Green synthesis of gold nanoparticles supported in Al-pillared bentonite using aqueous leaf extracts of Dracaena angustifolia and their use for reductive degradation of methyl orange

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Abstract. We obtained the green synthesis of gold nanoparticles (AuNPs) using suji leaf extract (Dracaena angustifolia) and used the AuNPs to reduce methyl orange. The active substance in suji leaf extract was determined using phytochemical tests to identify components such as terpenoid, steroid, alkaloid, polyphenol, flavonoid, and saponin. The catalyst Al–bentonite@AuNP was prepared by immobilizing HAuCl₄ in Al-pillared bentonite, which was then reduced using various concentrations of suji leaf extract [0.1 %–1 % (w/v)]. The AuNPs were characterized using UV–vis spectroscopy and transmission electron microscopy, and the Al–bentonite@AuNP catalyst was characterized using Fourier transform infrared spectroscopy and X-ray diffraction. The application of Al–bentonite@AuNP as catalyst in the reductive degradation of methyl orange yields a degradation percent of up to 34.5 %.

1. Introduction
Indonesia has many mineral resources, such as bentonite, which is clay first discovered in Fort Benton, eastern Wyoming. The supply of bentonite in Indonesia is about 380 million tons, which constitutes an important national asset that must be well used [1].

Cations Na⁺ and Ca²⁺ in the interlayer of bentonite can be interchanged with the Al polycation through the pillarization process and after calcination, the latter of which opens the bentonite interlayer supported by alumina pillars. The resulting pillarized material has a relatively large surface area and interlayer distance, has uniform pores, and is not fluffy (i.e., it is non-swelling). This renders the pillared bentonite thermally stable and allows it to be used as a catalyst. Pillarization agents are already widely used in the pillarization process and so have a good structure and chemical composition that result in thermal stability and attractive acidic properties.

AuNPs are unstable and susceptible to agglomeration into larger particles, which would destroy their catalytic activity. AuNPs are immobilized in pillared bentonite, which increases their stability. AuNPs thus offer a higher catalytic activity, especially for reactions between organic compounds [2]. In this research, the Al–bentonite@AuNP catalyst forms through the immobilization of HAuCl₄ in Al-pillared bentonite, and the catalyst is reduced using Suji leaf extract (Dracaena angustifolia).

2. Experimental method
Two to three kilograms of Suji leaves were washed thoroughly with water and then dried in open air for 1 week. Once dried, they were crushed using a blender to produce a dry Suji leaf powder. Up to 50 g of Suji leaf powder was mixed with 250 mL of methanol in a beaker. The mixture was then macerated for 7 days, stirring twice per day for 15 min. We used a maceration filtrate partitioned with n-hexane to dissolve the non-polar substances with a ratio of 1:1. The mixture was partitioned using a funnel and agitated to separate the mixture into two fractions: a methanol fraction and an n-hexane fraction.
The n-hexane fraction was subjected to phytochemical tests, and the methanol fraction was collected and concentrated using a vacuum rotator evaporator at temperatures below 50 °C. This produced an extract of the concentrated methanol fraction, which was partitioned using water and ethyl acetate solvent p.a at a ratio of 1:1. The mixture was partitioned using a funnel and agitated to separate the mixture. This yielded two fractions: a water fraction and an ethyl acetate fraction. The ethyl acetate fraction was subjected to phytochemical tests, and the water fraction was collected and evaporated using a vacuum rotator evaporator at 40 °C—70 °C. The next section presents the results obtained from the concentrated extract from the water fraction.

A total of 200 g of natural bentonite was collected from Nanggung Village, Bogor, West Java, and was crushed, heated in an oven at 1100 °C for 2 h, and filtered using a 200 mesh sieve. The bentonite was characterized using Fourier transform infrared (FTIR) spectroscopy. The bentonite was fractionated as follows: A total of 100 g bentonite was placed in a glass beaker and mixed with 2000 mL of distilled water. The solution was stirred using a magnetic stirrer for 30 min and then allowed to stand for 5 min. The precipitate formed was separated by decantation. These deposits are called “fraction one” (F1). The supernatant was allowed to stand for 30 min, and the precipitate obtained is called “fraction two” (F2). F1 and F2 were dried in an oven at 110 °C for 3 h and then screened using a 200 mesh sieve and characterized using FTIR spectroscopy. A total of 50 g of bentonite F2 was suspended in 2 × 500 mL of 1 M NaCl and then stirred for 2 × 24 h at a temperature of 700 °C (the same treatment was repeated twice). Finally, F2 was aged for 12 h. The precipitate was washed with distilled water, and the result was decanted until free of Cl⁻ ions, as indicated by the absence white AgCl precipitate upon adding two drops of 1 M AgNO₃ to 10 mL filtrate. The precipitate was dried in an oven at 1100 °C for 3 h to obtain a constant weight. The precipitate Na–bentonite was crushed and sieved through a 200 mesh sieve, and then characterized using FTIR spectroscopy.

A solution of pillared Al was prepared by adding coconut water filtered into a solution of 0.1 M AlCl₃, and aging while stirring for 2 days. Pillarization was performed by slowly adding a solution of AlCl₃ to a 2 %-by-weight suspension of Na–bentonite (5 g of Na–bentonite in 250 mL aquabidest) and then stirring the mixture for 24 h. Then, the solids were separated from the solution, washed, dried, and sieved with a 200 mesh sieve. Al–bentonite was successfully synthesized and was characterized using FTIR spectroscopy.

Chloroauric acid (HAuCl₄) was prepared by dissolving 99.99 % gold (Au) in aqua regia (a mixture of 32 % HCl: HNO₃ = 3:1) at a temperature of 1200 °C. The crystals obtained were then dissolved twice in aquabidest at 1250 °C to vaporize the residual NO gas. The HAuCl₄ solution was diluted with aquabidest up to concentrations of 1.0×10⁻⁶ M, which is the stock solution. Up to 5 mL of the 1.0×10⁻⁶ M HAuCl₄ solution was added to 1 mL of the Suji leaf extract (EDS), with a variation of the extract concentration of 0.1%–1% (w/v). The reaction product was characterized using a UV–vis spectrophotometer and transmission electron microscopy. A total of 1.0 g of Al-BNT was mixed with 10 mL of 1×10⁻⁶ M HAuCl₄ and stirred for 4 h. To this mixture was added 3 mL of EDS solution, and the mixture was stirred under a reactor Na lamp for 2 to 3 h. The Al–bentonite@AuNP that formed was centrifuged and washed twice with distilled water and then dried in an oven at 110 °C for 12 h. The Al–bentonite@AuNP was characterized using X-ray diffraction and FTIR spectroscopy.

To a mixture of 50 mL of methyl orange solution (2.3×10⁻⁵ M) and 100 mL of NaBH₃ (0.5% w/v) was added various masses of Al–bentonite@AuNP (50, 40, 30, and 20 mg) in a cuvette volume of 3.5 mL. The total volume of the mixture was achieved by adding 3.2 mL of aquabidest. The absorbance was measured as a function of time (for 10 min) by UV–vis spectroscopy at 464 nm.

3. Results and discussion

The percent concentration of Suji leaf extract in the water fraction was determined by evaporating in an oven 1 mL fractions of water on a previously weighed watch glass. The total mass was calculated to obtain the mass of the extract, and the percent concentration of Suji leaf extract was calculated using equation (1).

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\%\text{[EDS]} = \frac{\text{Mass extract (g)}}{1 \text{mL}} \times 100\%.
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(1)
Figure 1. FTIR Spectrum of EDS.

Figure 2. UV–vis spectra of AuNPs for several EDS concentrations from 0.1 % to 1 %.

The calculated percent concentration of Suji leaf extract is 6.36%. Figure 1 shows an FTIR spectrum of the EDS fraction of water, which reveals the benzene ring aromatic group (1622 cm$^{-1}$), the $\text{-OH}$ group (3381 cm$^{-1}$), and the aliphatic CN group (1058 cm$^{-1}$), showing that alkaloids, polyphenols, tannins, and chloroauric acid (HAuCl$_4$) were prepared by dissolving 99.99% gold (Au) in aqua regia (mixture of 32% HCl: HNO$_3$ 65% = 3:1) at 120 °C. The elevated temperature aims to evaporate the residual acid that may interfere with the reading of the UV–vis spectrum. Aqua regia was used because it can dissolve 8A group metals such as gold. HNO$_3$ acts as an oxidant which oxidizes Au$^0$ to Au$^{3+}$, whereas HCl donates a Cl$^-$ ion as a ligand with Au$^{3+}$ to form the complex [AuCl$_4$]$^-$. This, in turn, binds to H$^+$ to form HAuCl$_4$. The complete reaction is as follows (equation (2)):

$$\text{Au(s)} + \text{HNO}_3(\text{aq}) + 4 \text{HCl(aq)} \rightarrow \text{HAuCl}_4(\text{aq}) + \text{NO(g)} + 2 \text{H}_2\text{O(g)}$$

(2)

A preliminary synthesis test of AuNP was performed by adding 9 mL of 10$^{-4}$ M HAuCl, with 1 mL of EDS in concentrations of 1 %, 0.1 %, 0.01 %, and 0.001 % in a vial bottle at room temperature. EDS at concentrations of 0.01 % and 0.001 % does not form AuNP (the solution remains pale yellow), whereas the concentrations of 1 % extract (purplish-red solution) and 0.01 % extract (faded red solution) do form AuNPs. To determine the optimum extract concentration, we prepared EDS concentrations of 0.1 %, 0.3 %, 0.5 %, 0.7 %, 0.9 %, and 1 %. The mixtures were allowed to stand for several days and were characterized by UV–vis spectroscopy (see the results in figure 2). The concentrations of 0.3 %, 0.5 %, 0.7 %, 0.9 %, and 1 % all form AuNPs in purplish-red solution, although the 0.3 % concentration precipitates at the bottom of the vial, and the 0.1 % concentration does not form AuNPs (the solution remains clear).
Figure 3. UV–vis spectra of several methyl orange concentrations

Figure 4. FTIR spectra of Na–bentonite and Al–bentonite.

The UV–vis spectra (figure 3) show that the 0.3% concentration has an absorbance peak at 0.317. Thus, we can conclude that 0.3% is the optimum concentration of the extract for forming AuNPs.

Pillarization of bentonite with Al increases the basal spacing so that other particles (AuNPs in this case) can be inserted into the bentonite interlayer. Pillar polycations were prepared using coconut water media to replace the NaOH used in previous studies because the polycations can reduce the toxicity of the waste from this experiment. Figure 4 shows the FTIR spectra of pillared bentonite (Na–bentonite) and Al–bentonite. Peaks appear in both spectra at almost identical wave numbers. The FTIR spectrum of Al–bentonite reveals peaks at 3626 cm$^{-1}$ (the OH group bonded to Si), 1634 cm$^{-1}$ (OH bending), 1052 cm$^{-1}$ (Si–O–Si strain), 793 cm$^{-1}$ (Si–O bending), and 524 cm$^{-1}$ (Al–O–Si bending). Thus, bentonite with Al is successfully pillared.

The absorbance $A$ as a function of molar absorptivity is given by equation (3):

$$A = \varepsilon bc,$$

(3)

where $\varepsilon$ is the molar absorptivity (M$^{-1}$cm$^{-1}$), $b$ is the cuvette thickness (cm), and $c$ is the concentration (M).

The molar absorptivity of methyl orange (MJ) was determined by measuring the UV–vis absorbance spectra of various concentrations of MJ (4.055, 3.055, 2.055, and 1.055 $\times$ 10$^{-5}$ M). Next, the absorbance is plotted as a function of concentration, and a fit to the resulting line gives $A = 8100c - 0.0505$ with a regression of 0.9995 (see figure 3). The molar absorptivity is the slope of the line, which gives $\varepsilon$(MJ) = 8100 M$^{-1}$cm$^{-1}$. 


To determine the catalytic activity of Al–bentonite@AuNP, we degrade MJ using NaBH₄, with Al–bentonite@AuNP as the catalyst. The degradation of MJ using 0.1 M NaBH₄ was performed using various masses of Al–bentonite@AuNP (50, 40, 30, 20, and 0 mg) as the catalyst. The mass of Al–bentonite@AuNP was varied to determine how it affects the degradation of MJ (see figure 5). The result shows that, with increasing catalyst mass, the absorbance of MJ decreases and the color changes from orange to faded yellow. In other words, more catalyst mass causes more degradation of MJ.

The rate constant for the degradation of MJ was determined by comparing pseudo-first-order and pseudo-second-order reactions. The reaction is assumed to be pseudo-first order because it only depends on the concentration of the reactant MJ, whereas NaBH₄ may be considered fixed. The regression ($r$) of the second equation of the reaction-rate law is used as a parameter to determine the order and the value of the degradation rate constant. A greater regression coefficient $r$ indicates a more appropriate reaction order. The regression plot assuming pseudo-first order gives $r = 0.9967$, whereas the regression plot assuming second order gives $r = 0.7695$.

These results show that the regression coefficient is closer to unity when we assume a pseudo-first-order reaction, indicating that the MJ degradation reaction follows a first-order rate law. The reaction rate constant $k$ expresses how quickly the reaction progresses, which reflects the efficacy of the catalyst. The results give a reaction rate constant of $0.4911 \text{ min}^{-1}$, which shows that Al–bentonite@AuNP is an effective catalyst for the degradation of MJ. Note that previous work in MJ degradation using AuNPs reported a reaction rate constant of $0.0049 \text{ min}^{-1}$ [3]. These results indicate that AuNPs synthesized using suji leaf extract and supported on Al-pillared bentonite (Al–bentonite@AuNP) have better catalytic activity.

4. Conclusions
We used a water fraction of suji leaf extract (EDS) as a reducing agent in the green synthesis of Au nanoparticles (AuNPs) and found that the optimal concentration of EDS is 0.3 %. The AuNP solution has an absorption maximum at $\lambda = 543$ to 553 nm. Al–bentonite catalyst @ AuNP can be used to degrade MJ by up to 34.5 % through a pseudo-first-order reaction with a rate constant of $0.4911 \text{ min}^{-1}$.

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References
[1] Riyanto A 1996 Bahan Galian Industri: Bentonite (Bandung: Pusat Pengembangan Teknologi Mineral (PPTM))
[2] Campbell C T, Sharp J C, Yao Y X, Karp E M and Silbaugh T L 2011 Faraday Discuss. 152 227–39
[3] Gupta N, Singh H P and Sharma R K 2011 J. Mol. Catalysis A: Chem. 335 248–52