# AN INVESTIGATION ON THE REMOVAL OF ANIONIC AND CATIONIC DYES IN WASTEWATER BY USING SONO-PHOTOCATALYTIC OXIDATION PROCESSES

## SONO-FOTOKATALİTİK OKSİDASYON PROSESLERİ KULLANILARAK ATIKSULARDA ANYONİK VE KATYONİK BOYALARIN GİDERİMİ ÜZERİNE BİR İNCELEME

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*Geliş Tarihi / Received: 16.11.2021*
*Kabul Tarihi / Accepted: 19.12.2021*
*Derleme Makalesi/Review Article*
*DOI: 10.38065/euroasiaorg.908*

## ABSTRACT

Depending on the development of the industry, the problem of clean water caused by wastewater and other environmental problems have emerged. Today, industrialization has increased and environmental pollution has become an important problem. Wastes released into the aquatic medium from various industrial sources disrupt the natural stabilize and adversely affect living things and the ecosystem we live on. Therefore, the removal and treatment of dye wastes in river and lake waters has started to be a important environmental problem. Classical treatment methods are used for the removal of anionic and cationic dye wastes. However, classical wastewater treatment processes are not a good approach in terms of energy efficiency in the removal of dye waste. Sono-photocatalytic process is one of the preferred alternative processes for the removal of anionic and cationic dyes from wastewater. Sono-photocatalytic oxidation process is the simultaneous use of ultrasound waves and ultraviolet radiation with catalyst support as a result of the synergistic effect. The sono-photocatalytic treatment process greatly increases the efficiency of advanced oxidation processes and chemical reaction. The effect of the sono-photocatalytic process is greater than the combined effects of the two processes (sonocatalytic and photocatalytic process).

**Keywords:** Anionic and Cationic Dyes, Ultrasonic Irradiation, UV Irradiation, Hydroxyl Radical, Sono-photocatalytic Oxidation.

## ÖZET

Sanayinin gelişmesine bağlı olarak atık suların neden olduğu temiz su sorunu ve diğer çevre sorunları ortaya çıkmıştır. Günümüzde sanayileşme artmış ve çevre kirliliği önemli bir sorun haline gelmiştir. Çeşitli endüstriyel kaynaklardan su ortamına salınan atıklar, doğal dengeyi bozarak canlıları ve üzerinde yaşadığımız ekosistemi olumsuz etkilemektedir. Bundan dolayı, nehir ve göl sularındaki boya atıklarının uzaklaştırılması ve arıtılması önemli bir çevre sorunu olmaya başlamıştır. Anyonik ve katyonik boya atıkların gideriminde geleneksel arıtım yöntemleri kullanılmaktadır. Ancak boya atıklarının giderilmesinde klasik atıksu arıtma prosesleri enerji verimliliği açısından iyi bir yaklaşım değildir. Sono-fotokatalitik proses, anyonik ve katyonik boyaların atık sudan uzaklaştırılması için tercih edilen alternatif proseslerden biridir. Sono-fotokatalitik oksidasyon işlemi, sinerjik etki sonucunda ultrasonik ses dalgaları ve ultraviyole radyasyonun katalizör desteği ile birlikte kullanılmasıdır. Sono-fotokatalitik arıtma prosesi, ileri oksidasyon proseslerinin ve kimyasal reaksiyonun verimliliğini büyük ölçüde artırır. Sono-fotokatalitik prosesin etkisi, iki prosesin (sonokatalitik ve fotokatalitik proses) toplam etkilerinden daha büyüktür.

**Anahtar Kelimeler:** Anyonik ve Katyonik Boyalar, Ultrasonik Işınlama, UV Işınlama, Hidroksil Radikali, Sono-fotokatalitik Oksidasyon.

## 1. INTRODUCTION

Water pollution is generally defined as the deterioration of the physical chemical and biological properties and appearance of water in the medium. Organic substances that cause water pollution are dyes, drugs, detergents and pesticide waste (Abbassi et al., 2013). Today, the textile dye industry is one of the industrial sectors that use the most water. The textile industry produces wastewater containing dyestuffs and non-degradable substances (Bizani et al., 2006). Waste water produced by the textile dye industry creates hazardous environmental problems. Despite the use of modern technologies, the textile dye industry has the highest share among the industries that consume the most water and produces excessive amounts of wastewater (Kansal et al., 2009). Some wastewaters contain non-biodegradable dyestuffs. Industries that produce such wastewater include the textile, food and dye industries (Sidiras et al., 2011). The dyestuff wastes have undesirable effects in the environment where they are discharged. Due to their complex aromatic structure, they cause toxic and carcinogenic effects (Polat, 2010). In receiving waters, colored wastewaters prevent the transition of sunlight, harmful the living environment and also cause odor and visual pollution (Rida et al., 2013).

Wastewaters containing dyestuffs cause hazardous ecological problems in receiving environments even at very low concentrations. For this reason, in order to prevent the negative effects of dyestuffs on the environment, they must be treatment from wastewater before they are discharged into receiving environments (Arenas et al., 2017). Physical and chemical methods used for dye removal are electrochemical methods, filtration, flocculation, coagulation, adsorption, chemical oxidation. These methods have low removal efficiency in the degradation of dye wastes (Walker et al., 2003). In recent years, sono-photocatalytic (US/UV/Catalytic) process has become popular among advanced oxidation processes for the removal of dyes from wastewater. This process produces more hydroxyl radicals in the solution medium due to the synergistic properties of both the sonocatalytic effect and the photocatalytic effect (Danwittayakul et al., 2013). Photocatalytic oxidation is preferred because of it is effective advantages over other processes, high oxidation ability, applicable technology for removing dye wastewater and low cost parameters (Beata, 2017). The sono-photocatalysis treatment process which is preferred by researchers today, is the process with the highest removal efficiency of dye wastes among advanced oxidation processes. This hybrid process (sonolytic and photolytic) decrease the need to use physical conditions during oxidation (Lianga et al., 2017). The sono-photocatalytic oxidation process contributes to the efficiency of the degradation reactions of dye wastes by solving the problems related to the effect and surface area of the catalyst support compared to individual processes such as sonocatalytic and photocatalytic (Anju et al., 2012; Lianga et al., 2017).

### 1.1. Anionic and Cationic Dye Wastes

Dye molecules consist of two important components, auxochromes and chromophores which are responsible for color production. Anionic and cationic dyes can be classified according to their solubility, chemical structure and application areas due to their structural differences (Salleh et al., 2011). The dyes used in the textile industry are acid dyes, basic dyes, direct dyes, disperse dyes, reactive dyes and sulfur dyes (Paz et al., 2017). Dyestuffs connect to the surface on which they will give color by different physical interactions. These bonds; hydrogen bonds, Van der Waals and coordination bonds. In other cases, they interaction chemicaly with the covalent bonds (Marin et al., 2019).

Dyes are classified as cationic (basic), anionic (acid, direct and reactive) and non-ionic dyes (disperse) according to the application method (Li et al., 2011). Cationic dyes are substances that dissolve in water and give off positively charged ions (cations) to water when dissolved. The cationic property is found in the various types of dyes, especially the cationic azo dyes anthraquinone and solvent dyes (Khouni et al., 2020). Cationic dyes in acrylic, nylon and silk dyeing widely preferred. In addition to the toxic effect of this dye group they cause allergic derm inflammation, mutation and cancer (Ratnamala et al., 2012). Anionic dyes are substances that give off negatively charged ions when dissolved in water. The main classes of these dyes are triphenylmethane, nitro and azo dyes (Yagub et al., 2014). Anionic dyes are used in the polyamide, modified acrylic and polypropylene fibers. As they are organic sulfonic acids they cause harmful effects on humans (Ngulube et al., 2017). Non-ionic (disperse) dyes are insoluble in water. The basis of disperse dyes are benzodifuranone, nitro, styryl and azo dyes. Disperse dyes are used on the cellulose acetate, acrylic and cellulose fibers (Katheresan et al., 2018).

The textile industry is an effective component that causes hazardous threats to the environment and ecosystem and affects human health due to the discharge of wastewater containing various dye types into natural water resources considered as water pollution (Wong et al., 2019). Dye wastes decrease the transmission of sunlight to water and can reach humans through the food chain by accumulating in the aquatic plants and animals (Solis et al., 2012). In addition, dye wastes can cause functional damage to the kidney, liver, brain and central neural system of people by causing toxic and carcinogenic effects on the aquatic organisms (Singh et al., 2017).

## 2. METHODS

### 2.1. Ultrasonic Irradiation (US)

Ultrasonic irradiation is expressed as a sound wave with a frequency higher than the human hearing frequency. It is known to have a frequency ranging from 15 kHz to 500 MHz (Gholami et al., 2020). Acoustic cavitation is vibration waves that cause chemical and mechanical effects to accelerate the removal of dye wastes in the solution. Acoustic cavitation is formed during the vibration cycle. This process begins when the effect of negative pressure degradation up the water molecules (Adewu-Yi, 2005; Mahvi, 2009). The vibrations of acoustic cavitation result in the nucleation, growth and violent collapse as a result of chain reactions of gas filled microbubbles produced during compression cycles in solution (Pang et al., 2011).

Both the permanent and temporary bubbles are formed during ultrasonic cavitation. Both of these bubbles contribute to the chemical effects of ultrasonic cavitation (Kim et al., 2018). The dyestuffs in wastewaters can be oxidized by the energy and radicals released during the formation and destruction of bubbles caused by cavitation (Zhang et al., 2018). The reactions that take place during acoustic cavitation take place inside the bubble, at the bubble and solution interface and in the aqueous solution (Zhu et al., 2013). At high temperatures and with the help of oxygen dissolved in the aqueous solution dye molecules can be degradation (Song et al., 2012). Although molecules with high volatility are degradation directly in the bubble by cavitation, molecules with low volatility are not degradation in the bubble. These molecules are indirectly degradation as a result of their reaction with the radicals formed during cavitation (Yin et al 2011).

### 2.2. Ultraviolet Irradiation (UV)

Ultraviolet (UV) irradiation is a process that has a important effect on the treatment of dyes from wastewater. This process involves using light of the appropriate wavelength and transmits photons of light to ensure the removal of unwanted dye waste (Santos et al., 2016). The wavelength range of the UV spectrum is generally considered to be between 100 and 400 nm. Ultraviolet irradiation is generally examined in 3 groups. These groups are UV-A (315-380 nm), UV-B (280-315 nm) and UV-C (200-280 nm) irradiation (Kıranşan et al., 2015). Processes involving the interaction between dye wastes that cause chemical reactions by interacting with UV light are called photochemical reactions (Rong et al., 2015). Photochemical oxidation has approved to be an effective removal method in wastewater treatment systems, especially for the treatment of the complex molecules and dye wastes (Yang et al., 2016). Photochemical UV irradiation is divided into two different reactions, direct and indirect irradiation. Direct irradiation includes photon absorption by dye waste previous to any photochemical reaction (Nasirian et al., 2018).

## 3. RESULTS AND DISCUSSION

### 3.1. Sonocatalytic Oxidation Process

The realization of chemical reactions with the help of cavitation bubbles of the ultrasonic irradiation is named sonochemistry. Pressure and temperature are extremely high during ultrasonic cavitation reactions. This pressure and temperature can reach 1000 atm and 5000 K (Mason et al., 2011). As a result of events occurring under high temperature and pressure, water molecules and oxygen transform into effective radical species such as the hydrogen and hydroxyl radicals (Balachandran et al., 2016). Pyrolysis and radical reactions that occur as a result of the acoustic cavitation vibrations increase the efficiency of sonochemical degradation (Eqs. (1-5)) (Yashas et al., 2020).

$$H_2O + ))) \rightarrow \bullet OH + \bullet H \quad (1)$$

$$O_2 + ))) \rightarrow 2\ \bullet O \quad (2)$$

$$\bullet OH + \bullet OH \rightarrow H_2O + O\bullet \quad (3)$$

$$\bullet OH + H_2O \rightarrow H_2O_2 + H\bullet \quad (4)$$

$$H\bullet + \bullet OH \rightarrow H_2O \quad (5)$$

The sonochemical reaction mechanism of dye wastes is mainly carried out by thermal decomposition in the cavitation bubble and the formation of free radical reaction in the solution (Yap et al., 2019). There are many factors that affect the sonocatalytic cavitation and therefore the amount of reagents from ultrasound. Sonocatalytic reactions are affected by solution temperature, dissolved gases, ambient pressure and frequency of ultrasonic sound (Soltani et al., 2019). Reaction temperature is another parameter that affects ultrasonic cavitation. The effect of sonochemical reaction temperature on ultrasonic cavitation causes more bubbles to form as a result of speedy evaporation of the solvent with the increase in the vapor pressure (Diehl et al., 2018). It has been reported that increasing the temperature decreases the sonochemical reaction effect (Jun et al., 2020). The schematic representation of the sonocatalytic oxidation process is shown in Fig. 1.

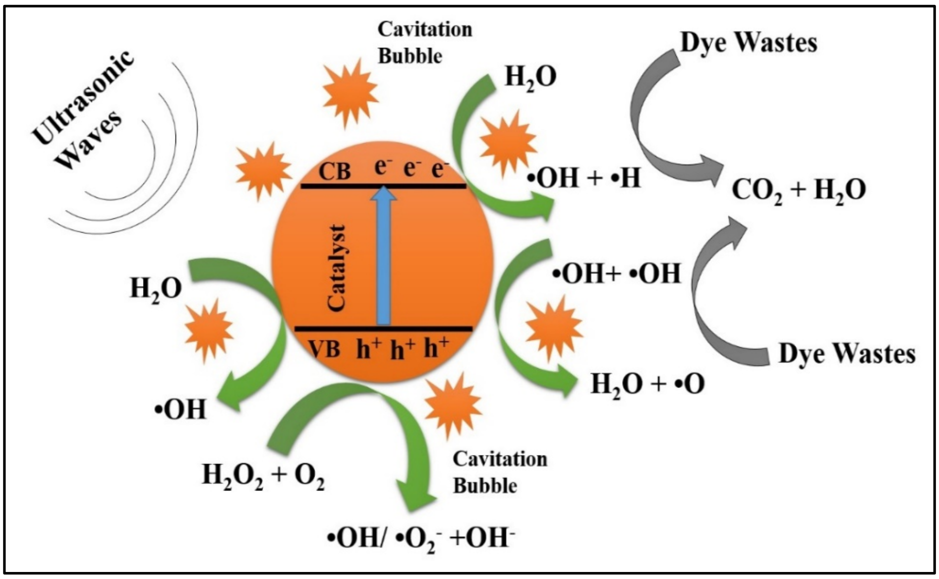


**Figure 1.** Schematic representation of the sonocatalytic oxidation process (Zhang et al., 2019).

It is known that the removal and degradation efficiency can be increased by adding different catalysts to the sonolytic oxidation process (Kim et al., 2018). The addition of an appropriate amount of catalyst (heterogeneous catalyst or hybrid catalyst) provides the formation of weak regions in aqueous solution, especially at the liquid-solid interface for nucleation of cavitation bubbles (Jorfi et al., 2018). These regions increase the rate of formation of bubbles, thus increasing the amount of radicals formed in the solution and increasing the removal and degradation efficiency of dye wastes (Khataee et al., 2015).

### 3.2. Photocatalytic Oxidation Process

Dye molecules (Dye) excited by photons of light are converted to the higher potential energy excited to the state (Dye*) by direct irradiation. Then the excited dye molecules can release the absorbed energy and return to the ground state or transform into intermediates by photochemical reactions (Soutsas et al., 2010). Photochemical oxidation reactions cause dye molecules to return into basic and harmless products such as $CO_2$ and $H_2O$ (Eqs. (6-9)) (Mukherjee et al., 2017).

$$\text{Dye} + \text{UV Light (A-B-C)} \rightarrow \text{Dye*} \quad (6)$$

$$\text{Dye*} \rightarrow \text{Dye} \quad (7)$$

$$\text{Dye *} \rightarrow \text{Intermediates (Radicals)} \quad (8)$$

$$\text{Intermediates} \rightarrow \text{Products} + CO_2 + H_2O \quad (9)$$

When a photocatalyst interaction with light of a certain wavelength, the energy of the photons transfers electrons from the valence band to the conduction band (Barzegar et al., 2019). In this process, an energy band gap ($h^+$) is formed in the valence band. This difference in load is one of the first important steps of the photocatalytic reaction. The electron double and holes formed come back together and give off the energy as heat to the environment (Eqs. (10-13)) (Khataee et al., 2017).

$$\text{Photocatalyst} \rightarrow e^-_{CB} + h^+_{VB} \quad (10)$$

$$e^-_{CB} + h^+_{VB} \rightarrow \text{Isı} \quad (11)$$

$$h^+_{VB} + H_2O \rightarrow OH^\bullet + H^+ \quad (12)$$

$$h^+_{VB} + OH^- \rightarrow OH^\bullet \quad (13)$$

As a result of these reactions, the risk of electron/hole double recombining and lose their activity is eliminated. As a result of photocatalytic and photochemical reactions on the catalyst surface, reactive hydroxyl radicals (OH•) are formed (Eqs. (12-13)) (Khataee et al., 2017). The schematic representation of the photocatalytic oxidation process is shown in Fig. 2.

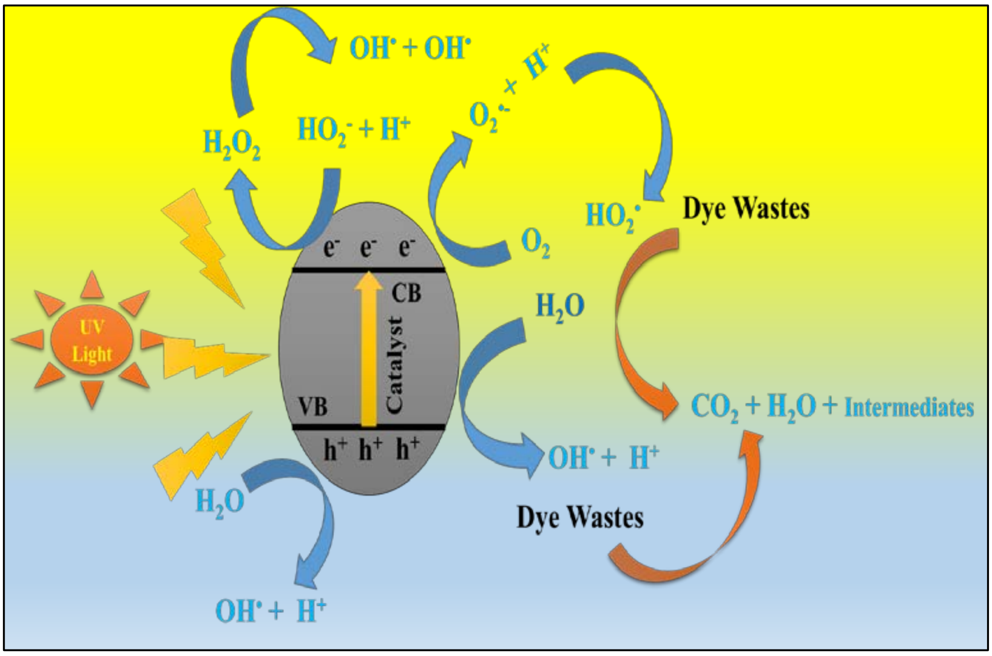


**Figure 2.** Schematic representation of the photocatalytic oxidation process (Roongraung et al., 2020)

As a result of photocatalytic reactions, superoxide ion radical reactions with water and reactive anions such as $O_2^{\bullet-}$, $HO_2^{\bullet}$, $HO_2^{-}$ are formed in the solution ambient (Eqs. (14-16)) (Sharma et al., 2018).

$$H^+ + O_2^{\bullet-} \rightarrow HO_2^{\bullet} \quad (14)$$

$$HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (15)$$

$$HO_2^{\bullet} + O_2^{\bullet-} \rightarrow O_2 + HO_2^{-} \quad (16)$$

### 3.3. Sono-Photocatalytic Oxidation Process Applications of Dye Wastes Removal

The sono-photocatalytic oxidation process is a hybrid sonolytic and photolytic process with catalyst support to increase the removal efficiency of dye wastes (Dinesh et al., 2016). The primary purpose of advanced oxidation processes is to decrease the treatment cost of the industrial wastes and to make dye wastes more harmless (Bahena et al., 2008). In order to make sono-photocatalytic oxidation more effective, there are three reasons that affect the mass transfer of dye wastes in the liquid phase. These reasons are the increase of hydroxyl radical (·OH) production, the formation of cavitation bubbles with the support of catalyst particles and catalyst surface (Hayati et al., 2020). The reaction rate is increased by the combination of the double effect of these two radiations (UV and ultrasound). Hydrogen peroxide is formed by the combining sonolysis with photocatalytic oxidation (Eqs. (17-20)) (Karim and Shriwastav, 2020).

$$H_2O \rightarrow)))) \rightarrow OH^{\bullet} + H^{\bullet} \quad (17)$$

$$H_2O_2 + H^{\bullet} \rightarrow H_2O + {}^{\bullet}OH \quad (18)$$

$$H_2O_2 + hv \rightarrow 2\ {}^{\bullet}OH \quad (19)$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow {}^{\bullet}OH + OH^{-} + O_2 \quad (20)$$

In the hybrid sono-photocatalytic reaction, the adsorption of dye contaminants to specific centers on the surface happened and the step that controls the reaction rate will be an important increase in the number of ultrasound active centers (Hapeshi et al., 2013). The schematic representation of the sono-photocatalytic oxidation process is shown in Fig. 3.

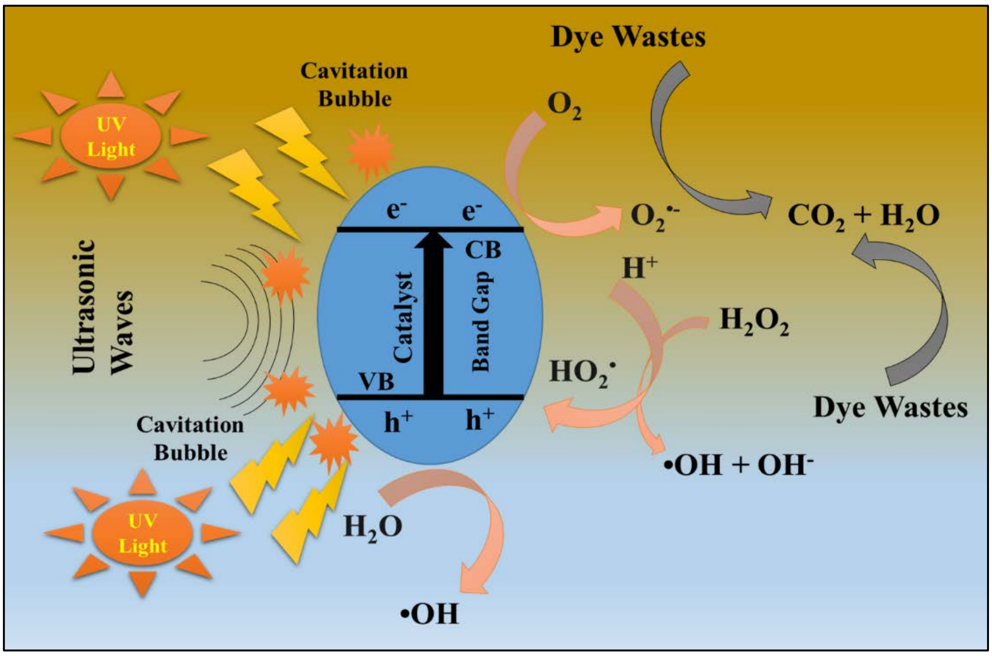


**Figure 3.** Schematic representation of the sono-photocatalytic oxidation process (Jorfi et al., 2018).

At the same time, under the turbulent conditions formed, the catalyst depending on the effect, suitable surface areas are created and increases suitable to the diffusion rates of dye wastes are observed (Xu et al., 2013). Applications of removal of the different dye pollutants by using sono-photocatalytic oxidation processes are given in Table 1.

**Table 1.** Applications of removal of the different dye pollutants by using sono-photocatalytic oxidation processes.

| Hybrid Process | Pollutants of Dye | Catalyst | Removal Efficiency | References |
|---|---|---|---|---|
| Sono-photocatalytic Oxidation (US/UV) | Direct Blue 71 (DB-71) | ZnO (Zinc Oxide) | ~100% | (Ertugay and Acar, 2014) |
| Sono-photocatalytic Oxidation (US/UV) | Methylene Blue (MB) | $NiMoO_4$ Nanosheets | 98.00% | (Dhanasekar et al., 2017) |
| Sono-photocatalytic Oxidation (US/UV) | Reactive Black 5 (RB-5) | $TiO_2$ | ~99.00% | (Kritikos et al., 2007) |
| Sono-photocatalytic Oxidation (US/UV) | Reactive Blue 19 (RB-19) | $TiO_2$ | 55.00% | (Siddique et al., 2014) |
| Sono-photocatalytic Oxidation (US/UV) | Basic Blue 9 (BB-9) | $TiO_2$ | 80.00% | (Gonzalez and Martínez, 2008) |
| Sono-photocatalytic Oxidation (US/UV) | Acid Yellow 23 (AY-23) | ZnO, Fe/ZnO Composite. | 98.00% | (Dinesh et al., 2016) |
| Sono-photocatalytic Oxidation (US/UV) | Acid Blue 113 (AB-113) | ZnO/Persulfate | 98.70% | (Asgari et al., 2020) |
| Sono-photocatalytic Oxidation (US/UV) | Acid Red 88 (AR-88) | $TiO_2$ | 45.00% | (Madhavan et al., 2010) |
| Sono-photocatalytic Oxidation (US/UV) | Brilliant Green | ZnO and CuO | 94.80% | (Gole et al., 2017) |
| Sono-photocatalytic Oxidation (US/UV) | Methyl Orange (Me-O) | $TiO_2$ | 91.50% | (Cheng et al., 2012) |
| Sono-photocatalytic Oxidation (US/UV) | Rhodamine 6G (Rh-6G) | $CuO/TiO_2$ | 63.30% | (Bokhale et al., 2014) |

## 4. CONCLUSION

As a result, the presence of a small amount of dye wastes in the water causes a toxic effect on aquatic organisms. It is very important to control the color removal and water quality in the wastewater where dye wastes can be seen at a high rate. Even a very small dye concentration, which can add important color to drinking water, is not suitable for human consumption. Removal of dyes from wastewater is an important environmental activity, not only in terms of the environment but also in terms of human health. Since the removal of dyes from wastewater is seen as an environmental problem and textile wastewater needs to be treatment, there is a need for hybrid methods that can effectively remove these dye wastes.

As a result of the hybrid effect of ultraviolet irradiation and ultrasonic irradiation, the sono-photocatalytic process is a method preferred by researchers over other advanced oxidation processes for removing dyes from wastewater. The sono-photocatalytic process can be designed and implemented as a pre-treatment step due to non-biodegradable and non-selective reactivity of dye residues. The combination of heterogeneous sonocatalytic and photocatalytic is assumed to be one of the most promising processes for completing the mineralization processes of dye wastes with high efficiency.

## ACKNOWLEDGMENTS

The authors would like to express special thanks to the University of Gumushane for supports.

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