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Usage of titanium nanomaterial for the decolorization of Methylene blue and Reactive Red 198 dyes by sonocatalysis

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ABSTRACT

The aim of this study was to use non-modified nano titanium dioxide (TiO_2) material to develop the sonocatalytic decolorization of Methylene blue (MB) and Reactive Red 198 (RR198) in aqueous solutions. The study is highlighted by the pH_{pzc} value of nano TiO_2. Electrostatic attraction or repulsion can occur due to anionic (RR198) and cationic (MB) dyes. The maximum sonocatalytic decolorization efficiency (%) of 95% for MB and 81% for RR198 were achieved with an initial dye concentration of 100 mg L^{-1}, a sonocatalyst dosage 0.25 g L^{-1} (MB) and 0.1 g L^{-1} (RR198), an initial pH of 6.55, ultrasonic power of 90 W and ultrasonic frequency of 53 kHz. The thermodynamic parameters showed that the process was feasible and exothermic. In addition, the usage of non-modified TiO_2 particles was found to be a feasible choice and give satisfactory results for the removal of aniline (cationic) and azo (anionic) dyes without the requirement of highly expensive modified methods.

Keywords: Methylene blue; Nano titanium dioxide; Reactive Red 198; Sonocatalysis

1. Introduction

The usage of dyes in different industries, such as the cosmetic, textile, chemical processing, food and dye industries, causes water pollution, particularly aesthetic pollution [1]. Dyes have a complex composition and are toxic and non-biodegradable [2]. A small amount of dye (<1 mg L^{-1}) is the leading visible color and pollution in water bodies instead of other colorless organic pollutants [3]. Therefore, the removal of dyes from aqueous environments is crucial. Various methods are used to remove dyes such as conventional treatment methods, physicochemical methods and biological methods. Despite physicochemical systems decolorization success, it has a number of problems with organic matter (carbon) removal. Studies have shown that biological systems are good for the removal of organic matter. However, questions have been raised about the biological systems such as colors are resistant to the microbial system.

In recent years, the usage of advanced oxidation processes (AOPs) for the removal of pollutants has sparked great interest. The reactive radicals ($OH^{\bullet}$, $O_2^{\bullet}$) can rapidly decolorize the dye molecules as a result of the production of these radicals by AOPs. The most commonly used AOPs are sonocatalysis, photocatalysis, sonolysis, ozonation and Fenton [4–9].

In the last decades, sonocatalysis has been widely taken great attention from AOPs, which can be used under mild operative conditions. With the sonocatalysis process, as a result of cavitation, microbubbles collapse, grow and produce free radicals, that is, $OH^{\bullet}$ and $OH^{\bullet}$ [10,11]. These radicals can transform less harmful pollutants and mineralize

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carbon dioxide and water [12]. In sonocatalysis, the presence of a solid catalyst provides more sites for cavitation and accelerates the reactions. Many sonocatalysts have been investigated in order to improve the catalytic activity by increasing the formation rate of cavitation bubbles [13]. Owing to its morphology and structure, titanium dioxide (TiO_2) is the most widely used as a sonocatalyst and it was found that its sonocatalytic activity is influenced [9].

In this study, TiO_2 nanoparticles were used for the sonocatalytic degradation of an azo dye, namely Reactive Red 198 (RR198), and a basic aniline dye, namely Methylene blue (MB). Factors influencing the performance of the degradation process, such as nano TiO_2 dose, solution pH, power density and ultrasonic frequency were investigated. The thermodynamic study has been also investigated.

2. Materials and methods

2.1. Materials and catalyst specifications

The TiO_2 anatase (anatase >99%, crystalline size 10 nm) was purchased from Ege Nanotek Kimya Sanayi (Turkey). The physical and chemical properties of the TiO_2 are shown in Table 1. The MB ($C_{16}H_{18}ClN_3S$), NaOH, H_2SO_4 and H_2O_2 were purchased from Merck (Germany). The RR198 ($C_{27}H_{18}ClN_7Na_4O_{16}S_5$) was procured from Eksoy Kimya Sanayi ve Tic. A.Ş. (Turkey). All of the chemicals were used as received without any further purification. All solutions were prepared using ultrapure water from a Milli-Q synthesis unit (Millipore, Germany).

2.2. Analysis and experimental procedure

A stock solution of dye was prepared using 1 g of dye dissolved in 1 L of distilled water. Dye solution of known concentration was prepared in distilled water, mixed appropriate amount of TiO_2 and dispersed in the ultrasonic reactor. The pH of the dye solution was adjusted using either H_2SO_4 or NaOH. The experimental procedure is given in detail in the previous study of Basturk and Karatas [14,15]. The residual dye concentrations were measured using a UV-Vis spectrophotometer (UV-1280, Shimadzu, Japan). During the course of a reaction, 1 mL of the dye samples was withdrawn using a micropipette, centrifuged and filtered to ensure the catalyst removal from the dye solution. The absorbance measurements were conducted with a maximum dye absorbance wavelength (λ_{max}) of 520 nm for RR198 and 664 nm for MB. The model solution was sonicated indirectly ultrasonic bath at a frequency of 35 and 53 kHz and 90 W ultrasonic power (KUDOS SK2210LHC Model). The characteristics of the selected dyes are shown in Table 2.

Table 1
Physical and chemical properties of nano titanium dioxide (TiO_2)

Purity	%99
Particle size	10 nm
Surface area	200 $m^2\,g^{-1}$
Color	White
Morphology	Spherical
Density	4.23 g cm^{-3}
Density (bulk)	0.06–0.10 g cm^{-3}

3. Results and discussion

3.1. Effect of catalyst dosage

The effect of sonocatalyst dosage on color removal (%) was evaluated in order to avoid an excessive amount of sonocatalyst application. The other operational parameters were set to constant values and the catalyst dosages were 0.05, 0.1 and 0.25 g L^{-1}. The removal efficiencies were 39%, 81% and 96% for RR198 and 21%, 75% and 95% for MB at the different catalyst dosages, respectively (Fig. 1). As can be seen from Fig. 1, the optimum catalyst dosages for RR198 and MB were 0.1 and 0.25 g L^{-1}, respectively. Increasing the catalyst dose increases the active sites on the catalyst surface [16,17], forms more microbubbles [18,19] and increases the $OH^{\bullet}$ and $O_2^{\bullet}$ radicals. Consequently, dye removal is increased [20,21].

As indicated in the literature, an excessive amount of sonocatalyst in the solution can result in the scattering of ultrasound and blocking the transmission of ultrasound waves and energy near to the surface of the sonocatalyst [17,22], which in turn decreases the active sites [23–25] and the removal rate of the sonocatalytic degradation reactions [26]. The increase in catalyst dose (i) causes an increase in the radicals, (ii) the more radicals act as a radical scavenger, (iii) the decrease intensity of the ultrasound waves [27].

Table 2
Characteristic of selected dyes

	Methylene blue	Reactive Red 198
CAS No.	122965-43-9	145017-98-7
Dye type	Basic aniline	Azo
Molecular weight	319.860	984.183
Molecular formula	$C_{16}H_{18}ClN_3S$	$C_{27}H_{18}ClN_7Na_4O_{16}S_5$
λ_{max}	664	520

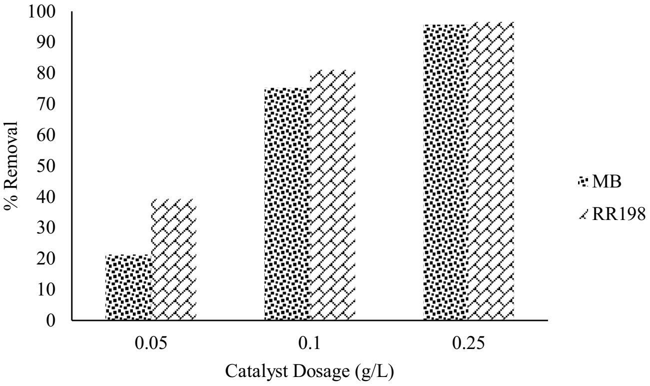

Fig. 1. Effect of catalyst dosage on the selected dyes ([RR198] = 100 mg L^{-1}; [MB] = 100 mg L^{-1}; pH = 6.55 (RR198); pH = 6 (MB); US frequency = 53 kHz; US power = 90 W).

3.2. pH effect

The solution pH value, which plays an important role in the sonocatalytic removal of the dye, is one of the most important parameters. The pH effect is related to the solution of the pH and the pH_{pzc} of the nano TiO_2 particles. In the literature, when the pH value was lower than the pH_{pzc} value, the surface charging of the nanoparticles was positive [28–30]. The TiO_2 was at the point of zero charge (pH_{pzc}) at pH 7.41. Thus, the TiO_2 surface was positively charged in acidic media ($pH < 7.41$) and negatively charged under alkaline conditions ($pH > 7.41$). Electrostatic attraction or repulsion can occur due to anionic (RR198) and cationic (MB) [31] pollutants [21]. The charge of the nano TiO_2 particles according to the pH_{pzc} value is shown Eqs. (1) and (2).

$$\mathrm{Ti^{IV}{-}OH + H^+ \rightarrow Ti^{IV}{-}OH_2^+} \qquad (pH < pH_{pzc}) \qquad (1)$$

$$\mathrm{Ti^{IV}{-}OH + OH^- \rightarrow Ti^{IV}{-}O^- + H_2O} \qquad (pH > pH_{pzc}) \qquad (2)$$

Under acidic conditions, the removal rate is higher at RR198 like as anionic dyes, in contrast, MB (Figs. 2 and 3). The electrostatic repulsion between hydroxide ions and negatively charged catalyst surface at the $pH > pH_{pzc}$. As a result, the removal rate of cationic dyes is higher [17,32]. On the contrary, when the pH value is higher than 7.43 (the pH_{pzc} value of the catalyst) the surface becomes negatively charged and there is an attraction between MB and catalyst surface [19]. Extremely high pH values have been found to be favorable even when anionic dyes hamper adsorption on the negatively charged surface [33].

3.3. Effect of power density and ultrasonic frequency on the decolorization of the selected dyes

In ultrasonic applications, the ultrasonic power dissipation is an important parameter as it affects the cavitational activity and the economic cost of the process is strongly associated with this parameter [34,35]. In addition, the increasing frequency of ultrasonic equipment reduces dye degradation [14]. Increasing the power density increases and the free radicals which accelerate the sonochemical reactions and enhances the removal of dye molecules [36,37]. This is in concordance with that observed in previous results [35,38–41]. The bubble formation increases with an increase in the power dissipation rate, which may lead to the turbulence generated by cavitational bubble collapse as well as micro jetting, in addition to yielding higher numbers of cavitation bubbles and hence higher yields of hydroxyl radicals [39,42,43]. The sonolytic degradation of the selected dyes increased with an increase in the power density of the system. The degradation of RR198 and MB was 21% at a power density of 30 W L^{-1}, 77% at 45 W L^{-1} and 84% at 90 W L^{-1}, respectively. Figs. 4 and 5 illustrate the decolorization of RR198 and MB at different power densities and frequencies. It can be seen that the increase in power density and frequency led to an increase in decolorization rate.

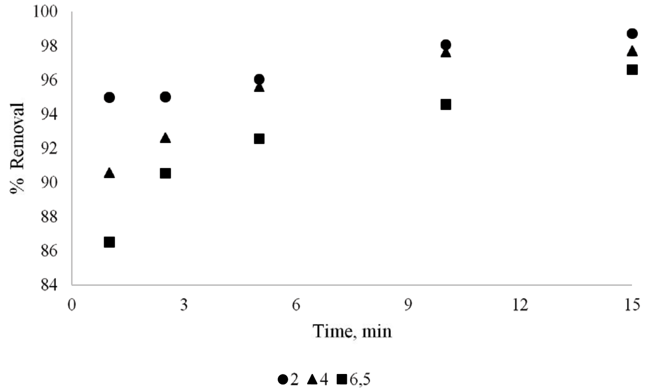

Fig. 2. pH effect on the removal of RR198 ([RR198] = 100 mg L^{-1}; US frequency = 53 kHz; catalyst dosage = 0.1 g L^{-1}; US power = 90 W).

3.4. Effect of initial dye concentration

The influence of initial dye concentration on the removal of RR198 and MB was another important factor investigated in this study. Fig. 6 presents the decolorization of the selected dyes at different initial dye concentrations. It can be observed that higher initial dye concentrations led to lower decolorization rates. This behavior is typical

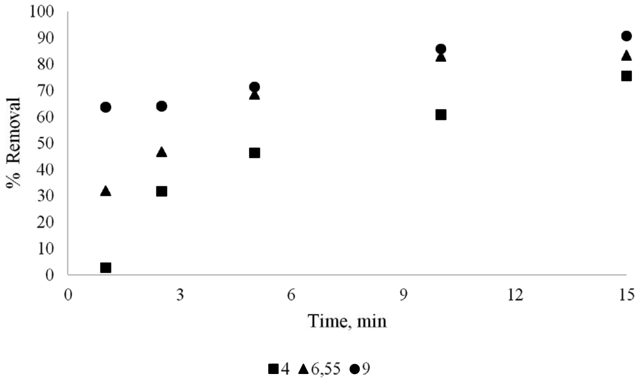

Fig. 3. pH effect on the removal of MB ([MB] = 100 mg L^{-1}; US frequency = 53 kHz; catalyst dosage = 0.25 g L^{-1}; US power = 90 W).

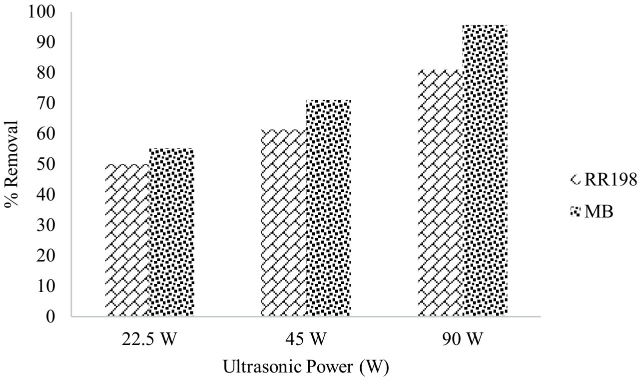

Fig. 4. Ultrasonic power effect ([MB-RR198] = 100 mg L^{-1}; US frequency = 53 kHz; catalyst dosage = 0.25 g L^{-1} (MB); catalyst dosage = 0.1 g L^{-1} (RR198); pH = 6.55 (MB); pH = 6.5 (RR198); time = 15 min).

of such sonochemical reactions [39]. The reason for this is that when the initial concentration of the selected dyes is increased, the hydroxyl radical is not increased correspondingly and the higher pollutant loading decreases the cavitational effects, thus, it is insufficient to completely destruct the organics [34,44]. Similar results have been reported in the literature [41,45]. Decolorization rate compared among only ultrasonic role, only TiO_2, and together ultrasonic role and TiO_2 and was shown at Figs. 7 and 8.

3.5. Thermodynamic study

Three thermodynamic parameters, namely entropy ($\Delta S°$), free energy change ($\Delta G°$) and enthalpy change ($\Delta H°$), were prescribed by the resulting equations [15,46,47] [Eqs. (3)–(5)]:

$$\Delta G = -RT\ln k \tag{3}$$

$$\ln k = \ln A - \left(\frac{E_a}{RT}\right) \tag{4}$$

$$\ln k = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{RT}\right) \tag{5}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), and k_L is the Langmuir constant (mol L^{-1}). $\Delta S°$ and $\Delta H°$ can be obtained from the slope and intercept $\ln k_L$ vs. $1/T$ according to Eqs. (3)–(5). The data regarding $\Delta S°$, $\Delta H°$ and $\Delta G°$ are given in Table 3. The negative values of $\Delta S°$ is a decrease in entropy in regard to the system. The process was thought to be exothermic due to the negative $\Delta H°$ values (Table 3). The positive value for the Gibbs free energy showed that the process was not spontaneous in nature. According to the results in Fig. 7, the removal rates of RR198 were 77% and 84% for sole TiO_2 and US, respectively. However, the removal rate of RR198 was 96% at US/TiO_2, due to the synergetic effect of both US and TiO_2. As can be seen from the results presented in Fig. 8, the removal rates for MB were 70% and 80% for sole TiO_2 and US. However, the removal rate was 95% at US/TiO_2, due to the synergetic effect of both US and TiO_2. According to the results, we cannot say certain expressions, also, the reaction pathway involved in the dye degradation is complex, with many unknown reactions occurring.

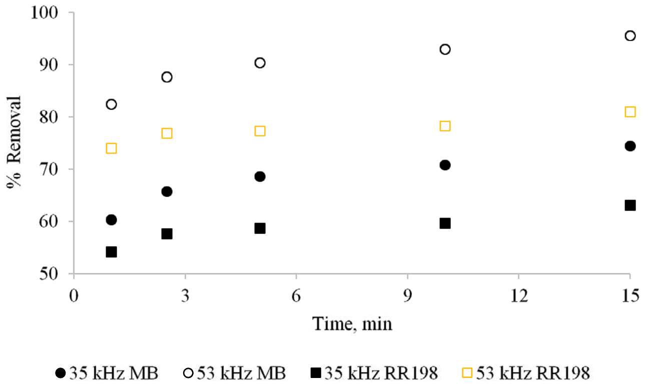

Fig. 5. Ultrasonic frequency effect ([MB-RR198] = 100 mg L^{-1}; US power = 90 W; catalyst dosage = 0.25 g L^{-1} (MB); catalyst dosage = 0.1 g L^{-1} (RR198); pH = 6.55 (MB); pH = 6.5 (RR198); time = 15 min).

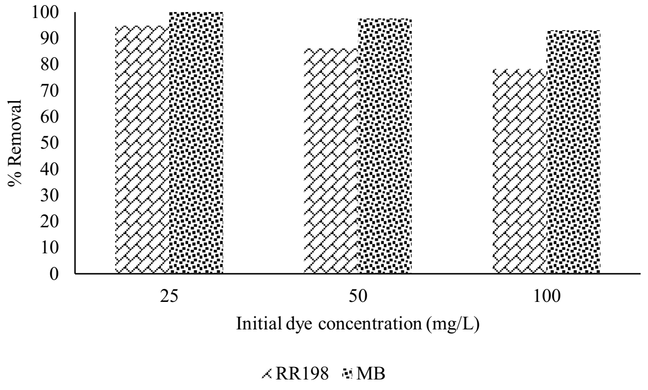

Fig. 6. Effect of initial dye concentration on the removal of the selected dyes (catalyst dosage = 0.25 g L^{-1} (MB); catalyst dosage = 0.1 g L^{-1} (RR198); pH = 6.5 (RR198); pH = 6.55 (MB); US power = 90 W; US frequency = 53 kHz; time = 10 min).

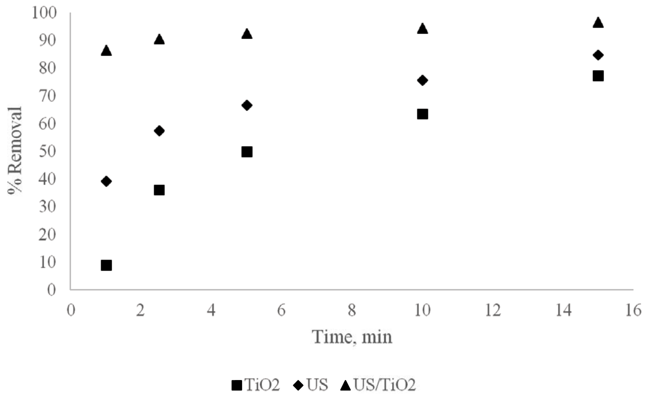

Fig. 7. Decolourization rate comparison among only ultrasonic role, only TiO_2, and together ultrasonic role and TiO_2 for RR198 (catalyst dosage = 0.1 g L^{-1} (RR198); pH = 6.5 (RR198); US power = 90 W; US frequency = 53 kHz; time = 10 min).

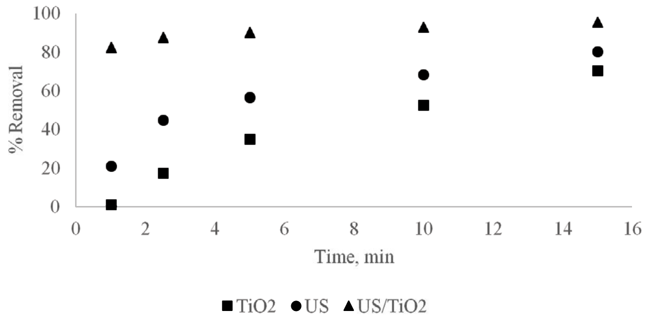

Fig. 8. Decolourization rate comparison among only ultrasonic role, only TiO_2, and together ultrasonic role and TiO_2 for MB (catalyst dosage = 0.25 g L^{-1} (MB); pH = 6.55 (MB); US power = 90 W; US frequency = 53 kHz; time = 10 min).

Table 3
Thermodynamic parameters for the decolorization of RR198 and MB by sono-oxidation

T (K)	MB			RR198		
	$\Delta S°$ (kJ mol^{-1} K^{-1})	$\Delta H° - E_a$ (kJ mol^{-1})	$\Delta G°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1} K^{-1})	$\Delta H° - E_a$ (kJ mol^{-1})	$\Delta G°$ (kJ mol^{-1})
273	–0.09	–32.4	9.97	–0.22	–73.6	5.77
293			6.11			4.22
303			5.67			3.96

4. Conclusions

In a brief, the nano TiO_2 particles also proclaimed the enhanced catalytic activity towards the removal of MB and RR198 dyes when excited by ultrasonic irradiation. The difference in the performance of the catalysts under ultrasound was attributed to different operational conditions with different dye types (cationic and anionic). This study showed that the maximum dye decolorization was achieved at 15 min, a neutral pH of 6.5 and a catalyst dosage of 0.25 g L^{-1} for MB, 0.1 g L^{-1} for RR198, US power 90 W and US frequency 53 kHz. High decolorization was obtained with high surface area, which enhanced the sonocatalytic reactions.

Hence, this study showed that nano TiO_2 can be used as an efficient sonocatalyst for the degradation of MB and RR198 dyes for treatment.

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