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Kinetics of 4-Nitrophenol Reduction with Black Tea Extract Conjugated Silver Nanoparticle Catalyst

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ABSTRACT

The 4-nitrophenol reduction process is one of the slow methods. One way to increase the rate of 4-nitrophenol reduction reactions is to use a catalyst. In this study, the catalyst used was silver nanoparticles conjugated by black tea extract. The stages that have been carried out in research are the synthesis of conjugated silver nanoparticles of black tea extract, the determination of the kinetic profile of 4-nitrophenol reduction, and the study of the influence of inorganic anions on the reduction of 4-nitrophenol with the presence of silver nanoparticle catalysts. The presence of conjugated silver nanoparticles of black tea extract has been shown to increase the kinetics of the degradation reaction of 4-nitrophenol compounds to 85 times compared to without nanoparticles by changing the value of the reaction rate constant from 0.00006 to 0.0051. The contribution of this research is to show that the presence of inorganic anions provides information on the decrease in the rate of reduction reactions of 4-nitrophenol.

1. Introduction

Nitrophenol is a yellow phenolic compound that has been used in various manufacturing sectors, ranging from the pharmaceutical industry (paracetamol), synthetic dyes (for leather), explosives, drugs, and pesticides (methyl/ethyl paration) [1]. This compound has been declared a toxic pollutant often found in waters by the United States Environmental Protection Agency - USEPA because it has been proven to harm organisms, even though the concentration of nitrophenol in water is low at 0.005 mg/L [2]. The specific nitrophenol compound most often found in industrial waste is 4-nitrophenol [3]. The 4-nitrophenol combination is considered to have high solubility in water and high resistance to biodegradation, thus making this compound relatively stable in the environment for years [4]. So far, several pollutant treatment methods have been related to removing 4-nitrophenol compounds in aquatic environments: coagulation, extraction, ion exchange, biological processes, and absorption methods [5].

In the pharmaceutical industry, 4-nitrophenol can produce 4-aminophenol, the raw material for paracetamol. Metal nanoparticles have shown good catalytic activity in the UV and visible light regions for applications in treating water pollutants [6]. Previous studies have shown that the use of silver (Ag) nanoparticles has good catalytic properties and is cheaper than the use of gold (Au), platinum (Pt), and palladium (Pd) nanoparticles, in which the catalytic efficiency of 4-nitrophenol becomes 4-aminophenol with silver nanoparticles has reached 100% [7].

In forming large amounts of nanoparticles, high surface energy is needed to create the surface area of nanoparticles [8]. Due to the presence of high surface energy, often the nanoparticles formed gather with each other to form irregular and unstable aggregates of particles. This aggregation process will be an obstacle to the functionality of nanoparticles, let alone for catalytic reactions [9]. Therefore, the manufacture of a nanoparticle must be supported by a conjugated capping agent in the nanoparticle system [10]. The existence of this agent serves to block the occurrence of aggregation while setting the size to be more uniform. In addition to affecting the size, the presence of conjugating agents also affects the properties of nanoparticles to be more effective in function [11].

One of the natural conjugating agents is the use of plant extracts. Plant extracts are reported to be stabilizers and reducers in synthesizing nanoparticles, resulting in uniformly sized nanoparticles without forming aggregates [9]. Generally, plant extracts that contain polyphenols are suitable for use as conjugated ligands to stabilize the surface energy of nanoparticles [12]. Black tea contains polyphenol compounds theaflavin and thearubigins that are worthy of being proposed as conjugating agents in this study [13].

In previous experimental studies, testing the functionality of nanoparticles against pollutant processing was often less concerned with other environmental factors, where testing was limited to being carried out within a pure water medium. Water contaminated with pollutants contains many inorganic anions from soil, rocks, and organisms [14]. Carbonate anions (CO_3^{2-}), nitrate-nitrites (NO_3^-, NO_2^-), and sulfates-sulfite (SO_4^{2-}, SO_3^{2-}) are the main inorganic anion groups often encountered in aquatic environments [15]. Therefore, the contribution of this study is to observe the influence of these environmental factors on the catalytic reaction speed of conjugated silver nanoparticles of black tea extract in reducing 4-nitrophenol pollutant compounds.

2. Research Methodology

2.1. Materials

The solution used in this study was based on $AgNO_3$, $NaBH_4$, 4-nitrophenol, Na_2SO_4, Na_2SO_3, $NaNO_3$, $NaNO_2$, and $CaCO_3$ which had a pro-analysis grade (p.a.). The black tea used in this study was commercial black tea from PT Sariwangi Agricultural Estate Agency Jakarta.

2.2. Procedures

1) Synthesis of Black Tea Extract Conjugated Silver Nanoparticles

Black tea extraction is performed by dissolving black tea into room temperature aqueous, in a ratio of 500 mg of black tea every 3.5 ml aqueous. The extraction process is carried out using microwave heat for 1 minute. The conjugated silver nanoparticles of black tea extract were synthesized by dripping a 1000 ppm $AgNO_3$ solution against a mixture of $NaBH_4$ and tea extract in a ratio of 9:1 (v/v). Dropping is done until the stirred solution of the mixture turns a bluish-red color, and it takes 5 minutes to balance.

2) Determination of 4-nitrophenol reduction kinetic profile

Determination of the optimum use of nanoparticles was carried out by testing five different solutions that were both reacted with 4-nitrophenol and measured with a UV-Vis spectrophotometer. This solution is prepared and mixed inside the vial in the following mixing order: aqueous, silver nanoparticles (AgNPs), $NaBH_4$, and 4-nitrophenol (4-NP). These five solutions are distinguished by the concentration of silver nanoparticles in the aqueous: 0, 5, 10, 15, and 20 μL in 2955 μL.

3) Effect of Inorganic Anions on the Catalytic Ability of Silver Nanoparticle in 4-Nitrophenol Reduction

The influence of anions is carried out by performing one of the variations at the stage of determining the kinetics of reduction with the addition of anions. The concentration of the final anion obtained is 1%. The result of 4-nitrophenol reduction was studied with the help of a UV-Vis spectrophotometer.

3. Results and Discussion

In this study, black tea was first extracted by immersion in water assisted by a microwave. Microwaves are used to speed up the extraction process and minimize the amount of water used, where the presence of microwave energy can disrupt the cell membrane system of black tea leaves.

Thus, the tea cell wall becomes damaged so that the water solvent can interact with the extract substances in black tea (polyphenol theaflavin and thearubigin compounds) [16].

In the synthesis process of silver nanoparticles conjugated black tea extract, the dropping stage of $AgNO_3$ solution (Ag^+ precursor) was carried out against a mixture of $NaBH_4$ and black tea extract. Dropping is carried out until a change in color to bluish-red is observed. Such a color change is one of the signs that silver nanoparticles have formed, according to the following reaction equation:

$$AgNO_3 + NaBH_4 \rightarrow Ag + \tfrac{1}{2} H_2 + \tfrac{1}{2} B_2H_6 + NaNO_3 \quad (1)$$

where positively charged silver (Ag^+) has been reduced to uncharged silver (Ag^0) or experienced a decrease in oxidation state [17]. From this small to large (bottom-up) synthesis method, the resulting homogeneous catalyst nanoparticles have been identified using UV-Visible, so that the spectrum shown in Fig. 1. is obtained. The UV-Visible absorption spectrum indicates the formation of a maximum absorption peak at a wavelength of 424 nm. The resulting absorbance is a form of optical properties of silver nanoparticles, namely surface plasmon resonance (SPR) nanoparticles.

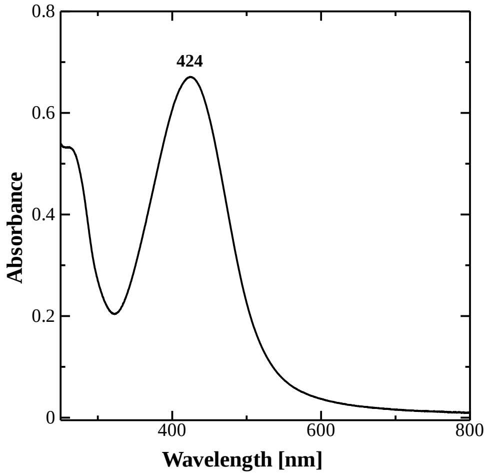

Fig. 1.UV-Visible absorption spectrum of silver nanoparticles

The next stage worked on is determining the kinetic profile of the 4-nitrophenol reduction. Fig. 2. presents the results of the UV-visible spectrum of 4-nitrophenol absorbance reduction. It is shown in Fig. 2. that there is a decrease in absorbance at a maximum wavelength of 4-nitrophenol.

Based on the UV-Visible spectrum in Fig. 2., the role of silver nanoparticle catalysts appears. In Fig. 2. (a), it can be seen that the reduction rate is prolonged, while the addition of a catalyst can accelerates the reduction rate according to Fig. 2. (b) to (e). As in [18], each metal catalyst's kinetics follows the first-order type's reaction equation. The first-order kinetics approach assumes that the rate of degradation kinetics is influenced only by the concentration of 4-nitrophenol. The concentration of sodium borohydride much higher compared to 4-nitrophenol, it can be assumed that the reaction rate of BH_4^- ions remains constant during the reduction reaction [19]. The result of the 4-nitrophenol reduction in Fig. 2. with a silver nanoparticle catalyst is determined to be of the reduction order, whose results are presented in Table 1.

Table 1. 4-Nitrophenol Reduction Reaction Rate Constant with Black Tea Extract Conjugated Silver Nanoparticle Catalyst

Catalyst	**Rate Constant**	
	k (minute^{-1})	***Difference of k value with 0 µL (multiple times)***
0 µL	0.00006	
5 µL	0.00510	85
10 µL	0.00920	153
15 µL	0.00990	165
20 µL	0.00920	153

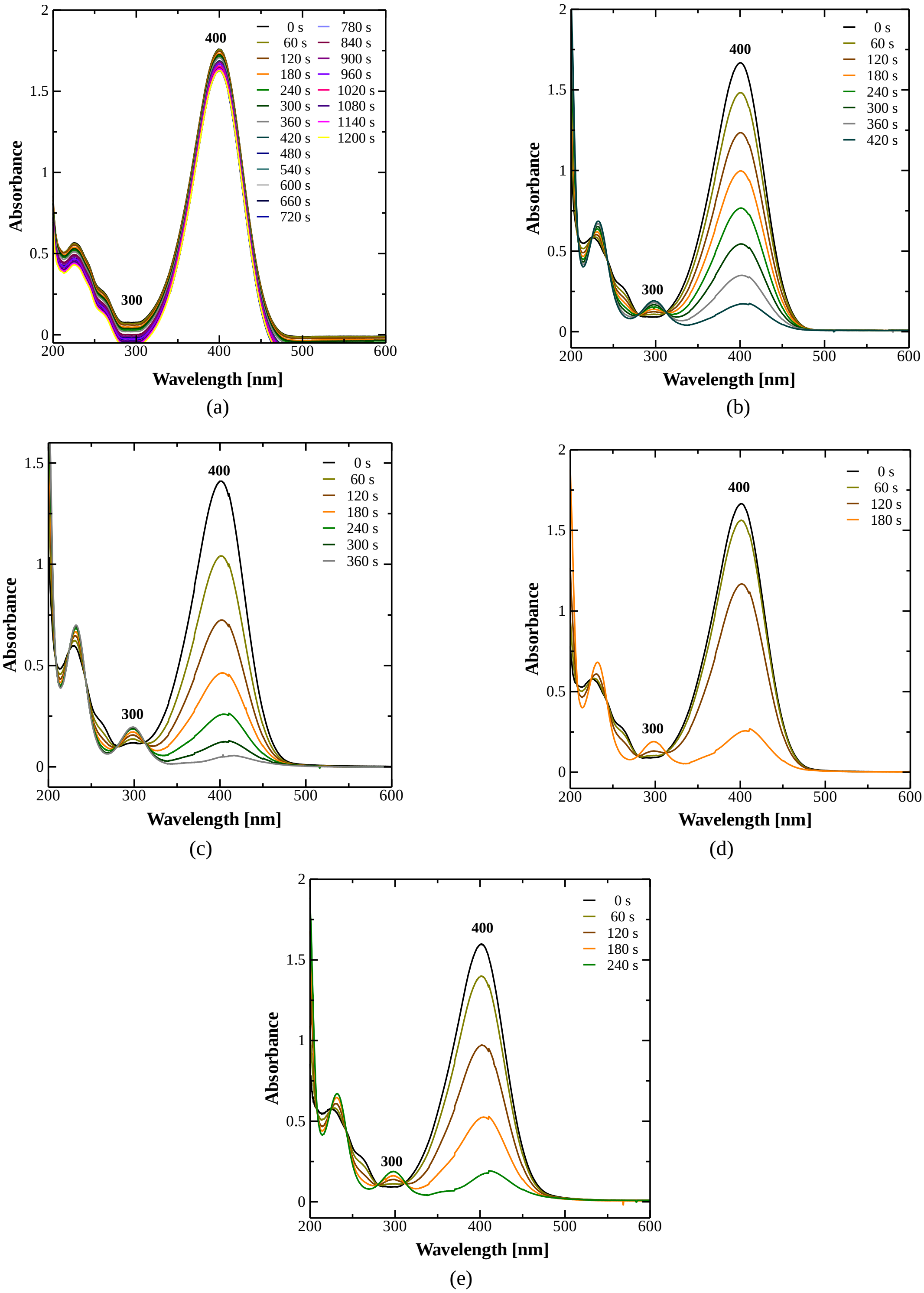

Fig. 2.UV-Visible spectrum reduction of 4-nitrophenol with the addition of black tea extract conjugated silver nanoparticle catalysts as much as (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20 μL

From the rated value of the reaction rate (k) obtained from quantitative calculations based on the first-order reaction rate equation, it can be scientifically known that the presence of nanoparticles gives a rate speed 85 times higher than without using a catalyst at all (the value of 85 is obtained from the comparison of the value of k in nanoparticles of 5 μL to 0 μL). It is proven that the presence of silver nanoparticles (5-20 μL) accurately accelerates the reaction rate of decreasing nitrophenol levels. When compared between the rated values of the reaction rate between the four other nanoparticle concentration variables, namely 5, 10, 15, and 20 μL, it can be known that the nitrophenol drop velocity sequence (sorted from fastest to late) occurs with the use of silver nanoparticles 15 μL > 20 μL ~ 10 μL > 5 μL.

The next stage is to study the influence of anions on the kinetics of 4-nitrophenol reduction. The addition of the selected catalyst is ten μL because it has the highest coefficient of determination value. Fig. 3 presents the result of a decrease in the concentration of 4-nitrophenol with the presence of inorganic anions. It is noticeable that the decreasing pattern is not very significant compared to the absence of inorganic anions.

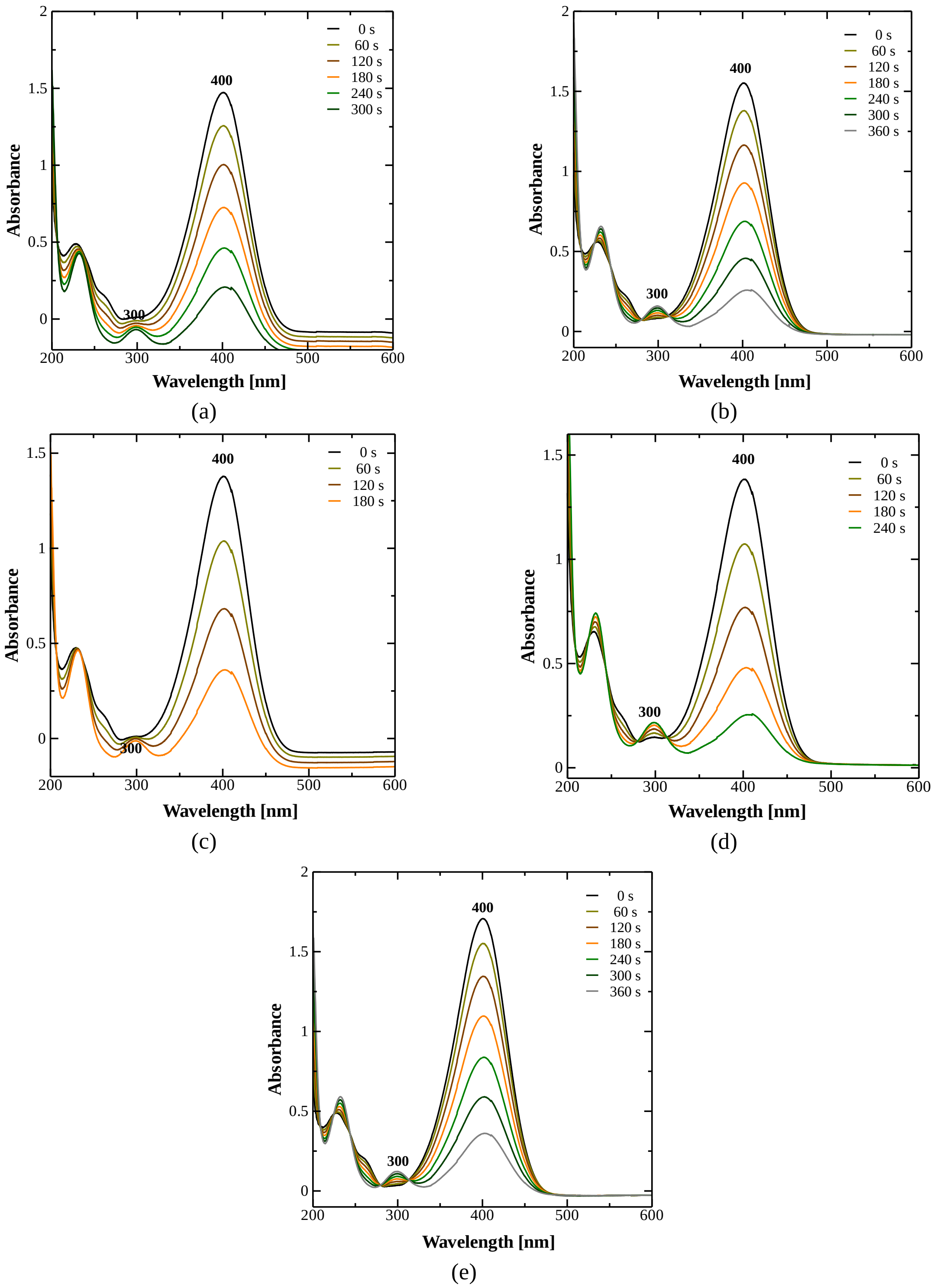

Fig. 3. A decrease in the concentration of 4-nitrophenol with the presence of (a) nitrate, (b) nitrite, (c) sulfate, (d) sulfite, and (e) carbonate ions

Table 2. The rated value of the reaction rate (k) of reducing 4-nitrophenol to 4-aminophenol

Anion	R^2	**Reaction Rate Constant**	
		k (minute $^{-1}$***)***	***Difference of k value with 0 μL (multiple times)***
without anions	0.9587	0.0084	
Carbonate	0.9366	0.0042	0.50
Nitrite	0.9356	0.0048	0.57
Nitrate	0.9187	0.0063	0.75
Sulfite	0.9665	0.0071	0.85
Sulfate	0.9690	0.0074	0.88

The data in Fig. 3. are processed based on first-order kinetics to obtain a consistent reaction rate. The results of the reaction rate constant presented in Table 2, the acquisition of information on the rated value of the reaction rate (k) confirms that the addition of inorganic anions into the mixed solution system will slow down the process of reducing 4-nitrophenol to 4-aminophenol. The order of nitrophenol drop velocity can be determined from the variable that gives the fastest to the slowest kinetic profile, namely the control variable ten μL > the sulfate variable > the sulfite variable > the nitrate variable > the nitrite variable > the carbonate variable. In this case, the catalytic ability of conjugated silver nanoparticles of black tea extract may decrease by 0.88 to 0.50 times when reduction 4-nitrophenols filled with anions in the aquatic environment, in particular carbonate, nitrite, and nitrate anions (a value of 0.88 obtained from the comparison of the k value on the sulfate anion variable to the ten μL control variable).

4. Conclusion

The presence of conjugated silver nanoparticles of black tea extract is able to increase the kinetics of the degradation reaction of 4-nitrophenol compounds to 85 times compared to without nanoparticles by changing the value of the reaction rate constant from 0.00006 to 0.0051. The presence of inorganic anions inside the reagent system will slow down 15 to 50 percent of the reaction rate of degradation of 4-nitrophenol by nanoparticles for 600 seconds, changing the value of the reaction rate constant from 0.0084 to 0.0042 (CO_3^{2-}), 0.0048 (NO_2^-), 0.0064 (NO_3^-), 0.0071 (SO_3^{2-}), and 0.0074 (SO_4^{2-}).

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