

Heavy Metal Waste Using Ch/AgNPs Synthesized by Gamma Radiolysis: Preliminary Study

D. Ariyanti^{1*}, K. T. Basuki¹, K. Megasari¹, Ismail², A. Abimanyu²,
H. Hamadi³, K. Rozana⁴

¹Department of Nuclear Chemical Engineering, Polytechnic Institute of Nuclear Technology, National Research and Innovation Agency, Babarsari 60 Street, Yogyakarta 55281, Indonesia

²Department of Electro Mechanic, Polytechnic Institute of Nuclear Technology, National Research and Innovation Agency, Babarsari Street, Yogyakarta 55281, Indonesia

³Department of Instrumentation Electronics, Polytechnic Institute of Nuclear Technology, National Research and Innovation Agency, Babarsari Street, Yogyakarta 55281, Indonesia

⁴Directorate of Laboratory Management, Research Facilities, and Science and Technology Park, National Research and Innovation Agency, Babarsari Street, Yogyakarta 55281, Indonesia

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ABSTRACT

Environmental issues had always been a problem for all countries in the world. Within a certain threshold, heavy metal waste in water and air must be considered. Various methods and instruments could be used for analysis of heavy metal waste levels. However, quick and accurate method needs to be upgraded in order to improve the efficiency of analysis. Ag nanoparticle is an alternative that could be used to detect the presence of heavy metal waste. Ag nanoparticles can be synthesized through reduction reaction with reductant agents from chemicals, biological compounds, and gamma irradiation. This research used qualitative analysis, utilizing chitosan stabilizer for Ag nanoparticles with gamma irradiation reductant in various doses, such as 7.5, 15, and 20 kGy. The results showed that AgNPs/chitosan was formed in the peak absorption range of 390-500 nm with optimum gamma irradiation dose of 15 kGy. In addition, AgNPs/chitosan has good sensitivity to detect Cr and Hg metals and was not sensitive to Cu and Pb metals.

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INTRODUCTION

One of the serious problem in Indonesia is environment pollution. Pollutants are produced from various sectors such as mining, energy and mineral, infrastructure, agricultural industry, manufacture, domestic, household, etc. Indonesian Central Bureau of Statistics released that water pollution by hazardous materials was 25.1 %, while soil pollution was 2.7 % from villages in Indonesia. One of the hazardous materials waste is the abundant heavy metal. Various types of heavy metals can pollute the environment. In their ionic form, heavy metals can be dissolved in water bodies or soil, such as mercury (Hg^{2+}), lead (Pb^{2+}), zinc (Zn^{2+}), copper (Cu^{2+}), cobalt (Co^{2+}), chromium (Cr^{6+}) etc. Indonesian Central Bureau of Statistics states that Pb levels in the blood

of children in Tangerang, Bogor, and Tegal exceed the threshold settled by WHO. The Ministry of Environment and Forestry also revealed that 68 % of rivers in Indonesia is heavily polluted [1].

This heavy metal waste has long-term effects such as cancer and congenital defects because of carcinogenic and mutagenic characteristics. In other way, metal pollution can decrease nerve function, causing mental retardation, acrodynia, and the most dangerous, Hunter Russell syndrome, due to the dissolution of heavy metals such as mercury in food [2]. Based on these environmental problems, the scientific research and development related to heavy metal detection is needed. Early detection of the presence of heavy metals is then used as the basis for policy making against the polluting sources. Several modern analytical methods have been used for heavy metal detection such as Raman scattering spectroscopy, X-Ray, AAS, HPLC, voltammetry, absorption spectroscopy, etc. However, these

*Corresponding author.

E-mail address: dhit001@brin.go.id

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analytical methods are relatively expensive instruments and require a relatively long time for sample preparation before analysis.

One alternative method that can be used as heavy metals detection is nanotechnology. Nanotechnology is a rapidly-developing science, both in terms of the method of producing nano-sized particles (nanomaterials) and its applications. Nanomaterials have many applications in health, industry, and environment. Currently, nanomaterials are intensively used as detector materials for chemicals, both heavy metals, pesticides, and proteins dissolved in the blood. This is due to the good sensitivity of the nanomaterial surface to chemicals. The sensitivity of nanomaterials to heavy metals can be analyzed by UV-Vis spectrophotometer. UV-Vis is a fast and easy method because it works based on the presence of chromophoric reagents or color carriers. Nanomaterials that work based on the color change response are also called colorimetric sensors [3].

Researches of colorimetric sensors that use nanomaterials for detecting heavy metals are widely available. Synthesized nanomaterials such as silver (AgNPs), platinum (PtNPs), and gold (AuNPs) are mostly carried out by chemical methods. Several studies have used chemical reducing agent in the form of sodium borohydride with different stabilizers. This stabilizer is reagent that functions as an anti-agglomeration to increase the stability of synthesized nanomaterials, PVP [4], mercaptobenzoheterocyclic [5], glutamine and histidine [6], sodium alginate [7], thiol functional group as chitosan [8], PEG [9], kappa(κ)-carrageenan and lambda(λ)-carrageenan (containing K 10.4 %, Ca 2.4 % and Na 0.7 %) [10], carboxymethyl cellulose [11], Cyclodextrin [12], PVA [3], etc.

Several experiments used bioreductor to reduce Ag^+ to Ag^0 , such as Babunah extract [13], apple extract bioreductors and Cyclodextrin [14], Vigna mungo beans extract [15], Malva Sylvestris extract [16], green algae [17], hyacinth leaf extract bioreductor [18], Muntingia calabura fruit extract bioreductor L. [19], and Passiflora flavicarva (passion) fruit extract bioreductant [20]. Based on the descriptions of previous studies, the novelty of this research is method in synthesizing silver nanoparticles (AgNPs) using radiolytic reduction of Co-60 gamma rays. The AgNPs synthesized use gamma rays as a reducing agent and chitosan stabilizer. Radiolytic reduction methods that employs gamma rays as a reducing agent is able to eliminate the number of chemicals needed, so it is more environmental friendly [21-24,32-35].

METHODOLOGY

Solution preparation

An amount of 0.5 gr of chitosan was dissolved in 25 ml of demineralized water and stirred for 20 minutes. AgNO_3 with different mass variations was dissolved in 25 ml of demineralized water and stirred for 20 minutes. The mass variations of AgNO_3 were 0.1, 0.2, 0.3, 0.4, and 0.5 gr, so that there are 5 variations of AgNO_3 solution. Each solution of chitosan and each variation of AgNO_3 solution are mixed, then added with 5 ml of isopropyl alcohol and 50 ml of demineralized water, then stirred for 60 minutes. In total, there were 5 solutions of AgNO_3 /chitosan with different variations of AgNO_3 , a total volume about 105 ml, and labelled [8].

Irradiation of AgNO_3 /chitosan solution to AgNPs/chitosan

Synthesized AgNO_3 /chitosan material was irradiated with gamma irradiation with a dose of 7.5, 15, and 20 kGy using ^{60}Co at gamma irradiator facility, Polytechnic Institute of Nuclear Technology, Yogyakarta [22].

Characterization of synthesized AgNPs/chitosan

Characterization of each synthesized AgNPs/chitosan was carried out by determining the maximum wavelength at its maximum absorbance using a UV-Visible instrument. The maximum wavelength indicates the range of particle sizes formed. The peak pattern formed indicates the particle distribution in the synthesized AgNPs/chitosan [13].

AgNPs/chitosan sensitivity test as a heavy metal detection colorimetric

The heavy metals sample in this study were Hg^{2+} , Pb^{2+} in $\text{Pb}(\text{NO}_3)_2$, Cu^{2+} in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and Cr^{6+} in $\text{K}_2\text{Cr}_2\text{O}_7$. Each mother liquid metal solution was prepared at a concentration of 500 ppm. For each sample above, 1 ml of solution was diluted in 10 ml demineralized water, and the final standard solution was 50 ppm [8,13,14]. This concentration is higher than previous experiments, since this is a qualitative analysis. Thus, the detection limit must be lowered. A total of 2 ml of the synthesized AgNPs/chitosan solution was added with 1 ml of each standard metal sample. Each solution mixture was recharacterized with a UV-Visible instrument and analyzed for sensitivity [8].

RESULTS AND DISCUSSION

Spectrum absorption UV-Vis of synthesized AgNPs/chitosan by gamma radiolysis

The formation of Ag nanoparticle from AgNO₃ solution, chitosan as stabilizer, and gamma radiation as reductor is characterized by color change from clear to brownish yellow colloid. The formation of AgNPs was identified by the presence of absorption peak at wavelength 390-500 nm on measurements using UV-Visible spectrophotometer. This range indicated wavelength of Surface Plasma Resonances (SPR) silver nanoparticles [25].

Figure 1 shows the absorption spectra of AgNPs/chitosan synthesis by radiolysis gamma on 7.5, 15, and 20 kGy irradiation dose. The characterization results with UV-Vis spectrophotometer showed that from AgNO₃/chitosan to nanoparticles (AgPNs/chitosan) due to reducing gamma irradiation occurred at an optimum dose of 15 kGy. At a dose of 15 kGy, an absorption peak in the wavelength 390-500 nm was formed. Meanwhile, the doses of 7.5 kGy and 20 kGy did not have absorption peaks in the wavelength range of 290-700 nm.

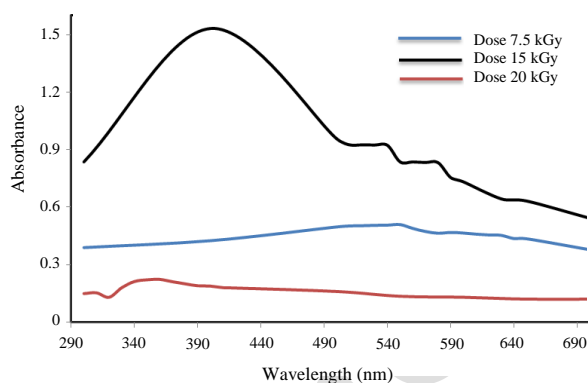
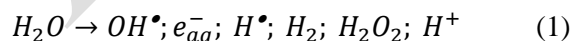


Fig. 1. Synthesis AgNPs/chitosan by radiolysis gamma on various doses.

The reaction of formation AgNPs/chitosan by gamma radiolysis began from water radiolysis with short half-lives ($\sim 10^{-10}$). Water radiolysis produced certain species which is able to reduce Ag⁺ to Ag⁰ through the reaction in Eq. (1) [26].



where the product of water radiolysis was solvated electron ($E^\circ H_2O/e_{aq}^- = -2,87 V_{NHE}$), hydrogen radicals ($E^\circ H^+/H^\bullet = -2,3 V_{NHE}$), H₂, H₂O₂, and H⁺. Both solvated electron and hydrogen radicals are strong reducing agent and can reduce Ag⁺ to Ag⁰ through mechanisms shown in Eqs. (2,3).



Stability of AgPNs/synthesized chitosan is still low, which is indicated by the formation of aggregates or deposits at the bottom of the bottle for more than two days. Ag⁰ nanoparticles will regroup to form larger particles. The formation of larger Ag particles will reduce the quantity of Ag nanoparticles, so that AgNPs no longer have good effectiveness as heavy metal detection materials.

Sensitivity test of AgNPs/chitosan synthesized by radiolysis gamma

Ag⁰ nanoparticles did not show peak absorption with Cu and Pb metals. This showed that there was no reaction that occurred between AgPNs/chitosan with Cu and Pb metals. In other words, it could be said that AgPNs/chitosan synthesized by gamma irradiation doses of 7.5 kGy (Fig. 2) was not sensitive to Cu and Pb metals.

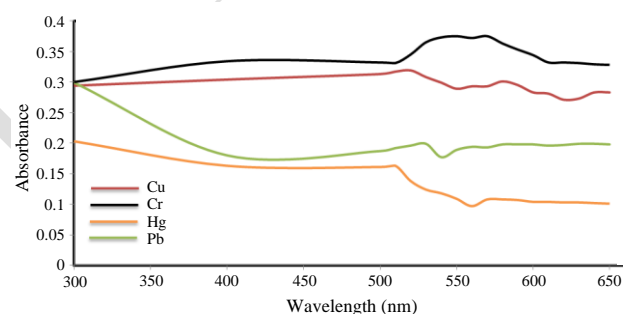


Fig. 2. Sensitivity test of AgNPs/chitosan synthesized by radiolysis gamma on dose 7,5 kGy.

Sensitivity test of synthesized AgNPs/chitosan was carried out by adding several types of simulated heavy metals, such as Cu, Pb, Cr, and Hg. Based on the UV-Visible absorption spectrum data Fig. 3, it was found that at gamma irradiation dose of 15 kGy, peak characteristics were formed in the wavelength range of 390-420 nm. The peak absorption showed Ag⁰ nanoparticles react with Cr and Hg metals, which means AgPNs/chitosan are sensitive to Cr and Hg metals. Data of absorbance and wavelength of Cr and Hg metals showed at Table 1.

Table 1. Peak absorption of reaction Cr and Hg with AgNPs/chitosan in optimum dose gamma irradiation 15 kGy.

Heavy metal	Peak Absorption	
	Absorbance	Wavelength (nm)
Cr	0.445	400
Hg	0.353	400

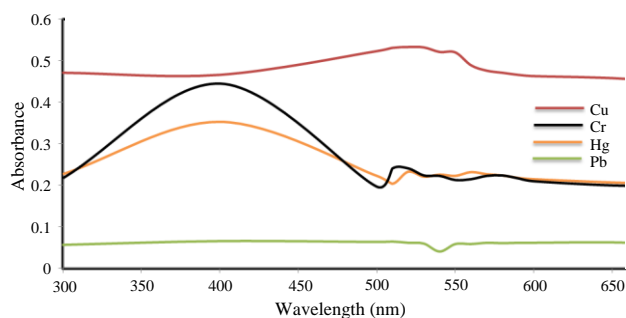


Fig. 3. Sensitivity test of AgNPs/chitosan synthesized by radiolysis gamma on dose 15 kGy.

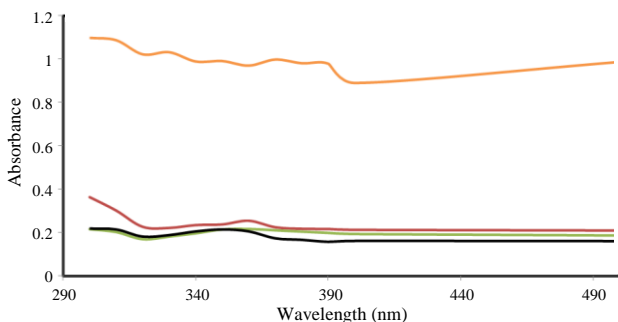


Fig. 4. Sensitivity test of AgNPs/chitosan synthesized by radiolysis gamma on dose 20 kGy.

Figure 4 showed that Ag^0 nanoparticles similarly did not show peak absorption with Cu and Pb metals on gamma irradiation dose of 20 kGy. This showed that there was no reaction that occurred between AgPNs/chitosan with Cu and Pb metals.

Mechanism reaction of reduction heavy metal with AgNPs/chitosan synthesized by gamma radiolysis

The oxidation reaction occurs due to a higher reduction potential value, so that the reaction takes place spontaneously. The mercury metal has a high reducing potential and functions as an oxidizer, and it can be detected using UV-vis spectroscopy and colorimetric sensing. Since Hg^{2+} ions have a larger reduction potential (+0.92 V) than Ag^0 (+0.8 V), they can be easily oxidized to Ag^+ ions and get reduced to Hg^+ . It seems like Chromium has high reducing potential and functions as an oxidizer. Cr^{6+} has larger reduction potential (+1.33 V) than Ag^0 (+0.8 V), so they can be easily oxidized to Ag^+ ions and get reduced to Cr^{3+} [27-29,31].

Figure 5 shows that no absorption peaks were formed in the reaction of Cu metal with AgNPs/chitosan synthesized at various gamma irradiation doses.

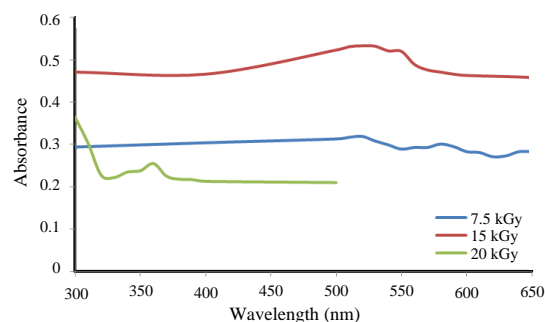
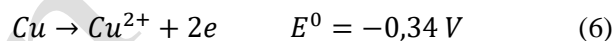


Fig. 5. Spectra absorption of AgNPs/chitosan and Cu metal on various gamma dose irradiation.

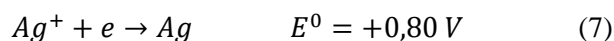
Standard reduction potentials of Cu Eq. (4) and Ag Eq. (5) are as follow.



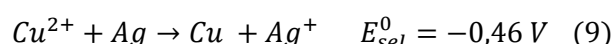
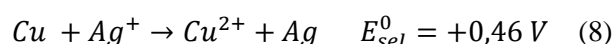
Reaction in anode (oxidation half reaction) is shown in Eq. (6).



Reaction in cathode (reduction half reaction) Eq. (7).



Overall reaction are summarized in Eqs. (8,9).



Overall reaction showed that potentials cell is negative. This result conduct that Ag nanoparticles was unable to reduce Cu^{2+} because standard potentials reduction of Cu^{2+} value is lower than that of Ag^+ . So, it is linear with absence of peak absorption in reaction between Cu and AgNPs/chitosan.

Figure 6 shows that no absorption peaks were formed in the reaction of Pb metal with AgNPs/chitosan synthesized at various doses of gamma irradiation.

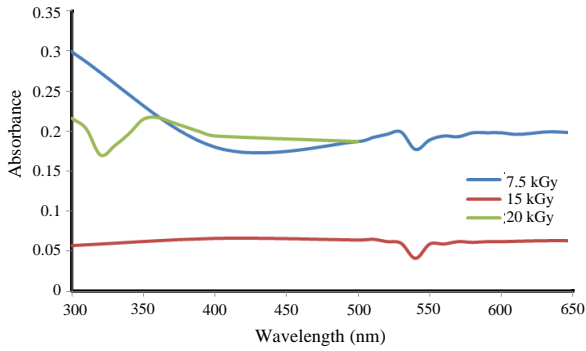


Fig. 6. Spectra absorption of AgNPs/chitosan and Pb metal on various gamma dose irradiation.

Standard reduction potentials of Pb is shown in Eq. (10).



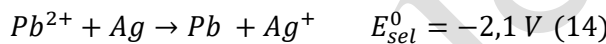
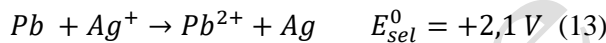
Reaction in anode (oxidation half reaction) is shown in Eq. (11).



Reaction in cathode (reduction half reaction) is shown in Eq. (12).



Overall reaction is summarized in Eqs. (13,14).



Overall reaction shows that potentials cell is negative. This result conduct that Ag nanoparticles also was unable to reduce Pb^{2+} because standard potentials reduction of Pb^{2+} value is lower than that of Ag^+ . So, this results is linear with absence of peak absorption in reaction between Pb and AgNPs/chitosan.

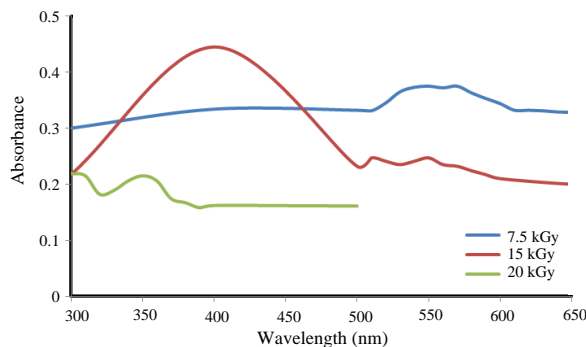
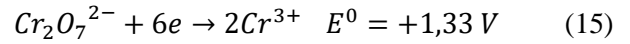


Fig. 7. Spectra absorption of AgNPs/chitosan and Cr metal on various gamma dose irradiation.

Figure 7 shows that absorption peaks (390-420 nm) were formed in the reaction of Cr metal with AgNPs/chitosan synthesized at 15 kGy doses of gamma irradiation. Standard reduction potentials of Cr is shown in Eq. (15) as follows.



Reaction in anode (oxidation half reaction) is shown in Eq. (16).



Reaction in cathode (reduction half reaction) is shown in Eq. (17).



Overall reaction is summarized in Eqs. (18,19).

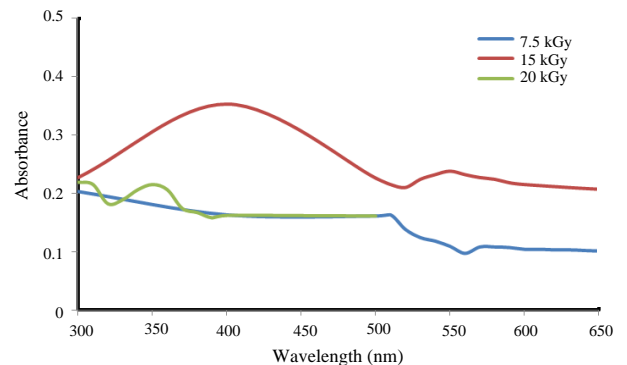
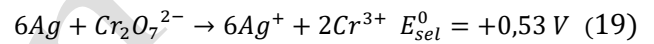
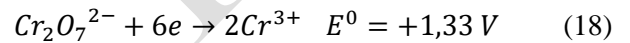
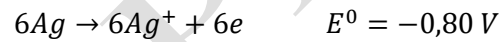


Fig. 8. Spectra absorption of AgNPs/chitosan and Hg metal on various gamma dose irradiation.

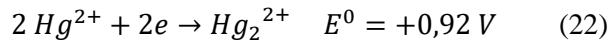
Figure 8 shows that small absorption peaks (390-420 nm) were formed in the reaction of Hg metal with AgNPs/chitosan synthesized at 15 kGy of gamma irradiation dose. In Eq. (19), overall reaction shows that potentials cell is positive. This result concludes that Ag nanoparticles could reduce Cr^{6+} because standard potentials reduction of Cr^{6+} value is higher than that of Ag^+ . Thus, it is linear with presence of peak absorption in reaction between Cr and AgNPs/chitosan. Standard reduction potentials of Hg is shown in Eq. (20).



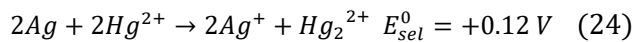
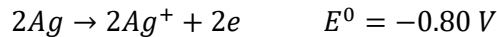
Reaction in anode (oxidation half reaction) is shown in Eq. (21).



Reaction in cathode (reduction half reaction) is shown Eq. (22).



Overall reaction is summarized in Eqs. (23,24).



In Eq. (24), overall reaction shows that potentials cell is positive. This result implies that Ag nanoparticles could reduce Hg^{2+} because standard potentials reduction of Hg^{6+} value is higher than that of Ag^+ . So, it is linear with presence of peak absorption in reaction between Hg and AgNPs/chitosan in Fig. 8.

The absorbance value is still low. This is because of low stability of AgNPs/chitosan. AgNPs/chitosan is unable to reduce heavy metals Cr and Hg in large quantities. Thus, the amount of low metal Cr and Hg that can be reduced by AgNPs/chitosan at a dose of 15 kGy is low. This preliminary study focused on qualitative analysis methods to detect other heavy metal presences. This method is a rapid methods, although gave lower precision and accuracy of contaminant value.

This research had similiarity with previous research conducted by Shahbaz et al. [28]. Researchers are currently working on developing new chemosensors for the qualitative and quantitative detection of metal ions. Among the methods developed for identifying cobalt ions, colorimetric and fluorimetric approaches are regarded as the best due to their ease of use, sensitivity, accuracy, linearity, and resilience. Hayati Hairom et al. [30] produced AgNPs from *Amomum subulatum* leaf extract using two distinct procedures: room temperature and heat treatment. The AgNPs manufactured using the heat treatment approach produced efficient results to detect Zn^{2+} . Synthesized AgNPs were investigated using basic UV-vis spectroscopy, which revealed an intense absorption band at 425 nm, which was validated by FTIR and SEM examination. The synthesized AgNPs shown a good colorimetric sensing property towards Zn^{2+} , shifting the color of the solution from yellowish-

brown to colorless and decreasing absorption intensity. The proposed detecting technique for the sensor has been discussed. The sensor had a good linear response towards Zn^{2+} . The proposed sensor was effectively employed to detect Zn^{2+} in drinking water samples.

CONCLUSION

AgNPs/chitosan can be synthesized at an optimum dose of 15 kGy than 7.5 kGy and 20 kGy. This is identified by color change from clear to brownish yellow colloid. Peak absorption is formed at 390-500 nm which is the SPR wavelength of silver nanoparticles. AgNPs/chitosan has good sensitivity to detect Cr and Hg metals and was not sensitive to detect Cu and Pb metals.

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AUTHOR CONTRIBUTION

D. Ariyanti and K.T. Basuki had contribution on conceptualization, methodology design, writing initial draft and revisions. K. Megasari, Ismail, H. Hamadi conducted data collection and sample analysis. A. Abimanyu and K. Rozana contributed on student supervision.

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