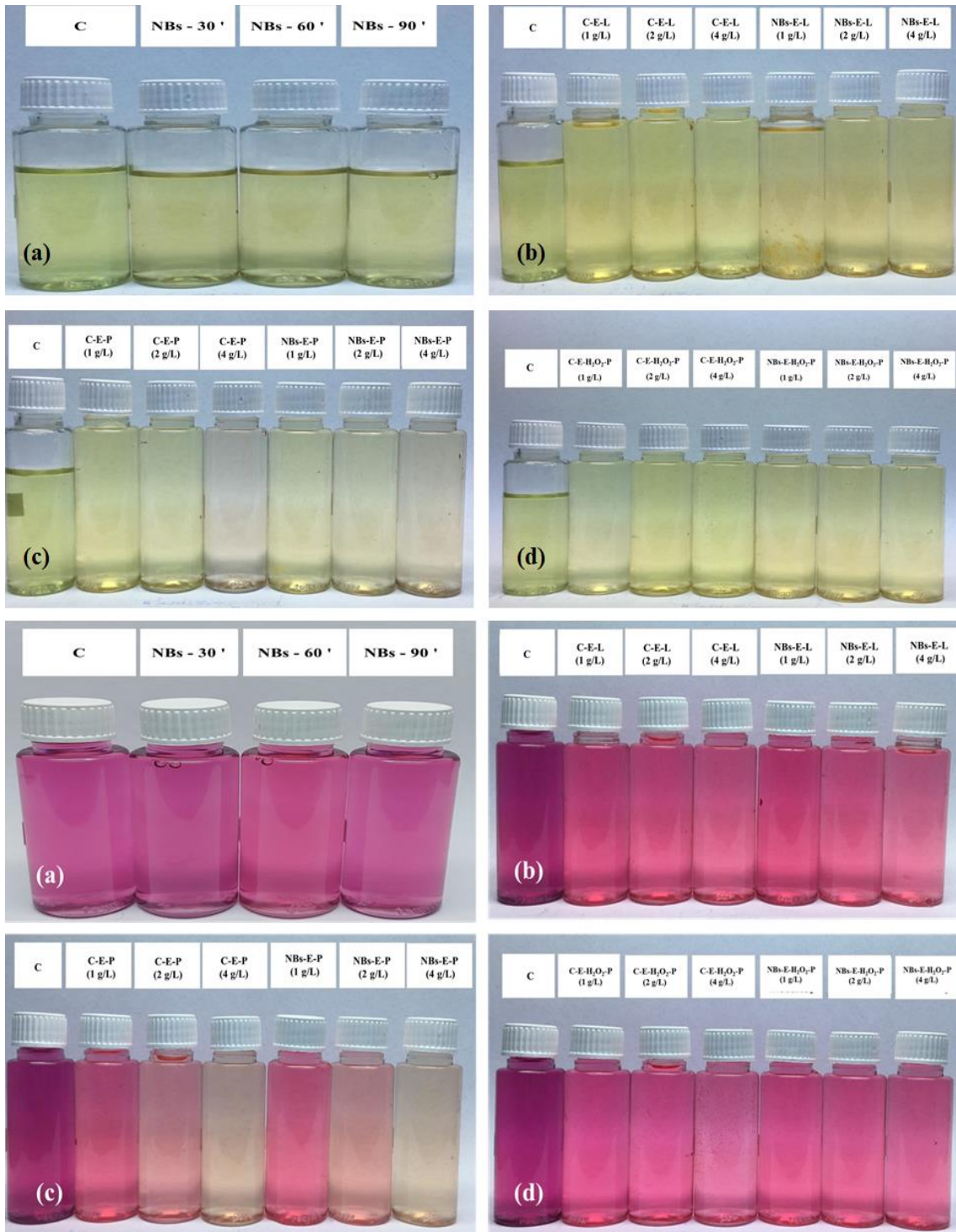


Figure 6. Images of the decolorization processes of medium shade green (top) and purple (bottom) dyes:
 (a) NBS, (b) C/NBs-E-L, (c) C/NBs-E-P, (d) C/NBs-H₂O₂-E-P

3.1.3 Decolorization of dark shade dyes

Transmittance values and baths images of the decolorization processes performed with different methods after the dark shade dyes are shown in Figure 7 and

Figure 8, respectively. The maximum absorbance wavelengths used in transmittance measurements are as follows, according to colors: 590 nm for blue, 420 nm for red, 590 nm for black.

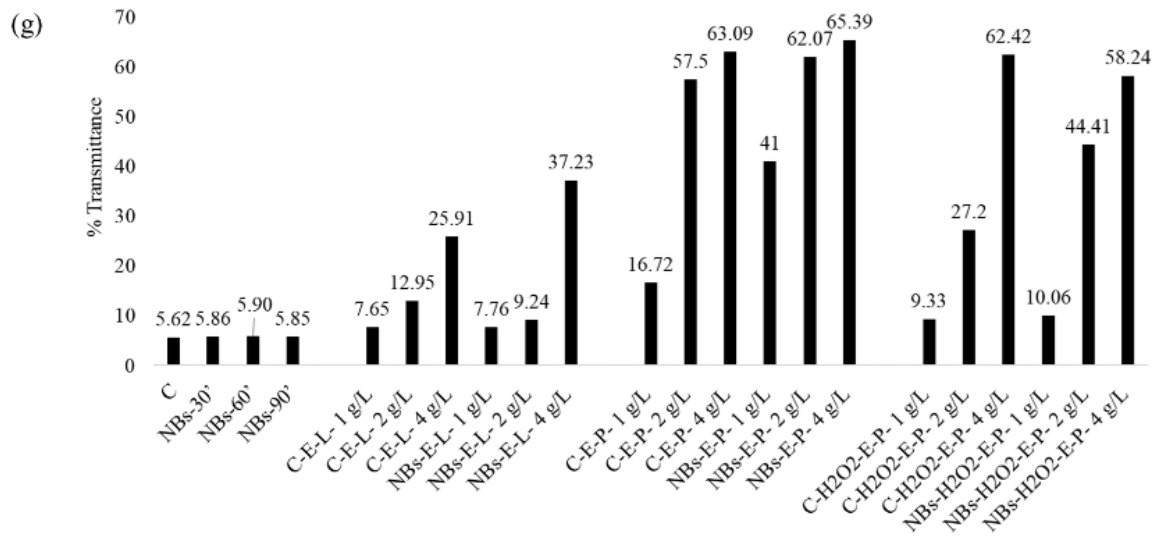
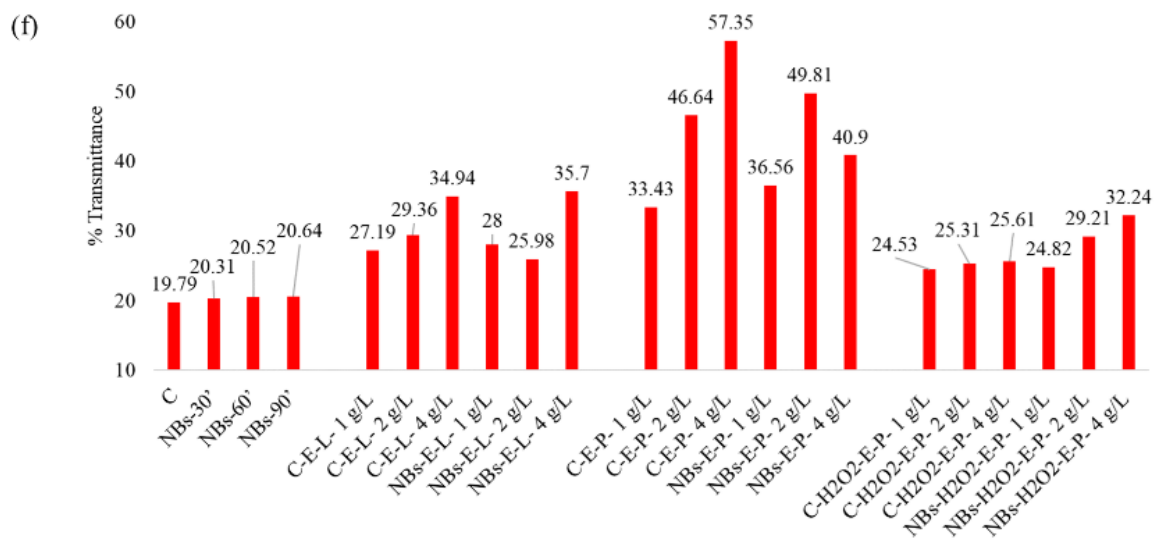
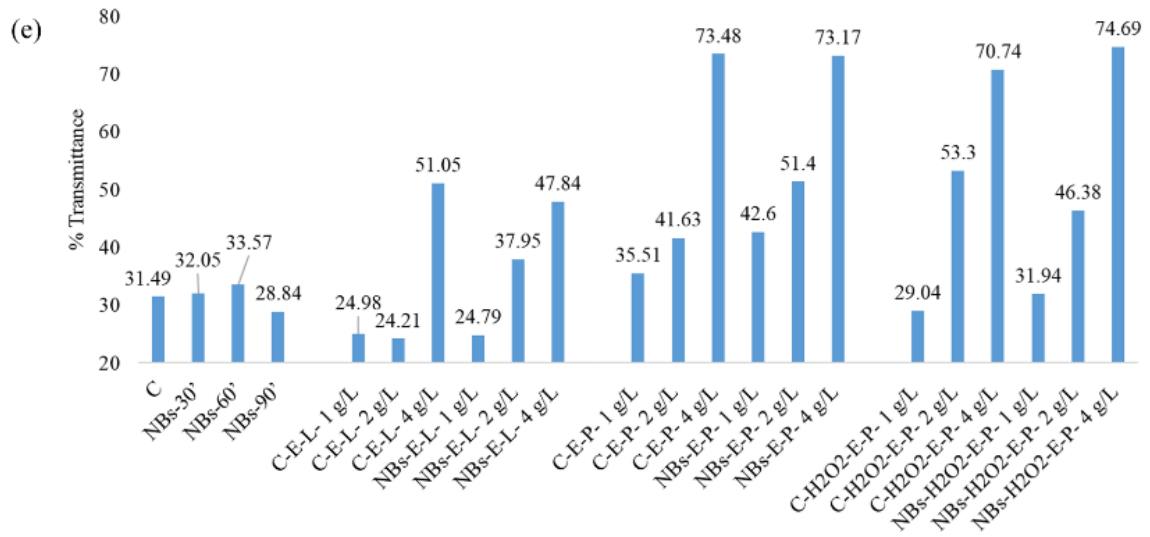


Figure 7. Transmittance values of the decolorization processes of dark shade dyes: (e) blue, (f) red, (g) black



Figure 8. Images of the decolorization processes of dark shade blue (top), red (middle), and black (bottom) dyeings: (a) NBS, (b) C/NBS-E-L, (c) C/NBS-E-P, (d) C/NBS-H₂O₂-E-P

Each of the decolorization methods increased the transmittance values of red and black colors compared to C. The reason why this case was not true for blue color was interpreted as decolorization caused color changes rather than color removing (Figure 8). The decolorization efficiency of NBs when used alone could have been increased by making them positively charged [21]. It was observed that usage of enzymes with NBs (NBs-E-) increased the decolorization efficiency. Since NBs increased enzyme activities, the use of enzymes with NBs provided higher rates of color removal [63]. The highest transmittance values in red and black colors were obtained from decolorization with peroxidase (C/NBs-E-P-) as other shades. The reason for this was thought to be enzyme-substrate compatibility [62]. There was also the possibility that laccase enzyme would provide higher color removal by using it in the presence of mediator [59]. In general, the use of enzymes with hydrogen peroxide adversely affected the activity of enzymes [60,61]. Although lower transmittance values were obtained with C/NBs-H₂O₂-E-P- in red and black compared to C/NBs-E-P-, the highest transmittance for blue was obtained from NBs-H₂O₂-E-P 4 g/L. It was also observed that 60 minutes was the optimum process time for decolorization with NBs.

Overall, except for navy blue and red, approximately 60% - 70% color removal was achieved in C/NBs-E-P- processes at the highest enzyme concentration (4g/L).

3.1 Chemical Oxygen Demand (COD)

COD values of some baths are given in Figure 9. In the COD measurement after decolorization, fuchsia was chosen for the light and black for the dark shade dyeings. In this figure, the COD values of the samples treated with NBs for 60 minutes were examined.

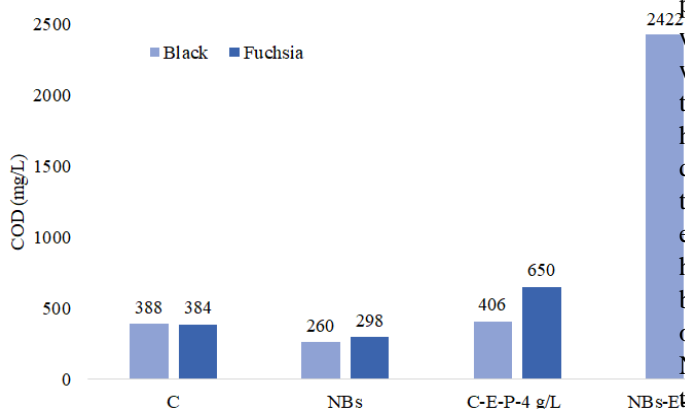


Figure 9. COD values of some decolorization baths

It was determined that the COD values of the wastewater samples (C) obtained after fuchsia and black dyeing were close to each other before they were subjected to the decolorization process. The COD value of the black “C” decreased from 388 mg/L to 260 mg/L after NBs decolorization processes, and that of fuchsia C from 384 mg/L to 298 mg/L. It is known that NBs provide degrading

of organic compounds [64] by producing hydroxyl free radical ($\bullet\text{OH}$) in water [15]. Comparison of dark (5.9 %) and light (50.52 %) shade decolorized with NBs showed that lower COD values were obtained from the dark shade. This could have been explained by the color removal of the dark shade dyeing, that is, the degrading molecules, was lower than the light shade dyeing. The increase in the COD values of the processes in which enzymes were used in decolorization compared to C and NBs was thought to be due to higher decolorization rate. Higher COD values were obtained in the NBs-E-P 4 g/L process compared to that of the C-E-P 4 g/L. Although these decolorization processes had similar decolorization rates, COD values were much higher in the processes using NBs. This could have been interpreted as enzymes whose activities increased with the use of NBs [63] could also cause degradation of numerous chemical structures. It was determined that the lowest COD value was obtained from the black NBs-60' decolorization process.

4. CONCLUSION

In the midst of the worldwide environmental movement towards a more sustainable and greener future, textile, as a completely integrated industry, is one of the focal points with a global market size of 1000.3 billion USD in 2020. Looking at the environmental impacts of the textile industry of this size reveals that wastewater is a major environmental barrier to the growth of the textile industry alongside other minor issues such as solid waste. Textile wet processing requires large quantities of fresh water such that about 50 L to 100 L of water is needed to make 1 kg of textiles. Annual textile production consumes about 93 billion cubic meters of water per year, which is equivalent to total water amount in 37 million olympic swimming pools. Considering the wastewater generated in each textile wet process is highly polluted, it is obvious that textile wastewater poses a great threat to the environment. When textile wastewater is not treated properly, it endangers both human health and the environment. In this article, the decolorization of textile dyeing wastewater with NBs technology, as a new water technology, and environmentally friendly enzymes (laccase and peroxidase) has been investigated. We found that the decolorization behavior of different dyes could be improved with the use of NBs technology as well as enzymes. The effectiveness of NBs in decolorization could have been increased by making them positively charged [21]. Processes using enzymes with NBs were very effective in color removal. These effects could have even been improved with the use of mediators [59]. As enzymes were used in increasing concentrations, their effectiveness in decolorization also increased. Hydrogen peroxide used together with peroxidase did not increase the color removal efficiency; on the contrary, it decreased the effect of the enzyme. It was interpreted as the hydrogen peroxide could have effected negatively peroxidase activity as stated in the literature [60,61]. While

NBs used alone in decolorization caused a decrease in COD values compared to those of the untreated samples, when used with enzymes, COD values increased. This could have been interpreted as a synergistic effect between enzymes and NBs. The use of NBs could have increased the activities of the enzymes [63], caused more molecules to be degraded and thus increased the COD.

In the literature, researchers have proposed various mechanisms related to the role of reactive species and hydroxyl radicals released in solutions on oxidizing dyes, supercritical reactions at the interface of the bubbles, and the degradation of dyes within the bubbles [25,65]. In other words, there are still many issues to be investigated regarding NBs. In the future, it is planned to develop this study in detail on the subjects mentioned below:

There is information in the literature that the highest color removal is achieved with the combined use of NBs with hydrogen peroxide [21]. In the next study, the combination of NBs-hydrogen peroxide will also be examined.

-Since it is known that electrostatic interaction between NBs, whose zeta potential can be controlled (negative or positive), and

dye components is effective on decolorization [66,67], it is planned to examine the effects of adding various surfactants or salts to solutions in future studies.

-It is known that the effect of NBs on decolorization is reduced as a result of rapid bursting due to excessive heat [64]. Since NBs was used with enzymes in this study, decolorization process temperatures were chosen according to the optimum operating temperatures of the enzymes. It was revealed that temperature optimization of decolorization process should also be done in future studies.

- Considering that laccase and peroxidase enzymes generally degrade azo dyes [68], it would be beneficial to select dyes by controlling their structures in future studies.

Acknowledgement

This work was supported by the Scientific and Technological Research Council of Turkey (TUBITAK) under TEYDEB 1505 – 5180061 (Yeni ve Çevreci Teknolojilerin Reaktif Boyama Sonrası Yıkamada ve Atık Suyun Dekolorizasyonunda Kullanımı). The authors wish to thank to TUBITAK.

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