

Development of a Rapid and Sensitive Probe for Colorimetric Detection of Ni²⁺ Ion in Water Sample by β -Cyclodextrin Stabilized Silver Nanoparticles

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Abstract: A rapid and selective colorimetric detection of Ni²⁺ was developed using silver nanoparticles (AgNPs) with β -cyclodextrin (β -CDs) as reducing and stabilizing agents. Characterization was assessed by spectrophotometer UV-vis, Fourier transform infra-red (FTIR), transmission electron microscopy (TEM), and particle size analyzer (PSA). The AgNPs- β -CDs were relatively stable after being stored for 5 months. The addition of Ni²⁺ to the AgNPs- β -CDs shifted the surface plasmon resonance (SPR) band at 409 nm. Synthesized AgNPs- β -CDs had a spherical shape and an average size of 25.07 \pm 0.66 nm (analyzed by TEM) and 33.63 \pm 0.25 nm, as confirmed by PSA. AgNPs- β -CDs as colorimetric sensors for Ni²⁺ ions had a good linear calibration curve at 409 nm with the R² value of 0.9993. The limit of detection (LoD) was found to be 33.30 ppb, while the limit of quantification (LoQ) was 111.0 ppb. This sensor had been applied to a seawater sample from Ancol Beach, North Jakarta, Indonesia and it exhibited good precision and accuracy. In this work, β -CDs-synthesized AgNPs were able to detect Ni²⁺ ions and were beneficial as an alternative method for Ni²⁺ screening in environmental samples.

Keywords: AgNPs; β -cyclodextrin; colorimetric sensor; Ni²⁺

■ INTRODUCTION

Nickel (Ni) has a wide range of applications in various fields, such as petroleum, coinage, textile, stainless steel manufacture, and printing. Due to being highly used, Ni has become a common contributor to water pollution. Ni²⁺ ion, a toxic environmental pollutant, harms aquatic ecosystems as well as human health. Therefore, Ni²⁺ presence in water is necessary to be detected. The detection of Ni²⁺ is developed through many techniques using several instruments, such as inductively coupled plasma optical emission spectrometry (ICP-OES) [1], atomic absorption spectrometry (AAS) [2], and UV-vis spectroscopy [3]. However, these methods are expensive,

time-consuming, and require trained personnel. Therefore, some alternative techniques have been developed to overcome the increasing demand for user-friendly and rapid metal detection [4]. A detection method based on nanoparticles as a colorimetric sensor offers more advantages than those methods due to their rapid, ease of use, affordability, and effectiveness in analyzing Ni²⁺ as a water pollutant [4-6].

Recently, silver nanoparticles (AgNPs) have been hugely studied for their applications as antibacterial agents [7-8], biosensors [9], catalysts [10-11], and colorimetric sensors [6,12-13]. AgNPs as colorimetric sensors have been an interesting topic to be developed

because they possess a unique characteristic, i.e., surface plasmon resonance (SPR). The SPR band of AgNPs was indicated by the appearance of a peak at 400–500 nm on UV-vis spectra and the yellow color of the solution [8,14]. Owing to this SPR characteristic, AgNPs have been widely used as an alternative method to detect Ni^{2+} based on the colorimetric assay. The change in SPR reflects the change in AgNPs' shape and size. The interaction occurring between AgNPs and Ni^{2+} will cause a change in AgNPs' shape and size as the SPR band and the color solution also change consequently [15].

Many works and studies report on various reducing and stabilizing agents used to prepare AgNPs these past years. Cyclodextrins (CDs) are water soluble and non-toxic cyclic oligosaccharides consisting of 6, 7, or 8 glucopyranose units (named as α -, β -, or γ -, respectively) linked by α -1,4 linkage [16]. β -CDs are commonly utilized in the synthesis of AgNPs due to their low cost compared to other CDs and their ability to have a dual role as both reducing and stabilizing agents simultaneously [17-21]. β -CDs have a toroidal shape with an inner cavity diameter of 0.78 nm [22]. The inner cavity of β -CDs acts as a host to form a stable inclusion complex with a guest molecule [16], while the hydroxyl groups of β -CDs exterior act as a reducing agent [19]. These abilities of β -CDs allow them to reduce and stabilize nanoparticles.

Previously, there have been studies about colorimetric sensors for Ni^{2+} ions from AgNPs that were synthesized by other capping agents. In this work, we synthesized AgNPs using β -CDs as a double role of reducing and stabilizing agents. This could reduce the excessive utilization of chemicals and make the synthesis procedure less time-consuming. The application of β -CDs as a stabilizing agent was investigated on the AgNPs stability over time. AgNPs- β -CDs were expected to be a rapid and sensitive colorimetric sensor for Ni^{2+} in real samples, in line with the SPR change when there was an interaction between AgNPs- β -CDs with Ni^{2+} that resulted in a change of color and particle size.

■ EXPERIMENTAL SECTION

Materials

Silver nitrate (AgNO_3), sodium hydroxide (NaOH),

nitric acid (HNO_3), iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3$), nickel(II) nitrate ($\text{Ni}(\text{NO}_3)_2$), magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$), chromium(III) nitrate ($\text{Cr}(\text{NO}_3)_3$), cobalt(II) nitrate ($\text{Co}(\text{NO}_3)_2$), palladium(II) nitrate ($\text{Pd}(\text{NO}_3)_2$), copper(II) nitrate ($\text{Cu}(\text{NO}_3)_2$), lead(II) nitrate ($\text{Pb}(\text{NO}_3)_2$), cadmium(II) nitrate ($\text{Cd}(\text{NO}_3)_2$), and tin(IV) chloride (SnCl_4) were purchased from Merck. Reducing and stabilizing agents β -CDs were supplied by Sigma Aldrich.

Instrumentation

The UV-vis spectra of samples were recorded by spectrophotometer UV-vis Agilent Cary 60 in the wavelength range of 200–800 nm. FTIR spectra were analyzed by Shimadzu IR Prestige 21 in the 400–4000 cm^{-1} range. Transmission electron microscope (TEM) Tecnai G2 20S-Twin Function was used to determine the morphology of AgNPs. The size of nanoparticles was examined using a particle size analyzer (PSA) Horiba LA-960. The content of Ni^{2+} in seawater samples was measured using atomic absorption spectroscopy (AAS) Agilent 280FS AA.

Procedure

Synthesis of AgNPs- β -CDs

The procedure of AgNPs- β -CDs synthesis was carried out under the optimum conditions as practised in our previous work [23]. AgNO_3 1.5×10^{-4} M was added to β -CDs 5.0×10^{-3} M as reducing and stabilizing agents at pH 12. The pH value of β -CDs was adjusted by adding NaOH 0.1 M. Each solution (5 mL) was mixed in a volume ratio of 1:1 and heated in a water bath at 98 °C for 5 min.

Stability test of AgNPs- β -CDs

The stability test was performed by having the AgNPs- β -CDs stored in the fridge at 4 °C for 5 months. The solution was next measured with a spectrophotometer UV-vis at room temperature, in the wavelength range of 200–800 nm.

Colorimetric response of AgNPs- β -CDs towards metals

Colorimetric response of AgNPs- β -CDs was investigated to several heavy metal ions, such as Fe^{3+} ,

Ni^{2+} , Mg^{2+} , Cr^{3+} , Co^{2+} , Pd^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , and Sn^{2+} . The detection of heavy metals was carried out by mixing AgNPs- β -CDs solution with 100 ppb heavy metal ion solution (1:1 volume ratio), then measured by spectrophotometer UV-vis at room temperature.

Other metal ion interference in the reaction of AgNPs- β -CDs with Ni^{2+}

By adding the inorganic matrix to the mixture of AgNPs- β -CDs and Ni^{2+} (AgNPs- β -CDs- Ni^{2+}), the interference test was determined. The AgNPs- β -CDs- Ni^{2+} solution was prepared by mixing 1 mL of AgNPs- β -CDs and 1 mL of 100 ppb Ni^{2+} . Then the solution was added by 1 mL of 100 ppb inorganic matrix solution (Fe^{3+} , Mg^{2+} , Cr^{3+} , Co^{2+} , Pd^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , and Sn^{2+}) and measured by spectrophotometer UV-vis. The AgNPs- β -CDs- Ni^{2+} solution which did not contain any matrix, was measured to compare the results.

Analytical performance

The calibration curve was plotted by putting the absorbance values at 409 nm versus the concentration of Ni^{2+} . The equation of $\text{LoD} = 3 \times \text{SD}/s$ and $\text{LoQ} = 10 \times \text{SD}/s$ were used to estimate the limit of detection (LoD) and the limit of quantification (LoQ), respectively, where SD is the standard deviation and s is the slope of the calibration curve. Repeatability and reproducibility were performed by analyzing the Ni^{2+} detection of AgNPs- β -CDs three times. The spiking method was done to investigate the

accuracy parameters. The determination of Ni^{2+} standard solution recovery value was determined in sea waters.

Application test to real samples

Seawater samples were collected from Ancol Beach, North Jakarta, Indonesia at three different spots. These samples were filtered with 0.45 μm filter paper and preserved with HNO_3 0.1 M until $\text{pH} < 2$ was reached. The mixture of AgNPs- β -CDs and sample (1:1 volume ratio) was measured by spectrophotometer UV-vis. While AAS measurement was used to analyze the sample as a comparison.

RESULTS AND DISCUSSION

Synthesis and Stability Test of AgNPs- β -CDs

AgNPs- β -CDs were formed through a redox reaction where Ag^+ was reduced to Ag^0 by OH groups of β -CDs. Simultaneously, the OH groups were oxidized to aldehyde and carboxyl groups [24]. The formation of AgNPs- β -CDs was confirmed by the yellow color solution and the SPR band at 412 nm with an absorbance intensity of 0.946 (as shown in Fig. 1). The size of produced AgNPs- β -CDs was relatively small as the SPR peak was sharp and narrow. Ndikau et al. [25] explained that the SPR sharpness depends on the size of nanoparticles. The size of AgNPs would be confirmed by the TEM and PSA analysis.

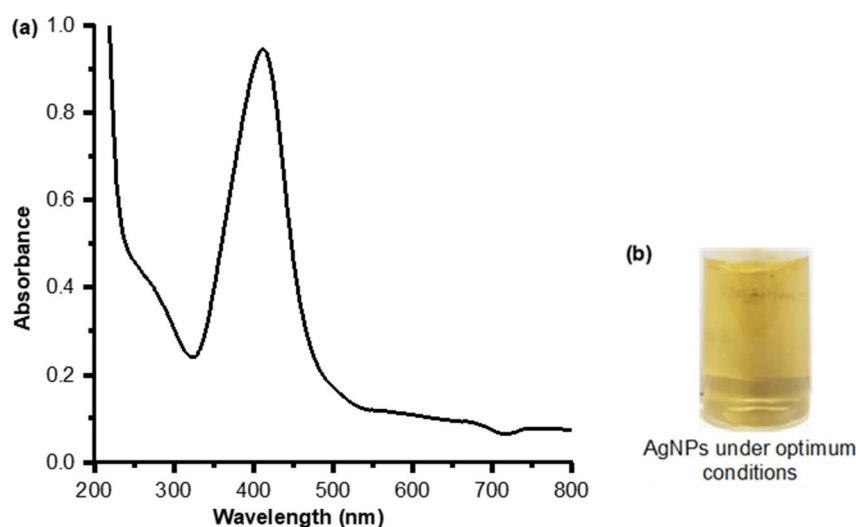


Fig 1. (a) UV spectra of AgNPs- β -CDs under optimum conditions (AgNO_3 1.5×10^{-4} M, β -CDs 5.0×10^{-3} M at pH 12, and 5 min of reaction time), and (b) the solution of AgNPs- β -CDs under optimum conditions

The stability of AgNPs- β -CDs was examined to describe the role of β -CDs as a stabilizing agent and to investigate its ability to stabilize silver nanoparticles over time. β -CDs were used as a stabilizing agent owing to their unique ability to form an inclusion complex with Ag so that the produced AgNPs- β -CDs were protected from heat, light, oxygen, and chemical reactions [26].

The AgNPs- β -CDs were stored in a capped bottle at 4 °C for 5 months. It was observed that there was no color change and no precipitate formed (Fig. 2). These factors showed that AgNPs- β -CDs were relatively stable after 5 months. The wavelength shift and increasing absorbance intensity could also be observed to study the AgNPs- β -CDs stability [27]. Fig. 2 showed the absorbance intensity increased by 0.036 (4.17%) due to the ongoing reduction process of Ag^+ to Ag^0 during the storage time. The wavelength of the SPR band did not go shift, but the peak was broadened after 5 months. It indicated that the AgNPs- β -CDs were slightly aggregated. However, it was considered that the AgNPs- β -CDs solution was still relatively stable after being stored for 5 months.

Colorimetric Response of AgNPs- β -CDs Towards Metals

An amount of 100 ppb solutions of some heavy metal ions such as Fe^{3+} , Ni^{2+} , Mg^{2+} , Cr^{3+} , Co^{2+} , Pd^{2+} , Cu^{2+} ,

Pb^{2+} , Cd^{2+} , and Sn^{2+} were tested to AgNPs- β -CDs to investigate the colorimetric response and then measured by spectrophotometer UV-vis. The UV spectra (Fig. 3(a)) showed that only Ni^{2+} caused a red shift from 409 to 414 nm and a decreasing absorbance of 0.095. The yellow color of the AgNPs- β -CDs solution also changed to greyish after being added by Ni^{2+} . Meanwhile, the other solutions were still the same. This color change happened within 5 s and was visible to the naked eye. As shown in Fig. 3(b), it was evidenced that the AgNPs- β -CDs could selectively detect the presence of Ni^{2+} ion rapidly compared to other ions.

Other Metal Ion Interference in the Reaction of AgNPs- β -CDs with Ni^{2+}

The interference test was assessed by spectrophotometer UV-vis which was carried out to determine the effect of other heavy metal ions on the AgNPs- β -CDs selectivity towards Ni^{2+} . As shown in Fig. 4, the absorbance intensity of AgNPs- β -CDs- Ni^{2+} 100 ppb did not significantly change after the addition of other heavy metal ions (100 ppb). It was evidenced that the AgNPs- β -CDs detection of Ni^{2+} was not affected by the presence of other heavy metal ions, which confirmed the good selectivity of AgNPs- β -CDs towards Ni^{2+} ion.

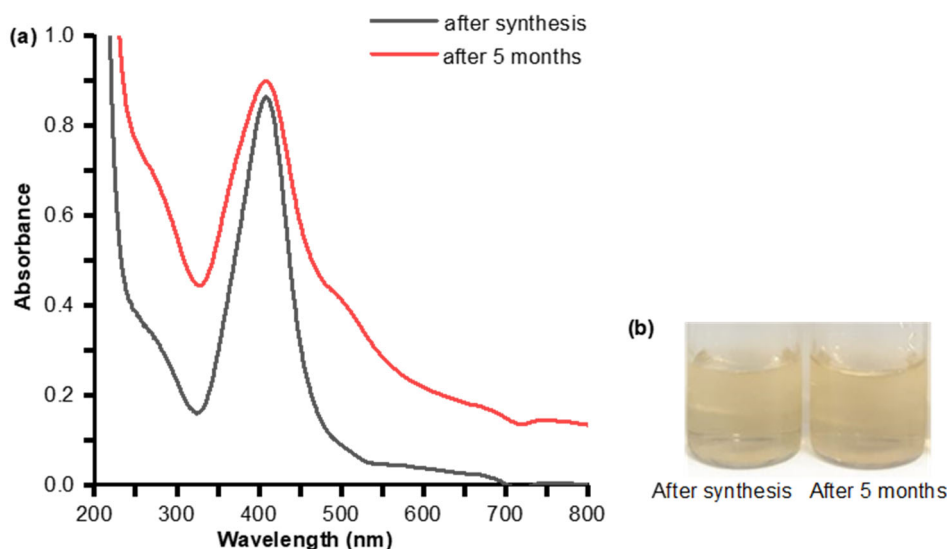


Fig 2. (a) UV spectra of AgNPs- β -CDs stability after 5 months, and (b) the solution of AgNPs- β -CDs after synthesis and after 5 months

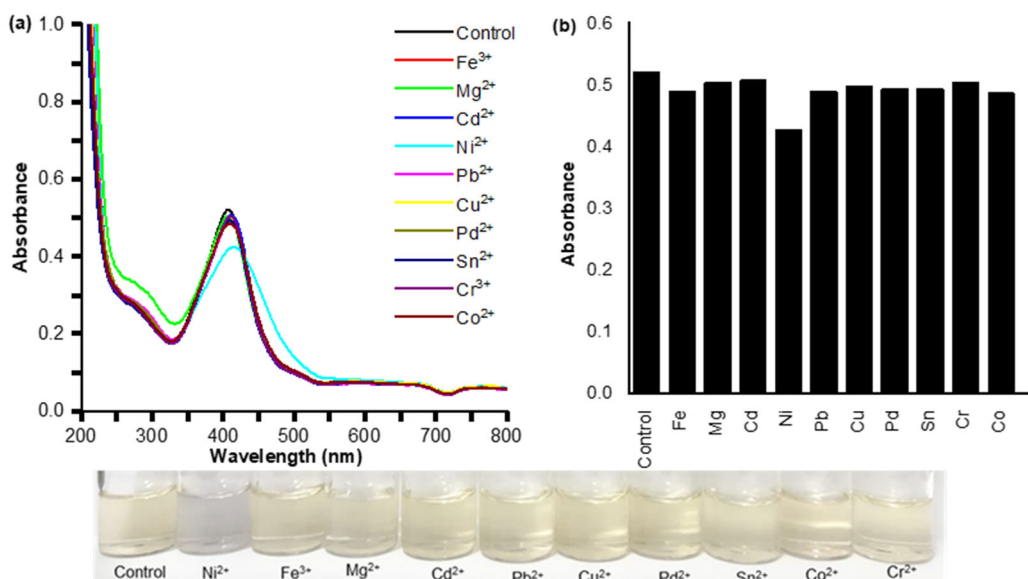


Fig 3. (a) UV spectra of AgNPs-β-CDs detection towards heavy metal solutions at a concentration of 100 ppb, and (b) AgNPs-β-CDs selectivity towards 100 ppb heavy metal solutions

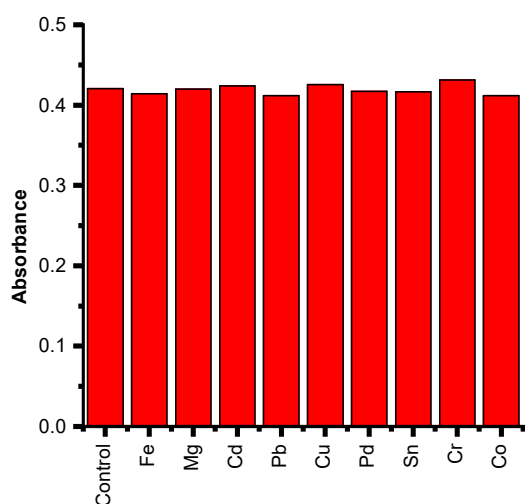


Fig 4. The bars representing the absorbance intensity of AgNPs-β-CDs-Ni²⁺ (409 nm) in the presence of 100 ppb of other heavy metal ions

Characterization

FTIR analysis

The addition of Ni²⁺ to AgNPs-β-CDs (AgNPs-β-CDs-Ni²⁺) showed the interaction between β-CDs and Ni²⁺ ion (Fig. 5 and Table 1). A peak at 3311 cm⁻¹ (AgNPs-β-CDs) was associated with O-H stretching, which was broadened and went shifted to 3348 cm⁻¹ in AgNPs-β-CDs-Ni²⁺ spectra. It explained that Ni²⁺ ion interacted with hydroxyl groups of β-CDs inner cavity [28]. There

was a peak attributed to CH stretching in AgNPs-β-CDs spectra at 2976 and 2918 cm⁻¹. Meanwhile, the ones in AgNPs-β-CDs-Ni²⁺ were shifted to 2922 and 2859 cm⁻¹. A weak peak at 1717 cm⁻¹ (AgNPs-β-CDs) and a strong peak at 1732 cm⁻¹ (AgNPs-β-CDs-Ni²⁺) were assigned to C=O stretching.

He et al. [28] revealed that Ni²⁺ interacted with the C-O bond of β-CDs, which caused a strong peak in AgNPs-β-CDs spectra (1051 cm⁻¹) change to a small peak

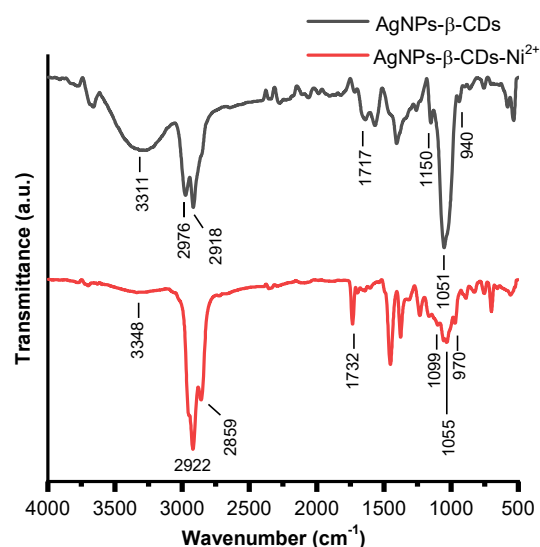
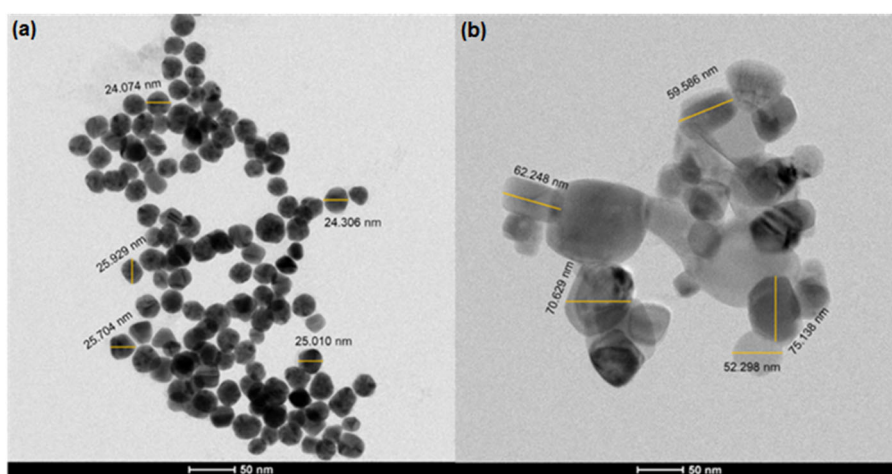


Fig 5. FTIR spectra of AgNPs-β-CDs and AgNPs-β-CDs-Ni²⁺

Table 1. Wavenumbers of AgNPs- β -CDs and AgNPs- β -CDs-Ni²⁺

AgNPs- β -CDs (cm ⁻¹)	AgNPs- β -CDs-Ni ²⁺ (cm ⁻¹)	Functional groups
3311	3348	O-H stretching
2976	2922	C-H stretching
2918	2859	C-H stretching
1717	1732	C=O stretching
1051	1055	C-O stretching
1150	1099	Asymmetrical C-O-C stretching
940	970	Symmetrical C-O-C stretching

**Fig 6.** The morphology and size of (a) AgNPs- β -CDs and (b) AgNPs- β -CDs-Ni²⁺ by TEM analysis

in AgNPs- β -CDs-Ni²⁺ (1055 cm⁻¹). There was an asymmetrical C-O-C stretching at 1150 and 1099 cm⁻¹ in the AgNPs- β -CDs and AgNPs- β -CDs-Ni²⁺ spectra, respectively. The peak corresponding to symmetrical C-O-C stretching appeared at 940 cm⁻¹ (AgNPs- β -CDs) and 970 cm⁻¹ (AgNPs- β -CDs-Ni²⁺).

TEM and PSA analysis

The synthesized AgNPs- β -CDs and AgNPs- β -CDs-Ni²⁺ were characterized by the TEM instrument. Fig. 6 revealed the morphology of AgNPs- β -CDs before and after interacting with Ni²⁺ ions. The average size of AgNPs- β -CDs was 25.07 ± 0.66 nm with a spherical shape (Fig. 6(a)). The addition of Ni²⁺ ion to AgNPs- β -CDs solution caused a size increase (with an average of 63.98 ± 8.09 nm) and particles to aggregate (Fig. 6(b)).

The size of formed AgNPs- β -CDs was confirmed by the PSA analysis. The measurement using PSA revealed that AgNPs- β -CDs had an average size of 33.63 ± 0.25 nm. Meanwhile, the AgNPs- β -CDs-Ni²⁺ was

73.43 ± 1.47 nm. There was an increasing size of particles after the addition of Ni²⁺ owing to the interaction between Ni²⁺ and AgNPs- β -CDs. The interaction led to aggregation because the SPR band got broadened and a red shift occurred [29-30]. The interaction of Ni²⁺ with AgNPs- β -CDs was illustrated in Fig. 7.

Ni²⁺ ion interacted with hydroxyl groups of β -CDs inner cavity through electrostatic interaction [28]. According to Kabbur et al. [31], Ni²⁺ ion had a size of 0.078 nm, and another study by Suárez-Cerda et al. [22] reported that the diameter of β -CDs inner cavity was 0.78 nm. Ni²⁺ ion had a smaller size than the inner cavity diameter of β -CDs, so Ni²⁺ could get into the β -CDs inner cavity and have interaction with the hydroxyl groups in line with FTIR data. It was also observed that the inner cavity of β -CDs had a negative charge due to complete deprotonation at pH 12, thus, the interaction was stronger as the Ni²⁺ ion had positive charges.

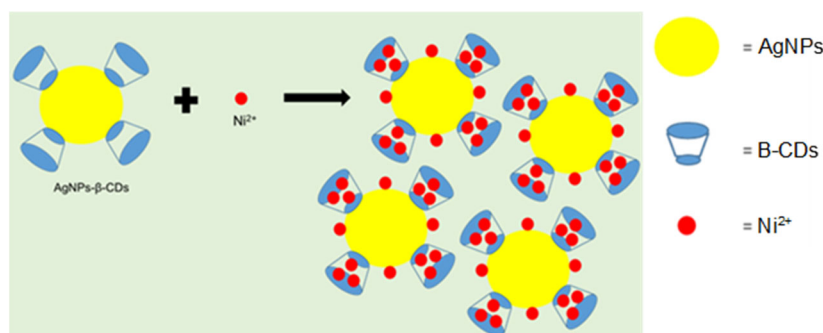


Fig 7. The illustration represents the interaction that happened between AgNPs-β-CDs and Ni²⁺

Analytical Performance

Linearity

The calibration curve linearity was carried out to evaluate the performance of colorimetric sensor AgNPs-β-CDs in detecting Ni²⁺ ions. Spectrophotometer UV-vis was used to measure the change of absorbance intensity at 409 nm. The difference between the initial absorbance intensity of AgNPs-β-CDs and the decreased absorbance intensity of AgNPs-β-CDs after Ni²⁺ addition was calculated to obtain the change of absorbance intensity (Δ_{Abs}). The Δ_{Abs} versus Ni²⁺ at a concentration of 100–500 ppb was plotted as a calibration plot (Fig. 8). The increasing concentration of Ni²⁺ led to an increased Δ_{Abs} as the SPR band was changed. The linearity equation obtained from the calibration curve was $y = 0.0002x - 0.0106$ with a correlation coefficient (R^2) of 0.9993. It proved that the R^2 obtained was categorized as a good linear regression value as the R^2 was ≥ 0.997 . The concentration level of Ni²⁺ in water samples could be determined by the linearity equation obtained. From the

dynamic linear range of the calibration curve, it also obtained the LoD value of 33.30 ppb and the LoQ of 111.00 ppb.

Table 2 shows the comparison between Ni²⁺ sensors using AgNPs-β-CDs and AgNPs with other stabilizing agents. AgNPs-β-CDs had more advantages than the previous studies [12,32-34], i.e., lower detection limit and the rapid colorimetric response towards Ni²⁺

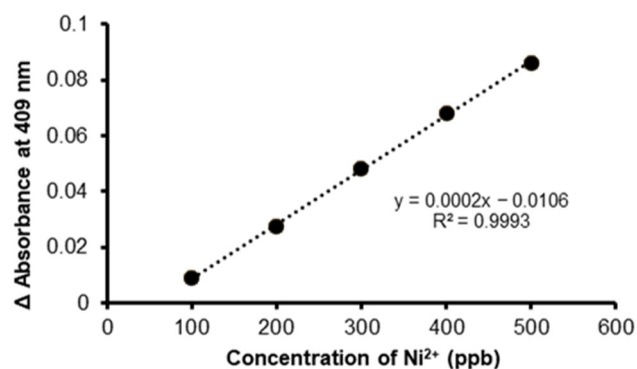


Fig 8. Calibration plot of AgNPs-β-CDs Δ_{Abs} at 409 nm versus the concentration of Ni²⁺

Table 2. The data comparison of AgNPs-β-CDs and various AgNPs as colorimetric sensors for Ni²⁺

Stabilizing agents	Samples	Analysis time (min)	LoD (ppb)	References
3-mercapto-1-propanesulfonic acid sodium salt (3MPS)	-	5	500	[12]
Citrate	Tap water	1	44.250	[32]
3,6-di(pyridin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine (H ₂ pytz)	-	2	554.6	[33]
Adenosine monophosphate and sodium dodecyl sulphonate	Tap water and lake water	5	35.4	[34]
β-cyclodextrin	Sea water	<1	33.30	This research

Table 3. The repeatability and reproducibility of AgNPs- β -CDs at 409 nm

Ni ²⁺ (ppb)	SD	Repeatability		Reproducibility	
		%RSD		%RSD	
		AOAC	Horwitz	AOAC	Horwitz
100	0.000168	0.031294	1.000000	3.288019	1.000000
200	0.000900	0.172146	0.900929	0.442867	0.900929
300	0.000582	0.116802	0.847591	0.450230	0.847591
400	0.000493	0.107833	0.811673	8.311422	0.811673
500	0.000520	0.119042	0.784864	8.460454	0.784864

Table 4. The accuracy of AgNPs- β -CDs for detecting Ni²⁺ in seawater samples

Samples	Spiked (ppb)	Detected (ppb)	Accuracy (%)
Sample I (1.33 ppb)	250	252.31	100.39
Sample II (1.33 ppb)	250	272.91	108.63
Sample III (1.33 ppb)	250	227.14	90.32

less than 1 min. It proved that this research developed a Ni²⁺ colorimetric sensor which provided a better sensitivity and more rapid detection.

Repeatability and reproducibility

The precision method of the Ni²⁺ colorimetric sensor using AgNPs- β -CDs was determined by examining the repeatability and reproducibility. Repeatability was performed where the measurement of absorbance intensity was done in triplicates at 409 nm on the same day, under the optimum conditions. Reproducibility was carried out by measuring the absorbance under the optimum conditions at 409 nm on 3 different days. The %RSD results of both repeatability and reproducibility (Table 3) were lower than the maximum acceptable %RSD according to AOAC (15%) and Horwitz (22.6%) for the Ni²⁺ concentration level of 100 ppb [35]. It was evidenced that AgNPs- β -CDs as Ni²⁺ colorimetric sensors gave acceptable precision results.

Accuracy

The accuracy test was determined by measuring 3 different seawater samples spiked by 250 ppb Ni²⁺ standard solution with a spectrophotometer UV-vis. The results were stated as %Recovery. Table 4 enlisted the recovery value of Ni²⁺ in the seawater samples at the range of 90.32–108.63%. González et al. [35] revealed that the acceptable %Recovery range of 250 ppb Ni²⁺ concentration level was 80–110%. It was implied that the colorimetric sensor of Ni²⁺ using AgNPs- β -CDs could give

Table 5. The results of Ni²⁺ concentration in seawater samples (n = 3)

Samples	AgNPs (ppb)	AAS (ppb)
Sample I	19.95	20
Sample II	19.95	20
Sample III	19.95	20

accurate results as the obtained recovery values were lower than the maximum acceptable percentage.

Application Test to Real Samples

AgNPs- β -CDs as a Ni²⁺ colorimetric sensor were applied to seawater samples collected from Ancol Beach, North Jakarta, Indonesia at three different points. It was performed to assess the Ni²⁺ concentration in the samples. Those samples were filtered by a 0.45 μ m filter paper and preserved by HNO₃ until pH < 2. The measurement with AAS was carried out to compare the Ni²⁺ concentration results.

Table 5 shows the measurement results of Ni²⁺ concentration using AgNPs- β -CDs and AAS. AgNPs- β -CDs as colorimetric sensors provided good results compared to AAS. These data proved that AgNPs- β -CDs could be applied as a colorimetric sensor for Ni²⁺ in seawater samples.

CONCLUSION

This current work inferred that β -CDs as reducing and stabilizing agents could form relatively stable

AgNPs- β -CDs after 5 months. AgNPs- β -CDs as a rapid and selective colorimetric sensor for Ni²⁺ was successfully developed, which was indicated by the yellow color of the solution turning into greyish. This sensor could exhibit good performance as the R² of the linear calibration curve obtained was 0.9993 with an LoD value of 33.30 ppb and an LoQ value of 111.0 ppb. No interference of other ions affected the detection. Furthermore, the precision and accuracy were satisfying for the measurement of Ni²⁺ in seawater. Hence, this sensor could be beneficial for the detection of Ni²⁺ ions in real water samples.

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■ AUTHOR CONTRIBUTIONS

Farrah Nurkhaliza: data curation, investigation, formal analysis, writing-original draft; Ahmad Fathoni: investigation, validation, supervision; Muhammad Eka Prastya: validation, methodology, supervision; Zetryana Puteri Tachrim: validation, supervision; Abdul Aji: validation, supervision; Agustina Sus Andreani: conceptualization, formal analysis, funding acquisition, investigation, methodology, supervision, validation, writing-review & editing.

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