

Development of a colorimetric sensor based on tapioca starch and gold nanoparticles for the detection of cadmium residues in fish products

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Summary

Fish is consumed by many people around the world. However, fish may contain various pollutants such as heavy metals like mercury, cadmium, lead, iron, copper and nickel, with Cd being one of the most toxic elements. Therefore, this work focused on the development of a sensitive and selective colorimetric detection using a film of tapioca starch and gold nanoparticles (TS-AuNP) in the presence of Cd in fish. The detection mechanism was based on the aggregate formation between AuNP and Cd, associated with a colour change from red to purplish grey. The detection limit was $13.21 \text{ mmol}\cdot\text{l}^{-1}$ and the response was linear in the range from $6 \text{ mmol}\cdot\text{l}^{-1}$ to $12 \text{ mmol}\cdot\text{l}^{-1}$ ($R^2 = 0.9935$). The limit of quantification was calculated to be $40.04 \text{ mmol}\cdot\text{l}^{-1}$. Notably, the biodegradable film was successfully used for the determination of Cd in seven different fish species. These results show that the developed biodegradable film was successful in detecting the presence of Cd in fish samples.

Keywords

heavy metal; cadmium; gold nanoparticles; biodegradable film; colorimetric sensor; fish

Cadmium (Cd) is one of the most dangerous heavy metals classified as a grade I carcinogen by the International Agency for Research on Cancer [1]. Even at low contents, cadmium can harm the environment and human health. It has bioaccumulation qualities, which means that it accumulates in living organisms like marine critters or plants. Cd is a rare element in the Earth's crust with a content of $0.10\text{--}0.15 \text{ mg}\cdot\text{kg}^{-1}$ and $1.1 \times 10^{-4} \text{ mg}\cdot\text{kg}^{-1}$ in the oceans. Cd can pass to fish in water or sediment in marine life, thus entering the food chain and posing a threat to humans [2]. The contamination by Cd has become a global issue in the aquatic environment due to its bioaccumulation and biomagnification capabilities. When marine species ingest Cd from their food and the environment, it builds up in their bodily tissues over time, and the content of Cd increases and multiplies as it passes

through each link in the food chain. Agency for Toxic Substances and Disease Registry (ATSDR) reported [3] that the Cd exposure increased in 2008 among persons who regularly consume fish and shellfish. Furthermore, anthropogenic activities like metal mining, industrial processing and waste disposal are among the leading contributors that release heavy metals into the atmosphere via the soil, water and air [3].

Cd is easily absorbed by the human body and will build up primarily in the liver and kidney, impairing renal intake and lung inhalation. It will also accumulate in various organs between the ages of 10 and 35 [4]. Due to mobility qualities and chemical similarity to calcium in charge and ionic radius enable also its replacement [5]. In Japan, an epidemic of Itai-Itai disease caused by Cd toxicity in the contaminated Jinzu River basin

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of Toyama in the early twentieth century took place. The main symptom of the illnesses is renal tubular dysfunction, bone softening caused by vitamin D deficiency or osteomalacia, and osteoporosis, which are caused by competition with calcium and other nutrients. The toxicity of Cd has been associated with carcinogenic consequences such as breast and lung cancer, heart failure and congenital impairment, which lead to genetic anomalies [5, 6]. Hence, assays with excellent selectivity, sensitivity and speed are necessary.

Several methods such as gas chromatography-mass spectrometry, high-performance liquid chromatography, supercritical fluid chromatography or capillary electrophoresis are commonly used due to their great sensitivity and accuracy. However, these methods require costly equipment and/or are cumbersome and time-consuming, necessitating the use of large, expensive analytical instruments and skilled operators [7].

Colorimetric techniques have gained popularity in recent years because of their ability to provide on-the-spot detection of Cd using only naked eye, without any special equipment, while also being cost-effective and convenient. Gold nanoparticles (AuNP) are recommended for colorimetric sensors over other metal nanoparticles because of their high extinction coefficient, strong surface plasmon resonance (SPR) absorption in the visible wavelength spectrum and increased sensitivity of colour-tunable optical properties [8, 9]. The interaction between analytes of interest and sense elements is essential to acid-base interactions, hydrogen bonding, dipolar and multipolar contacts, molecule complexation and van der Waals interactions [10].

Colloidal gold, also known as AuNP, is a remarkably stable nanomaterial that has been used by researchers all over the world. Generally, the diameter of AuNP particles ranges from 1 nm to 100 nm [11]. AuNP is widely used in electronic devices, environmental monitoring, biomedicine and food safety for screening due to its unique physico-chemical properties. Regarding the SPR properties of AuNP, its maximum characteristic absorption peak wavelength shifts in the UV-visible region with changes in particle size, morphology and interparticle distance, which accompanied by a colour change [12].

In the field of biosensing technology, natural polymers such as tapioca or maize starch are commonly used in the form of a sensing film due to their biodegradability and film-forming properties, as well as their availability, accessibility and low cost compared to other natural polymers. The mechanical properties of starch films are mainly de-

termined by their content, as they are composed of amylose and amylopectin, where amylose contributes to good film-formation properties [13]. In this study, a simple, straightforward, and rapid colorimetric method for detecting cadmium ions (Cd^{2+}) using AuNP was designed to detect Cd^{2+} in the fish samples. The tapioca starch (TS) film was used as a carrier for the colorimetric reagent to enable the on-site detection. The detection process was based on the affinity level of the heavy metals towards AuNP. The reaction of chloroauric acid with sodium citrate resulted in the aggregation of AuNP, led to the formation of negatively charged AuNP on the surface and remained dispersed in the solution after being stabilized by citrate ions. The sensing mechanisms of AuNP with Cd is based on electrostatic interaction where Cd ions (with a charge of +2) exert an attractive force on the negative surface of gold nanoparticles. The stability of the solution is weakened when Cd is mixed with the AuNP solution by an agitation process, resulting in a purplish-grey colouration of the solution

MATERIALS AND METHODS

Materials

Chloroauric acid (HAuCl_4), sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, $\geq 99.0\%$), gold (III) chloride trihydrate ($\text{HauCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$), cadmium (99.5%), nickel (99.7%), iron ($\geq 99.99\%$), mercury ($\geq 99\%$), copper (99.999%), and lead (99.95%) were obtained from Sigma-Aldrich (St. Louis, Missouri, USA).

Tapioca starch (TS) was obtained from a supermarket in Kota Kinabalu (Malaysia). All solutions were freshly prepared for analysis using ultrapure water.

Preparation of gold nanoparticles

AuNP solutions were prepared by general reduction of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ from HAuCl_4 according to TAN and LEE [14] with some modifications. About 200 ml HAuCl_4 solution (approximately $10 \text{ mg} \cdot \text{l}^{-1}$, prepared from $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was reduced with 4.0 ml $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ solution ($10 \text{ g} \cdot \text{l}^{-1}$). After vigorous stirring, the solution was boiled at 150°C . The solution was heated continuously for approximately 30 min until a colour change from yellowish to wine-red was observed.

Preparation of tapioca starch with gold nanoparticles film

The biodegradable film was prepared following a method of WONGNIRAMAİKUL and LIMSAKUL

[15] with slight modifications. An approximately 0.5 g of TS in 10 ml of distilled H₂O was heated on a hot plate at 100 °C. The solution was stirred continuously until the solution became viscous and clear. After the solution cooled to room temperature (approximately 25 °C), AuNP solution was mixed into TS solution in a 1:1 ratio and stirred continuously until a homogenous solution was formed. Approximately 100 µl of it was transferred to the cap of a 1.5 ml snap-on microtube and dried in an oven at 70 °C for 30 min. The thin wine-red film was obtained for further analysis.

Characterization of film

Morphological properties

The surface of TS and TS-AuNP films was characterized using scanning electron microscopy (SEM) with FEI Quanta 200 FEG (Krefeld, Germany) instrument [16].

Mechanical properties

Thickness (d) of the films was measured using a micrometre (Wilkens-Anderson, Chicago, Illinois, USA). Five random measurements were taken and the mean was calculated.

Density (D) of the film was calculated by taking thickness (d), mass (m) and area (A) of the film using Eq. 1:

$$D = \frac{m}{A \cdot d} \quad (1)$$

Physicochemical properties-

The film was weighed (W_0) and oven-dried at 105 °C for 24 h and then weighed again (W_1). Then, the dried films were immersed in 30 ml of distilled water and allowed to stand for 24 h at room temperature (approximately 25 °C). The swollen films were then filtered and weighed (W_2). The final weight (W_3) was determined after the films were oven-dried again for 24 h at 105 °C.

The moisture content (MC), swelling power (SP) and solubility (S) of the films were calculated using the following equations:

$$MC = \frac{(W_0 - W_1)}{W_0} \times 100 \quad (2)$$

$$SP = \frac{(W_2 - W_1)}{W_1} \times 100 \quad (3)$$

$$S = \frac{(W_1 - W_3)}{W_1} \times 100 \quad (4)$$

For the biodegradability test, the films with initial dry weight (W_i) were placed in a container and covered with soil at a depth of 2 cm from the surface. The test was performed after 7, 14 and

21 days to obtain a final weight (W_f). The biodegradability rate (B) was calculated using the following formula and expressed in percent:

$$B = \frac{(W_i - W_f)}{W_i} \times 100 \quad (5)$$

Sensitivity of cadmium detection

Cadmium powder at 6–12 mmol·l⁻¹ reacted with TS-AuNP film. A UV-Vis spectrophotometer λ35 (Perkin Elmer, Waltham, Massachusetts, USA) was used to measure the colour changes of these solutions at 400 nm to 800 nm. The absorption spectra were recorded and the calibration curve was constructed. The limit of detection (LOD) and limit of quantification (LOQ) were calculated using the following equations, where σ is the standard deviation and S is the slope of the calibration curve [17]:

$$LOD = \frac{3\sigma}{S} \quad (6)$$

$$LOQ = \frac{10\sigma}{S} \quad (7)$$

Colour analysis

The visible colour was evaluated by combining three primary colours in various proportions of red (R), green (G) and blue (B). A Galaxy smartphone (Samsung, Seoul, South Korea) with applications ON Color Measure v. 8.0 (PotatootreeSoft, sine loco) and Color Lab (H&H Color Lab, Raytown, Missouri, USA) were used for the RGB analysis. For image analysis and photo retouching, free software XnView (XnSoft, Reims, France) and ImageJ (National Institutes of Health, Bethesda, Maryland, USA) running on a normal personal computer were utilized, respectively. A device with an RGB sensor (TCS34725, RGB Sensor, Adafruit Industries, New York, New York, USA) was utilized to gather the RGB values. For data collection and manipulation, this device was attached to a single-board Arduino Uno microcontroller (Arduino, Turin, Italy). The white, high-brightness LED in this sensor emits light and illuminates the surface being targeted. The detector measures the amount of light that is transmitted by this surface. The photodiodes in this sensor are arranged in a 4×3 array, with filters on each pair of 3 diodes for the R, G and B hues. Due to this, the hue angle (H) was determined using the three separate equations (Eq. 8–10).

$$H_R = \frac{(A_G - A_B)}{(R_{max} - R_{min})} \quad (8)$$

where H_R is hue angle of red, A_G is absorbance

of green, A_B is absorbance of blue, R_{max} is maximum absorbance of red and R_{min} is minimum absorbance of red.

$$H_G = 2 + \frac{(A_B - A_R)}{(G_{max} - G_{min})} \quad (9)$$

where H_G is hue angle of green, A_B is absorbance of blue, A_R is absorbance of red, G_{max} is maximum absorbance of green and G_{min} is minimum absorbance of green.

$$H_B = 4 + \frac{(A_R - A_G)}{(B_{max} - B_{min})} \quad (10)$$

where H_B is hue angle of blue, A_R is absorbance of red, A_G is absorbance of green, B_{max} is maximum absorbance of blue and B_{min} is minimum absorbance of blue.

Statistical analysis

All data were presented as mean \pm standard deviations and analysed using SPSS version 25.0 (IBM, Armonk, New York, USA). One-way analysis of variance (ANOVA) was used to assess differences in total Cd concentration in seven fish species, followed by a post-hoc Tukey's test. ANOVA was performed at a 5% level ($p < 0.05$) to test for significant differences between samples [18].

RESULTS AND DISCUSSION

TS and TS-AuNP films were successfully prepared on the cap of a 1.5 ml snap-on microtube as shown in Fig. 1A and Fig. 1B. TS was selected as a natural biodegradable film because it helped

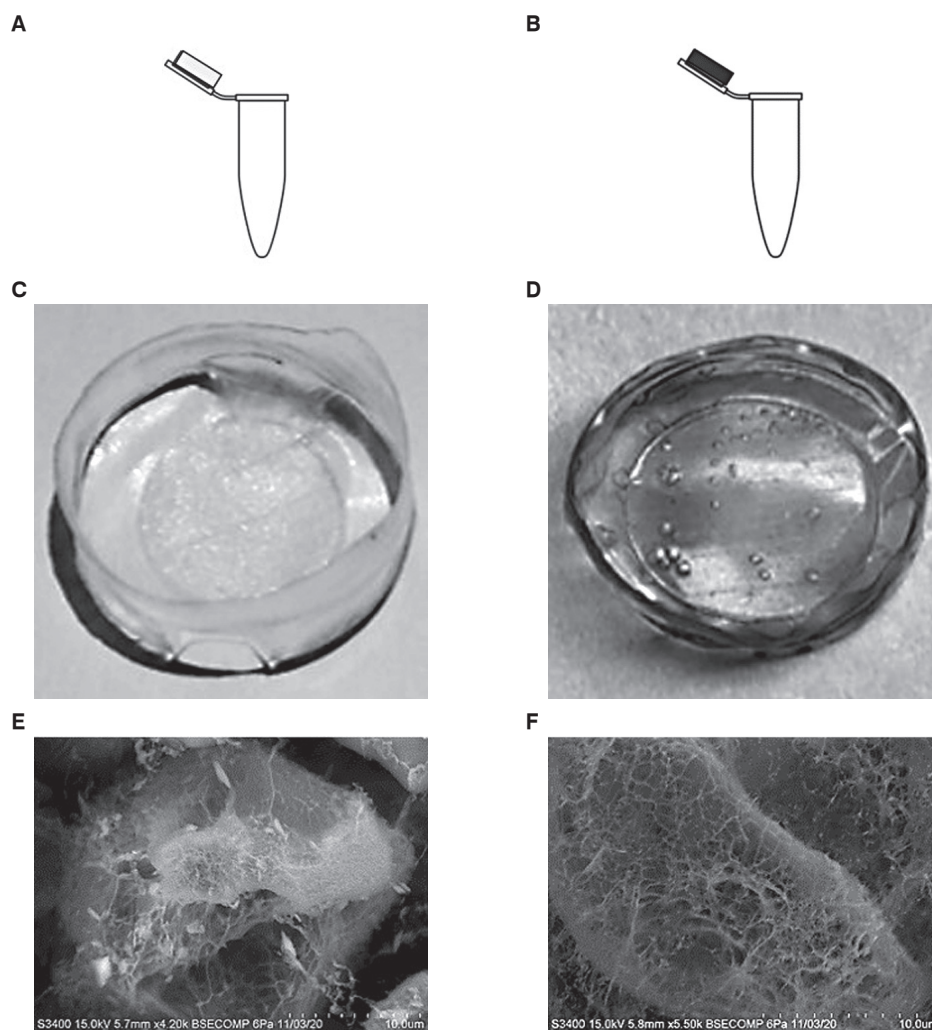


Fig. 1. Schematic diagram and scanning electron microscopy images of film.

A – illustration of tapioca starch film on a cap, B – illustration of tapioca starch-gold nanoparticles film on a cap, C – tapioca starch film, D – tapioca starch-gold nanoparticles film, E – SEM image of tapioca starch film (magnification $\times 4.2$) and F – SEM image of tapioca starch-gold nanoparticles film (magnification $\times 5.5$).

Tab. 1. Physical properties of the films.

Parameter	Tapioca starch	Tapioca starch with gold nanoparticles	<i>p</i> -value
Thickness [mm]	0.023 ± 0.006 ^a	0.043 ± 0.006 ^b	0.013
Density [g·cm ⁻³]	74.370 ± 0.350 ^a	38.930 ± 1.330 ^b	0.001
Moisture content [%]	0.1 ± 0.1 ^a	0.8 ± 1.0 ^b	0.294
Swelling power [%]	4.0 ± 0.8 ^a	5.0 ± 0.4 ^a	0.126
Solubility [%]	0.3 ± 0.1 ^a	0.4 ± 0.3 ^a	0.723

Values represent mean value ± standard deviation. Different superscript letters (in row) indicate significant difference at $p < 0.05$ ($n = 3$).

to form a clear TS film (Fig. 1C), while a cloudy film was provided by maize starch [15]. Therefore, TS was selected as the carrier for the colorimetric reagent, which consists of AuNP. The incorporation of TS and AuNP resulted in a slightly red-wine film, as shown in Fig. 1D. Size, surface composition and morphological properties of TS film and TS-AuNP film were analysed by SEM as shown in Fig. 1E and Fig. 1F. The SEM images showed that TS had a smooth surface, while the film with AuNP had a homogenous surface with multiple aggregates.

Mechanical properties

The incorporation of a colorimetric reagent affects the thickness of biodegradable films. As a result, it can significantly affect the physico-chemical properties and stability of the films. As presented in Tab. 1, the results showed significant differences ($p < 0.05$) in thickness between TS film and TS-AuNP film. According to the results, the incorporation of AuNP caused a slight increase in the thickness of TS-AuNP film compared to TS film. Meanwhile, the density of both films could be calculated based on the obtained thickness. The calculated density also showed a significant difference ($p < 0.05$) between TS and TS-AuNP films. The added AuNP caused the differences in the density of both films in the developed film, which reduced their density.

Physico-chemical properties

Moisture content (*MC*), swelling power (*SP*) and solubility (*S*) of the film are essential as they contribute to the biodegradability of the films [19]. Based on Tab. 1, there were no significant differences ($p > 0.05$) in physico-chemical properties between TS film and TS-AuNP film. TS-AuNP film showed increased *MC*, *SP* and *S* compared to TS film. The study indicated that incorporating AuNP in the starch film resulted in a significant increase in *MC*, *SP* and *S* of film. These results were

related to the increase in the film's hydrophilicity caused by AuNP and their ability to form a stable colloidal suspension in water [20].

The soil degradation process analysed the biodegradability test of TS film and TS-AuNP film after 21 days. Generally, the process of biodegradation is assisted by the microorganisms and microflora present in the soil, such as fungi, bacteria and protozoa [21]. Both films showed significantly increased *B* ($p < 0.05$) after 21 days. This result indicates that the films were biodegradable and the materials in the film can be released into the soil. Tapioca can also act as a carbohydrate source for the microflora present in the soil and help to rapidly degrade the films. In addition, an increase in water absorption by AuNP also leads to degradation of the films [21].

Selectivity test

As presented in Fig. 2, Cd showed a significant colorimetric response towards AuNP compared to other metal ions, as a significant increase in the absorption was observed at a wavelength of 620 nm. Hg^{2+} showed no noticeable changes. Meanwhile, the colour of AuNP upon adding Pb^{2+} changed from red-wine to violet with a slight increase in absorption, compared to Cd^{2+} , at 549 nm. Fe^{2+} provided similar colour changes from red-wine to purplish-grey. Ni^{2+} absorption spectrum had a maximum at 615 nm with colour changes from wine-red to grey.

Colour analysis

The RGB colour model was developed based on Maxwell's colour theory and was based on three primary colours: red, green, and blue [22]. The colour of the films changed from red to purplish-grey by tapioca starch-gold nanoparticles films reacting with Cd solutions. Theoretically, as the concentration of Cd solution increases, the hue angle decreases and the colour becomes darker, as shown in Tab. 2.

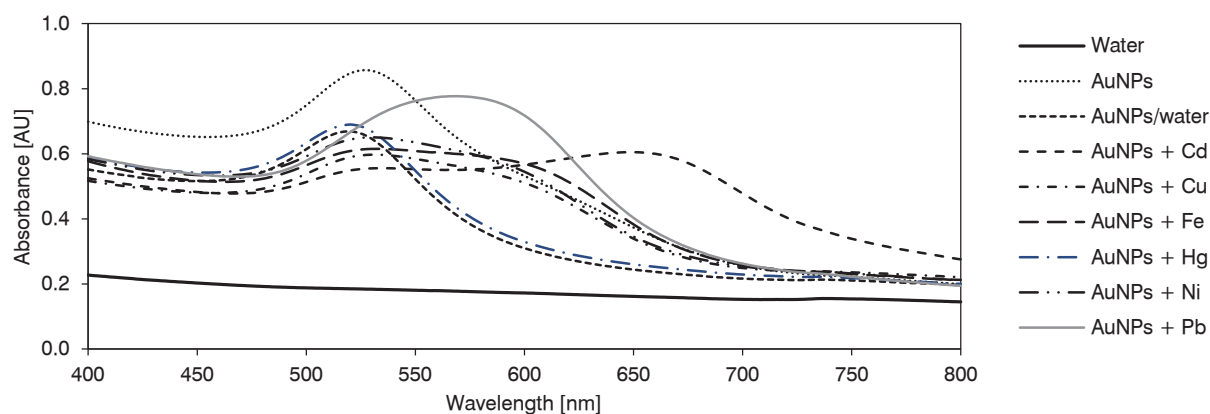


Fig. 2. Absorption spectra of different of heavy metals.
AuNPs – gold nanoparticles.

Tab. 2. Colour of the detection system at various cadmium concentrations.

Cd concentration [mmol·l ⁻¹]	Hue angle [°]	Colour description
6	300.0	Granite grey
7	283.3	Grey
8	296.0	Purplish-grey
9	350.0	Purplish-grey
10	283.3	Purplish-grey
11	283.3	Purplish-grey
12	285.9	Purplish-grey

Tab. 3. Cadmium concentration in fish samples found in various fish samples.

Fish sample	Cd concentration [mmol·l ⁻¹]	
	Spiked	Found
<i>Thunnus obesus</i>	0	32.03
<i>Scomberomorus commerson</i>	0	18.22
<i>Euthynnus affinis</i>	0	11.01
<i>Nemipterus furcosus</i>	0	5.53
<i>Selar crumenophthalmus</i>	0	10.52
<i>Priacanthus lovetii</i>	0	10.89
<i>Megalaspis cordyla</i>	0	7.49

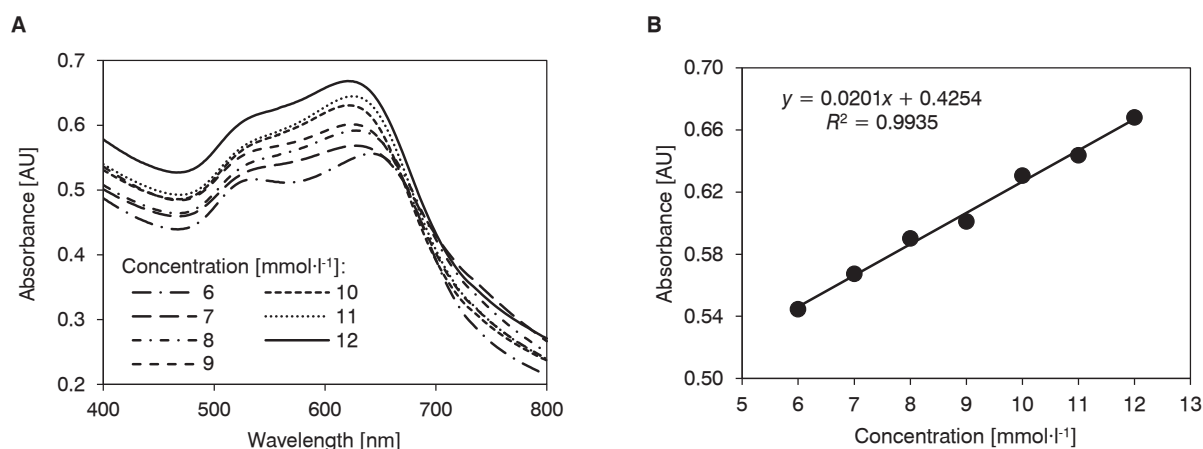


Fig. 3. UV-vis spectra and calibration curve of colorimetric response linearity.

A – UV-Vis spectra of the system reacting with Cd²⁺, B – calibration curve of colorimetric response to Cd²⁺ at 520 nm.

Detection in solution

Representative curves of the UV-Vis spectra and the linearity of the colorimetric response of AuNP in the Cd concentration range from 6 mmol·l⁻¹ to 12 mmol·l⁻¹ are shown in Fig. 3. The colour changes and absorbance spectra of the AuNP were determined when the target analytes were deposited on the surface of the AuNP. As shown in Fig. 3A, the UV-Vis absorbance spectra of AuNP showed a maximum at approximately 520 nm and the solution was of red-wine colour. The addition of Cd caused the absorbance of AuNP at 520 nm to gradually decrease, as well as the colour changed from red-wine to purplish-grey, with the absorbance at 620 nm increasing accordingly [23, 24]. Moreover, the absorbance values at 520–620 nm corresponded to the state of dispersion due to the aggregation of AuNP. Concomitantly, the calibration curve showed a linear response with $R^2 = 0.9935$, as shown in Fig. 3B. The values of *LOD* and *LOQ* were calculated to be 13.21 mmol·l⁻¹ and 40.04 mmol·l⁻¹, respectively. Hence, these developed TS-AuNP films had excellent sensing performance for the detection of Cd²⁺.

Detection in fish samples

Seven deep-sea fish species were tested, namely, *Thunnus obesus*, *Scomberomorus commerson*, *Euthynnus affinis*, *Nemipterus furcosus*, *Selar crumenophthalmus*, *Priacanthus lovetii* and *Megalaspis cordyla*. Only edible parts of the fish were used in the study by omitting the bones and organs. Results on Cd²⁺ detection in fish samples are shown in Tab. 3. All the species were found to be contaminated with Cd²⁺ ranging from 5.53 mmol·l⁻¹ to 32.03 mmol·l⁻¹, which is more than the permissible value for Cd²⁺. The amount of Cd²⁺ in the selected fish species from the fish market Kota Kinabalu was high due to uncontrolled anthropogenic activities contributing to water pollution and entering the fish [25, 26].

CONCLUSION

Throughout the studies, a biodegradable TS-AuNP film was developed and successfully used for detection of Cd²⁺, with a rapid change in colour from red-wine to purplish-grey in an agitation process that weakens the stability of the solution. The SEM images in this study showed that TS-AuNP film had a homogenous surface with many aggregations, which exhibited the properties of AuNP and density, and was only slightly thicker than TS film. In addition, TS-AuNP film showed

a significant biodegradation rate after 21 days, which was attributed to the increased water uptake of AuNP compare to the control. Interestingly, Cd²⁺ showed an effective colorimetric response towards AuNP compared to other heavy metal ions (Hg²⁺, Ni²⁺, Fe²⁺, Pb²⁺ and Cu²⁺). The results also showed that an environmentally friendly colorimetric sensor with fast detection prepared in this study was successful in detecting Cd²⁺ in fish samples. The TS-AuNP film is easier to use for on-site food safety applications than conventional methods.

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