Rapid Synthesis of PbO-NPs Photocatalysts, Investigation of Methylene Blue Degradation Kinetics

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Abstract

The study focused on the green synthesis of lead oxide nanoparticles (PbO-NPs) using green tea extract and its use for photocatalytic degradation. The effect of experimental conditions such as green tea extract concentrations and reaction temperatures on the structure and size of PbO-NPs has been investigated. Reaction temperatures of 25, 50 and 85 °C and green tea extract concentrations of 5, 10, 20, 40, 80 and 100 mg/mL were used for preparing of PbO-NPs. Amount of the phenolic acid contained in the green tea extracts was determined according to the Folin-Ciuceltau method. The synthesized PbO-NPs were further confirmed by UV–visible Spectroscopy, Fourier Infrared Transformation Spectroscopy (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive (EDX) analysis. Tetragonal and orthorhombic morphology of PbO-NPs were observed in SEM images. While the crystallite structure of the PbO-NPs was obtained for the samples prepared using 5 and 10 mg/mL extract concentration for all reaction temperatures, the amorphous structures of PbO-NPs were seen for the samples prepared using extract concentrations of 20, 40, 80 and 100 mg/mL. Finally, PbO-NPs catalyst was tested for the degradation of methylene blue (MB) under UV light. The effect of dye concentration, catalyst amount and pH on degradation were investigated. By determining suitable experimental conditions, MB degradation reached 89% with PbO-NPs in 60 minutes. The reaction kinetics of MB removal from aqueous solution under UV lamp and in the dark media were compared for first-order and second-order reaction kinetics.

1. INTRODUCTION

Important developments in nanomaterial production and applications have increased the interest of scientists in nanotechnology [1]. Today, the discovery of nanoparticles has gained a lot of momentum as a result of its unique properties. Metal and metal oxide nanoparticles are widely used in the industrial applications because of having optical, electronic, mechanical, magnetic, biomedical, sensory and catalytic properties [2-4]. There are different forms of lead oxides such as PbO, PbO$_2$, Pb$_2$O$_3$, Pb$_3$O$_4$, and Pb$_{12}$O$_{19}$. Lead oxide (PbO) is recognized as an important industrial material that can be used in batteries, composite electrode, optical sensor, reusable catalyst and glass industry [4-9]. In addition, the band gap changes according to the lead-oxygen ratio. It has been reported that the color of PbO is yellow, Pb$_3$O$_4$ is red and Pb$_{12}$O$_{19}$ is brown. However, special attention has been paid to PbO nanostructures due to the photoconductive properties of these nanomaterials [9].

Among the synthesis methods of nanoparticles, there are different techniques such as chemical, physical, mechanical and biological methods [10]. Chemical and physical synthesis methods of nanoparticles are both costly and have harmful effects such as hazardous waste generation. In addition, harmful chemicals can adhere to the surface of nanoparticles, limiting their use for biological purposes [4]. Therefore, the researchers proposed "green" synthesis, a simple, economical and environmentally friendly approach to

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produce metal oxide nanoparticles. Environmentally known, sustainable and green synthesis methods enchant nanotechnology researchers due to problems accompanying traditional chemical methods. Therefore, the production of nanoparticles by green synthesis is considered a more suitable way for the synthesis and use of functional nanomaterials [11-13].

Table 1. Some plants and nanoparticles used in green synthesis

| Plants                        | NPs       | References |
|-------------------------------|-----------|------------|
| Cocos nucifera L              | Pb-NPs    | [1]        |
| Lavender leaf                 | AuNPs     | [10]       |
| Cynometra ramiflora leaves    | Iron oxide| [11]       |
| Pomegranate peel              | CuO       | [12]       |
| Parsley leaf                  | ZnO       | [14]       |
| Quince seed Mucilage          | ZnO       | [15]       |
| Cuminum cyminum seed powder   | Pb-NPs    | [16]       |

There are few studies on the preparation of lead oxide nanoparticles using the green method and some examples are given in Table 1. The bacterial pellets of Bacillus toyonensis species were used for synthesis of lead oxide nanoparticles (PbO-NPs) [17]. Lead nanoparticles were prepared by using Jatropha curcas L. latex extract and they claimed that could be potential applications in lead batteries, catalysis etc.[18]. Although, green synthesis of PbO-NPs has been successfully reported using some plants extracts, however there are no reports available in the literature about green synthesis of PbO-NPs using green tea extract. The polyphenolic compounds found in green tea mainly contain flavonoids, flavones, phenolic acids and similar species. Tea polyphenols, often referred to as catechins, are flavonoids with the basic α-phenylbenzopyran structure [19]. Phenolic compounds have high antioxidant potential and electron reducing ability. Antioxidants reduce metal ions; therefore green synthesis of nanoparticles is preferred [20, 21].

Methylene blue (MB) causes water pollution. It has also been reported to have various harmful effects such as irritation, cyanosis, tachycardia, vomiting and diarrhea when exposed [22]. It has also been reported that MB undergoes reductive anaerobic degradation, which causes the formation of carcinogenic products [23]. In addition, dyes that cause discoloration of water can adversely affect the photosynthesis process. To produce efficient photocatalysts, photocatalytic systems that can work effectively under visible light are needed. Colored molecules absorbs visible light and reduces the amount of light needed for photosynthesis to occur. Therefore, the water ecosystem may be damaged [24]. Ferrites, metal oxides, metal sulphides and semiconductors are used as photocatalysts in the decomposition of organic pollutants [25].

The aim of this study is to synthesize PbO-NPs using green tea extract as a reducing agent and to investigate properties of nanoparticles using various techniques. The obtained PbO-NPs were used in the removal of methylene blue under UV lamps and in the dark environment.

2. MATERIAL METHOD

2.1. Materials

Lead acetate trihydrate (Pb(CH₃COOH)₂.3H₂O) and hydrochloric acid (%37 HCl) were purchased from Merck. The Folin-Cioceltau reagent used in the total phenolic content analysis was purchased from Carlo Erba. Gallic acid (C₇H₆O₅) and sodium carbonate (Na₂CO₃, 99%) were purchased from Sigma Aldrich. Methylene blue was purchased from Isolab Chemicals Sodium hydroxide (NaOH) was purchased from Fluka. Dried green tea leaves were purchased from local markets for the extract to be used in nanoparticle synthesis.

2.2. Preparation of Extracts

Dry green tea leaves of certain grams (0.5, 1, 2, 4, 8, 10 g) were extracted by brewing using 100 mL of deionized water under heat of 70 °C for 15 minutes. Then the extract was obtained by filtering from the green tea leaves and used freshly.
2.3. Folin-Cioceltau Method

Plant extracts have chain breaking activity and active oxygen removal. For this reason, polyphenols, which are antioxidants and act as free radical terminators, have the feature of reducing metal compounds. In this study, the total phenolic acid content of green tea extracts was determined by Folin-Cioceltau method. The method is based on the transfer of electrons from phenolic compounds to acid complexes determined spectrosocopically at 765 nm in alkaline medium. The method based on the determination of the amount of Gallic acid equivalent to the amount of polyphenol is widely applied to determine the polyphenol content of plants [21]. Gallic acid calibration curve is prepared with the help of UV-Vis spectroscopy. Results obtained from the regression equation of the calibration curve are shown as mg Gallic acid equivalents per a mL of extract.

2.4. Synthesis of PbO-NPs

Green synthesis of PbO-NPs was carried out by adding 0.1 M lead acetate into 100 mL of aqueous green tea extracts, followed by mixing at different temperatures for 1 h. Once the solution had cooled to room temperature, it was centrifuged at 2000 rpm for 5 minutes to collect the precipitates. After the precipitate obtained was settled in centrifuge, it was dried at 60-65 °C (Figure 1). Table 2 shows the experimental conditions for preparing PbO-NPs.

![Diagram of PbO-NPs synthesis](image)

**Figure 1. Schematic representation of PbO-NPs synthesis with green tea extract**

2.5. Characterization

Scanning electron microscopy (SEM) analysis of obtained PbO-NPs was done using a Tescan Mira 3 XMU SEM machine. Powder X-ray diffraction was performed using X-ray diffractometer, Rigaku Miniflex 600 X, with CuK radiation = 1.5405Å over a wide range of Bragg angles (2θ=5-90°). Fourier transform infrared spectroscopic measurements were done using Bruker (Tensor II) spectrophotometer. UV-Vis spectra of PbO-NPs were recorded in the wavelength range of 200-400 nm using the Schimadzu 2600 spectrophotometer. In photocatalytic degradation studies, 400-800 nm range of wavelength region was used.
2.6. Photocatalytic Degradation

The photocatalytic properties of the PbO-NPs were evaluated by a 366 nm UV lamp (Merck) in the photodegradation of MB. In the experimental setup, the dye solutions were closed with a box and the UV lamp was turned on inside the box, and the solutions were exposed to irradiation. Experiments were carried out with aqueous MB solutions (10 ppm) using a certain amount of PbO-NPs catalyst. Initially, the resulting suspension was stirred in the dark for about 30 minutes to establish the adsorption/desorption equilibrium of the dye. It was then irradiated for 60 minutes at room temperature throughout the experiment. At selected time intervals (every 15 minutes), a 1 mL sample was taken and their spectra at absorbance at 664 nm MB were examined using a UV–Vis spectrophotometer.

The degradation efficiency of MB has been calculated (Equation (1)) as:

\[
\%\text{Degradation} = \frac{(C_0 - C)}{C_0} \times 100
\]  \hspace{1cm} (1)

Where \(C_0\) and \(C\) expressed in the formula are the dye concentration at the beginning and after irradiation at time \(t\).

Table 2. Experimental conditions used to prepare PbO-NPs (mixing time: 1 h)

| Green tea extract concentration (mg/mL) | Temperature (°C) | Code of synthesized PbO-NPs |
|----------------------------------------|------------------|-----------------------------|
| 5                                      | 25               | 50                          | 85                          | PbO-5                        |
| 10                                     | 25               | 50                          | 85                          | PbO-10                       |
| 20                                     | 25               | 50                          | 85                          | PbO-20                       |
| 40                                     | 25               | 50                          | 85                          | PbO-40                       |
| 80                                     | 25               | 50                          | 85                          | PbO-80                       |
| 100                                    | 25               | 50                          | 85                          | PbO-100                      |

3. RESULTS AND DISCUSSION

In this study, the amount of total phenolic acid in green tea extracts that were prepared at various concentrations (5, 10, 20, 40, 80 and 100 mg/mL) was determined by the Folin–Cioceltau method and the results were presented in Table 2 [21]. A calibration curve of gallic acid (ranging from 10 to 375 mg/ml) was prepared by UV–Vis. Gallic acid was chosen as the standard compound and the total amount of phenolic substance was expressed as mg/mL. When calculating gallic acid equivalent using the standard curve equation: \(y = 0.0042 \times +0.2014\) (Figure 2), where \(y\) is absorbance at 765 nm, \(\times\) is total phenolic content in the green tea extracts. It can be seen from the table that the total amount of phenolic acid increased proportionally with the increase in the green tea extract concentration.
Figure 2. Standard Curve of Gallic Acid

UV-Vis spectroscopy detects the concentration of solute in a solution by measuring absorption. Concentration and absorption are proportional. In addition, Concentration and absorption vary depending on the presence of absorbent species in the solution. It has been reported that lead nanoparticles can be analyzed in the range of about 200 nm to 400 nm with a UV-Vis spectrometer [17]. Figure 3 shows UV-Vis spectra and the formation of PbO-NPs changing the color of solution from white to yellow. The Figure 3 illustrates that the green tea extract (5 mg/mL), prepared PbO-NPs (PbO-5) and lead acetate have absorption peaks at 211, 238-272 and broad peak about 224 nm, respectively.

| Table 3. Amount of total phenolic acid in green tea extracts |
|------------------------------------------------------------|
| **Green tea extract concentration (mg/mL)** | **Total Phenolic acid (mg/mL)** | **Absorbans (λ max: 765 nm)** |
|------------------------------------------------|-------------------------------|-----------------------------|
| 5                                              | 286.57                        | 1.40                        |
| 10                                             | 292.52                        | 1.43                        |
| 20                                             | 354.43                        | 1.69                        |
| 40                                             | 359.19                        | 1.71                        |
| 80                                             | 380.62                        | 1.80                        |
| 100                                            | 402.05                        | 1.89                        |

The formations of PbO-NPs with different green tea extract concentrations were monitored by UV-Vis spectra at various intervals (Figure 4). The UV-Vis spectrum of synthesized PbO-NPs exhibited the peaks at 238, 216, 213, 213, 217 and 223 nm for extract concentrations of 5, 10, 20, 40, 80 and 100 mg/ml, respectively. The results show the formation of PbO-NPs [18]. As the green tea extract concentration increases, the peak attributed to the polyphenol appears in the spectra of PbO-NPs at 272 nm. PbO-NPs may have been functionalized by polyphenols and complex structure may have emerged [26]. The result is also confirmed with the SEM and XRD analysis.
Three syntheses were performed at 25, 50 and 85 °C using different green tea extract concentrations to investigate the effect of synthesis conditions on morphology and particle size of PbO-NPs (Figure 5(a)-(c)). According to XRD data, the crystalline pattern of PbO-NPs is only seen in the samples that were prepared using 5 and 10 mg/ml extract concentration (PbO-5, PbO-10). The presence of PbO in the samples has been illustrated with peaks at 27.6, 27.9, 27.42, 34.08, 34.24 and 34.36° (Figure 5) [18, 27]. These peaks appearing near 27° and 34° in the XRD spectra indicate orthorhombic and tetragonal PbO [9]. It can be seen in Figure 5 that as the concentration of green tea extract increases, defined crystalline peaks of PbO-NPs disappear and the pattern turns into an amorphous structure. This behavior could be due to polyphenols that are capped on the PbO-NPs surface [28]. The large peaks at around 27° and 34° have been obtained for all samples that were synthesized at reaction temperatures of 25, 50, 85 °C with extracts concentrations of 5, 10, 20, 40, 80, 100 mg/mL.

Figure 3. UV–Visible spectra and pictures showing the color change during the formation of PbO-NPs (reaction temperature of 25 °C).

Figure 4. UV–visible spectra of green tea extract and prepared PbO-NPs using different extract concentration at 25 °C.
The average crystallite sizes of the PbO-NPs were determined using the Scherrer's Equation (2) [29]

\[ D = \frac{0.9\lambda}{\beta\cos\theta} \]

(2)

In the Equation, \( D \) is the average crystallite size, \( \lambda \) is the wavelength of CuK\( \alpha \), \( \beta \) is the full width at half maximum of the diffraction peak and \( \theta \) is the Bragg's angle. Since the presence of crystalline pattern of PbO-NPs has been only obtained from the samples prepared using 5 and 10 mg/mL extract concentration, the average crystallite sizes were calculated for these samples. The crystallite sizes were calculated to be 6.47 and 1.72 nm at 25 °C, and 2.44, 2.05 nm at 50 °C, and 3.39, 1.61 nm at 85 °C for samples with 5 and 10 mg/mL green tea extracts, respectively (Table 4). It has been seen from the table that the crystalline size of nanoparticles is decreased by temperature and extract concentration.

**Table 4. Average crystallite sizes of prepared PbO-5 and PbO-10**

| Reaction temperature (°C) | PbO-5 | Peak position (2\( \theta \)) | PbO-10 | Peak position (2\( \theta \)) |
|---------------------------|-------|-------------------------------|--------|-------------------------------|
| 25                        | 6.47  | 27.36                         | 1.72   | 27.3                         |
| 50                        | 2.44  | 26.86                         | 2.05   | 27.38                        |
| 85                        | 3.39  | 27.24                         | 1.61   | 27.26                        |

**Figure 5.** XRD pattern of PbO-NPs prepared at a) 25, b) 50 and c) 85 °C with green tea extracts concentrations of 5, 10, 20, 40, 80, 100 mg/mL.

FTIR spectra of PbO-NPs 4000-500 cm\(^{-1}\) range are shown in Figure 6. The effect of green tea extracts concentrations and reaction temperature on nanoparticle formation was investigated. The broad peaks at 3410 cm\(^{-1}\) in the spectra of lead oxide nanoparticles expressing hydroxyl groups are attributed to characteristic bands of polyphenolic compounds [27, 30]. The peak around 1520 cm\(^{-1}\) represents the stretching-bending vibration of O-H. The peaks appearing around 1045, 1048 and 1052 cm\(^{-1}\) are attributed to the bending vibration of C-O [27]. The absorption peaks at 667, 661 and 663 cm\(^{-1}\) indicate the presence of Pb-O and Pb-O-Pb bonds. Peaks located between 500-900 cm\(^{-1}\) are defined as metal-oxygen stretching.
vibrations [27, 31, 32]. FTIR spectrum shows that identical characteristics peaks of PbO-NPs have not
changed as increased the reaction temperature while the peaks appeared to weaken with the extract
concentration increased.

Figure 6. FTIR spectrum of PbO-NPs prepared at a) 25, b) 50 and c) 85 °C with green tea extracts
concentrations of 5, 10, 20, 40, 80, 100 mg/mL

Figure 7 shows the SEM images of PbO-NPs prepared at different reaction temperature (25, 85 °C) and
green tea extract concentrations (40, 80 mg/mL). The SEM images illustrate that the particles exhibit a
nanoscale tetragonal and orthorhombic morphology (Figure 7). The images also point out that the size of
particles ranges from 20 to 100 nm. It was observed that the particle size increased with the increase of the
extract concentration in the samples synthesized at 25°C and 85°C. The extract may have led to
agglomeration of nanoparticles. It has been reported that various factors such as reaction time and precursor
concentration can change the particle size and shape [32]. As a result, it shows that the polyphenol
concentration in the extract is effective in the formation of the structure and size of the nanoparticles [33].
SEM studies showed that the sample prepared at 85 °C has smaller particle size than that prepared at 25 °C
and points out uniform particles. In addition, the presence of only lead and oxygen elements in the EDX
graph of nanoparticles indicates that the nanoparticle is of high purity (Figure 8) [32].

It was decided to continue the photocatalytic degradation studies with PbO-NPs synthesized at 40 mg/mL
extract concentration and 25 °C reaction temperature. The effect of these experimental conditions as a
photocatalyst was investigated, since the process is easy to apply and synthesis is made with less energy
consumption.
Figure 7. SEM images of PbO-NPs prepared a) 40 mg/mL extract, 25 °C, b) 40 mg/mL extract, 85 °C c) 80 mg/mL extract, 25 °C and d) 80 mg/mL extract, 85 °C

Figure 8. EDX spectrum of PbO-NPs (40 mg/mL extract concentration, 25 °C reaction temperature)
3.1. Photocatalytic Activity

In photocatalytic degradation studies, dye concentration is one of the main parameters affecting the degradation efficiency [34]. Methylene blue (MB) is defined as a cationic dye. Some researchers have reported that the hydroxyphenyl group contained in natural polyphenols interacts with cationic dyes via ionic ion and ionic dipole forces. Such functional groups have permanent dipoles due to electronegativity from the oxygen elements. In addition, negative charges arise due to the loss of hydrogen ions in the aqueous solution. Complex compounds have been reported to occur between polyphenols and cationic dyes [35]. The photodegradation provided by semiconductor PbO-NPs depends on various parameters such as pH, catalyst amount and time [24]. In the photocatalytic activity experiments, the solution of MB prepared with distilled water was used as organic impurity. The predicted possible decomposition reaction of PbO is given by Equations (3)-(5)

\[
PbO + h\nu \rightarrow PbO (h) + PbO (e) \\
PbO (h) + MB \rightarrow \text{Degradation product} \\
PbO (e) + MB \rightarrow \text{Degradation product}.
\]

The operating conditions during photocatalytic degradation of MB were shown in Table 4. According to the results, the highest dye degradation was achieved as 89%. In order to reach maximum degradation efficiency, effect of pH, concentration of dye and amount of PbO-NPs were examined in range of 2–10, 5-15 ppm, and 0.5–1 mg/mL, respectively (Table 5). As seen in Table 5, the highest dye degradation was achieved with 89% and the lowest with 28% dye removal.

| Run no. | pH | Catalyst loading (mg/mL) | Initial dye concentration (ppm) | Degradation (%) |
|--------|----|--------------------------|-------------------------------|-----------------|
| 1      | 4  | 1                        | 10                            | 89              |
| 2      | 4  | 0.5                      | 10                            | 48              |
| 3      | 4  | 1.5                      | 10                            | 28              |
| 4      | 4  | 1                        | 5                             | 36              |
| 5      | 4  | 1                        | 15                            | 38              |
| 6      | 2  | 1                        | 10                            | 57              |
| 7      | 7  | 1                        | 10                            | 49              |
| 8      | 10 |                           | 10                            | 79              |

The degradation of MB dye was carried out by taking different amounts of PbO-NPs, initial concentrations of MB and different pH of MB solutions (Figure 9 (a,b,c)). It is observed that the percentage of MB degradation increases until amount of catalyst 1 mg/mL then decrease. The reason for the maximum degradation (89%) obtained in 1 mg/mL catalyst may be the increase of active sites on the surface of the catalyst as the amount of catalyst increases [36]. This is probably because the number of absorbed photons and dye molecules increases as the amount of PbO-NPs increases [37]. It was determined that there was a decrease in the degradation of the dye when the amount of catalyst reached 1.5 mg/mL. This may be due to both increased light scattering and decreased penetration of light passing through the solution (Figure 9a). Dye removal decreased from 89% to 28%. This phenomenon may be explained by decrease in the passage of irradiation through the sample [24, 37].

It has been reported that at high dye concentration, the color of the solution darkens and the path length of photons entering the solution decreases, and only a few photons can reach the photocatalyst surface thus, the percentage of degradation diminished as the absorption of photons decreased [24, 34]. As seen in Figure 9b, when the dye concentration increased from 5 ppm to 10 ppm, the dye degradation increased. It has been also reported, when the amount of dye exceeds a certain level, more dye molecules will be adsorbed on the photocatalyst surface and the active sites of the catalysts will decrease [37]. This may be the reason for the decrease in the percentage of degradation in the MB solution of 15 ppm.

The effect of dye pH on degradation of MB under UV lamp using 1 mg/mL of PbO-NPs is given in Figure 9c. degradation of dye was observed as 57%, 89%, 49% and 79% for pH 2, 4, 7, and 10, respectively. The pH values of the suspensions were adjusted with HCl and NaOH solutions. Most of the semiconductor
oxides show amphoteric behavior [38]. Lead is known as an amphoteric metal. Amphoteric metals have the ability to react with both bases and acids [39]. Since the change in the pH of the solution affects the surface of the catalyst, it allows the dye molecules to separate. Therefore, it causes a change in adsorption and reaction rate [40]. Hydroxyl radicals are formed in alkaline conditions and thus the dye solution removes rapidly [24]. However, it has been reported that the degradation rate of some azo dyes may increase as the pH value decreases [38]. For this reason, it has been determined that PbO-NPs have high removal at both pH 4 and pH 10.

Figure 9. MB degradation irradiation under UV lamp for 60 min a) amount of catalyst, b) initial dye concentration c) pH of dye solution

Dye removal was achieved by adsorption in the dark environment. To understand the adsorption mechanism on dye removal and the effect of UV light on photodegradation, the experiment was conducted under dark conditions. The experiments were repeated at predetermined initial dye concentration (10 ppm), catalyst amount (1 mg/mL) and pH (4 and 10) values. In the adsorption removal studies carried out in the dark environment, a sample was taken every 30 minutes and studied for 180 minutes. The effect of acidic and basic environment was examined in dark environment by selecting pH 4 and pH 10 where removal was high. It is seen in the Figure 10 that the removal obtained after 180 minutes in dark environment is reached in 60 minutes under UV light. It has been found that UV light accelerates the MB's removal mechanism compared to the dark environment [34]. As shown in Table 6 at pH 4 and pH 10 after 180 minutes, 87.6% and 84.5% removal was achieved, respectively.
Figure 10. Photocatalytic degradation of MB with PbO-NPs at dark media: a) pH=4 b) pH=10, under UV light c) pH=4, d) pH=10 (1mg/mL PbO-NPs, 10 ppm MB)

Figure 11. Kinetic plots of pH and the effect of light on MB degradation. Dark media with a) First-order, b) Second order and under UV lamb, c) First-order, d) Second-order

Experiments were carried out under certain working conditions to study the photocatalytic degradation kinetics of methylene blue (pH=4 and pH=10, methylene blue concentration 10 mg/L, photocatalyst dosage 1 mg/mL). Studies have revealed that the photocatalytic degradation of organic dyes conforms to first-order
kinetics [34, 36]. The work of MB Photocatalytic degradation kinetics can be explained according to the first-order and second-order model and is expressed according to the following Equations (6) and (7):

\[ \ln \left( \frac{C_t}{C_0} \right) = -k_1 t \]  \hspace{1cm} (6)
\[ \frac{1}{C} - \frac{1}{C_0} = k_2 t \]  \hspace{1cm} (7)

C₀ and C expressed in the formula are likewise the MB concentration at the start and time t, where t is the irradiation time in minutes, k is the apparent rate constant. \( k_1 \) is the rate constant for first order, \( k_2 \) is the rate constant for second order reaction kinetics. In order to calculate the photocatalytic rate constants of the PbO-NPs photocatalyst, \( \ln(C_0/C) - t \) change graphs were drawn and their slopes were calculated. Similarly, for the second order kinetic model, t values against \( \frac{1}{C} - \frac{1}{C_0} \) were plotted and \( k_2 \) was calculated from the slope. All the plots displayed a linear association with good correlation coefficients.

Figures 11 a and b show under dark media and c and d under UV lamp, first-order and second-order reaction kinetic patterns, respectively. It can be expressed according to \( R^2 \) values, where the adsorption of MB dye in PbO-NPs in the dark media to first-order kinetics \( (R^2 = 0.9784) \) for pH 4 and second-order kinetics \( (R^2 = 0.8699) \) for pH 10. On the contrary, the photocatalytic removal reaction kinetics under UV lamp match the first order reaction kinetics for pH 4 and pH 10. Calculated rate constants are given in Table 6.

**Table 6. Pseudo-first-order kinetic parameters for the degradation of MB with PbO-NPs under different pH conditions**

| pH | Under UV Lamp (60 min) | Dark Media (180 min) |
|----|------------------------|----------------------|
|    | Degradation (%) | \( k_1 (\text{min}^{-1}) \) | \( k_2 (\text{min}^{-1}) \) | Removal (%) | \( k_1 (\text{min}^{-1}) \) | \( k_2 (\text{min}^{-1}) \) |
| 4  | 89.9 | 0.038 | 0.036 | 87.6 | 0.017 | 0.032 |
| 10 | 79.9 | 0.026 | 0.016 | 84.5 | 0.014 | 0.015 |

The highest efficiency (%89.9) in photocatalytic removal of MB with PbO-NPs was achieved under UV lamp and at pH 4 (Table 6). As a cationic dye, MB provides high efficiency removal in the presence of OH ions, generally under alkaline conditions. But in our study, degradation efficiency reached its highest value at pH 4. This may be because lead is an amphoteric metal. In addition, the anionic extract on the PbO-NPs surface synthesized with green tea extract may react with MB.

**4. RESULTS**

The reason why green synthesis has attracted so much attention from researchers in the last decade is that it is an easy, inexpensive, and harmless method. The synthesis of PbO-NPs in green tea extract in our study supports this idea. Green tea extracts were used as a reducing agent for the preparation of PbO-NPs and PbO-NPs were successfully synthesized. It is seen from the study that both the concentration of green tea extract and the processing temperatures have an influence on structures of nanoparticles. The formations of PbO-NPs were confirmed by a UV-Spectrometer by the absorption peak position and also by characterization studies using SEM, FTIR and XRD. The sizes of the synthesized particles ranged from 20 to 100 nm as seen from the SEM images. This study reveals that green synthesis of PbO-NPs using green tea extracts can be an inexpensive and efficient method and a suitable alternative instead of chemical methods for the synthesis of metal oxide nanoparticles. In addition, the sizes of nanoparticles can be controlled by amount of total phenolic acid.

From the photocatalytic results of MB on the PbO-NPs catalyst, it can be seen that the photodegradation rate of MB increases with decrease pH. When the degradation under dark environment and UV light is compared, it was determined that MB degradation under UV light accelerated by decreasing from 180 minutes to 60 minutes. PbO-NPs synthesized using green tea extract are thought to be suitable and sufficient for methylene blue extraction from water.
ACKNOWLEDGEMENTS

This work was supported by the Cumhuriyet University Scientific Research Projects Unit (CUBAP) as Project Number M725.

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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